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Metal Ion Exchange of Square-Planar Nickel(II) Tetraglycine with Polydentate Amines[1]

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The exchange of nickel ion from yellow, diamagnetic, square-planar nickel(II) tetraglycine, NiG^{2-}, to polydentate amines takes place in two measurable steps from pH 10.5 to 12. The initial rapid reaction is first order in NiG^{2-} and zero order in hydrogen ion, buffer, and polydentate amine concentrations and yields an identical first-order rate constant for five different polydentate amines. The simplest formulas for the yellow mixed complexes produced in the initial rapid reaction are NiGen, (NiG)$_2$dien, (NiG)$_3$trien, (NiG)$_3$EDTA, and (NiG)$_5$tetren. The presence of excess polyamine converts in a slower reaction the yellow mixed complexes to octahedral complexes of nickel(II) and amines. In general, this slower reaction is independent of pH and buffer concentration, first order in mixed complex, and zero or first order in excess polydentate amine. The double-exchange reaction of NiG^{2-} and Cu(trien)$^{2+}$ exhibits complex kinetics and is zero order with respect to cupric complexes and first order with respect to nickel complexes in both directions.

When 1 equiv of base is added to a solution containing equimolar amounts of nickel(II) ion and glycylglycylglycylglycine (tetraglycine, abbreviated as just G in this paper) simple chelation at the terminal amino group and the first carbonyl oxygen atom takes place yielding a blue, octahedral, paramagnetic complex, NiG^{+}. To attain a pH of 10, an additional 3 equiv of base must be added corresponding to the titration of the three amide hydrogens.[2] Binding to nickel ion now occurs at the amino nitrogen and at three planar, *trans* amide nitrogens to give the yellow, square-planar, diamagnetic[3] complex NiG^{2-}. The amide hydrogen ionizations are not instantaneous and all three take place in a narrow pH range with pK_a values from 8.1 to 8.3 yielding a fully formed NiG^{2-} complex above pH 10. Despite the increasing negative charge on the complex, the ratios of the three nickel ion promoted amide hydrogen ionization constants are even less than those calculated on a statistical basis for equivalent and independent groups. Owing to the cooperative nature of diamagnetic complex formation, at the midpoint in the titration of the three amide hydrogens, the solution has lost half its original paramagnetism and is half as yellow as when 4 equiv of base has been added, indicating that half the nickel ions in the solution are octahedral and simply chelated and half are ringed by a plane of four nitrogen donors. Exchange of nickel ion between diamagnetic NiG^{2-} and excess tetraglycine is slow.[3] Cupric ion promotes amide hydrogen ionization at a lower pH than nickel, but in this case the ionizations occur in a normal noncooperative manner.[2] The yellow color of nickel complexes observed with peptides also occurs in proteins[4] and is the analog of the biuret color of cupric ion in similar environments.[5]

This paper presents a kinetic study of the change in nickel ion stereochemistry from diamagnetic square planar as the fully ionized nickel tetraglycine complex is converted to a paramagnetic octahedral one due to chelation with polydentate amine ligands. The amines employed in this study are ethylamine, ethylenediamine (en), diethylenetriamine (dien), triethylenetetramine (trien), tetraethylenepentamine (tetren), and ethylenediaminetetraacetic acid (EDTA).

Experimental Section

Nickel(II) ion was added as the chloride. Tetraglycine was purchased from Nutritional Biochemicals. Salts en·2HCl and EDTA disodium salt from Eastman Organic Chemicals and trien·2H$_2$SO$_4$ from Baker were used as received. Liquids dien and tetren from Eastman were vacuum distilled and the middle third was retained. All other materials were high-quality reagents. A Cary Model 14 spectrophotometer and Beckman Model G pH meter were employed.

Kinetic constants were evaluated from plots of the log of absorption differences *vs.* time over a range of several half-lives. For the fast formation reactions a critical reagent was injected by means of a syringe through a light-proof hole cut into the top of the sample compartment of a Cary 11 recording spectrophotometer into a cell containing the other reagents in solution. All kinetic and equilibrium experiments reported in this paper were conducted at 25.0° and at 0.5 ionic strength controlled with KCl.

One of the problems in investigating reagents of metal ions without a pH Stat[6] is the choice of buffer for control of pH. In the pH 10–11.5 region required in this work, the carbonate–bicarbonate buffer seemed appropriate so that most of the earlier experiments were performed in this system. When some experiments exhibited a dependence on buffer concentration, we searched for another buffer system and settled on triethylamine. Most of the results quoted in this paper are derived from experiments employing triethylamine as a buffer as it does not exhibit the deficiencies of the carbonate system. When the results obtained in the carbonate system differ in some way, this fact is stated briefly at the appropriate place in the following section.

Results

Addition of ethylamine to a solution containing the square-planar nickel(II) tetraglycine complex NiG^{2-}

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[1] This paper is abstracted from the M.S. theses of N. W. H. Ma and D. A. White, both 1965, from which more details may be obtained. The research was supported by a grant from the National Science Foundation.

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[5] A. S. Brill, R. B. Martin, and R. J. P. Williams in "Electronic Aspects of Biochemistry," B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1964, p 519.

[6] H. L. Conley, Jr., and R. B. Martin, *J. Phys. Chem.*, **69**, 2914, 2923 (1965).

yields no apparent change in the absorption maximum at 412 mμ where the molar extinction coefficient is 195. Addition of any one of several polydentate amines to a solution containing the yellow complex yields an initial rapid decrease in absorption followed by a slower decrease yielding, in the presence of sufficient amine, spectra identical with that of the octahedral nickel complex of the amine. The spectra of all intermediate complexes formed after the initial rapid reaction also absorbed maximally at 412 mμ with molar extinction coefficients, based upon the amount of nickel ion present, of 140–170.

The initial rapid decrease in absorption on addition of a polydentate amine to a yellow solution containing NiG^{2-} was investigated under a variety of conditions. At 25.0° and 0.5 ionic strength, the variations in concentrations were as follows: NiG^{2-}, 3–5 $\times 10^{-3}$ *M;* triethylamine buffer, 0.08–0.16 *M;* pH 10.5–11.6; en, 4–12 $\times 10^{-3}$ *M;* dien, 2–8 $\times 10^{-3}$ *M;* and trien, tetren, and EDTA, all 2–4 $\times 10^{-3}$ *M*. In addition, in the case of dien, runs were also performed at pH 12.95 in the absence of buffer. The result of 84 experiments conducted over the range of these conditions establishes that the rate is independent of the particular polydentate amine and its concentration, buffer concentration, and pH and is dependent upon the first power of the NiG^{2-} concentration. First readings were taken at 5 sec by means of the injection technique described in the Experimental Section. From the continuous record of absorption decrease *vs.* time, data were converted to log plots. From the slopes of log $(A - A_0)$ *vs.* time plots, where A_0 corresponds to the absorption of the intermediate complex formed after the initial rapid reaction, the first-order rate constants obtained for each polydentate amine are shown in Table I. Standard deviations ranged from 0.0025 to 0.0033 sec^{-1}. Not only is the reaction rate independent of polydentate amine concentration, but it is also independent of the amine employed. Greater rates were found for trien and EDTA in carbonate buffers, and these experiments are not considered further here.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR INITIAL RAPID REACTION OF POLYDENTATE AMINES WITH NICKEL(TETRAGLYCINE)$^{2-}$ AT 25.0°

Amine	Rate constant, sec^{-1}	No. of experiments
en	0.034	17
dien	0.037	24
trien	0.038	15
EDTA	0.040	14
tetren	0.037	14

Since the initial rapid reaction with a half-life of 19 sec is virtually complete before the slower reactions is appreciably underway, a condition exists that is favorable for investigation of the equilibrium formation of intermediate complexes formed from NiG^{2-} and the five polydentate amines. In order to determine the formula of the complex, the method of continuous variations was applied to solutions containing varying ratios of NiG^{2-} and polydentate amines at constant total concentration. In all cases a plot of the difference in absorption between that expected assuming no complex formation and the experimental value *vs.* the mole fraction of NiG^{2-} added to the solution yielded distinct triangular-shaped curves; one example, that for trien, is shown in Figure 1. The point of intersection of the straight lines shown in Figure 1 occurs at a mole fraction of NiG^{2-} of 0.75 corresponding to a 3:1 NiG^{2-} to trien mixed complex. This surprising result is reflected in the formulas of the mixed complexes formed with the other polydentate amines. The numbers of NiG entities found per polydentate amine molecule are as follows: en, 1; dien, 2; trien, 3; tetren, 5; EDTA, 3. The method of continuous variations has been subjected to criticism especially in solutions where several intermediate complexes might exist.[7] For both concentrations the lines in Figure 1 at high mole fractions do not pass through the ordinate value of zero at unit mole fraction. The trien case shown in Figure 1 exhibits the largest such discrepancy found for any amine in this work and suggests the existence of other complexes in solutions with low mole fractions of trien. On the other hand the distinctness of the maximum near 0.75 mole fraction in Figure 1 and the evident high equilibrium constant for formation of the complex indicate that in a solution of this composition the 3:1 NiG^{2-} to trien complex is the predominant species. Identical results were obtained in all cases for the formulas of the mixed complexes when the molar ratio method was applied. Several experiments performed in the trien system showed that the absorption is unaffected by the presence of 20% excess tetraglycine indicating that the amine is not expelling tetraglycine from the coordination sphere of nickel ion in forming the 3:1 NiG to trien complex.

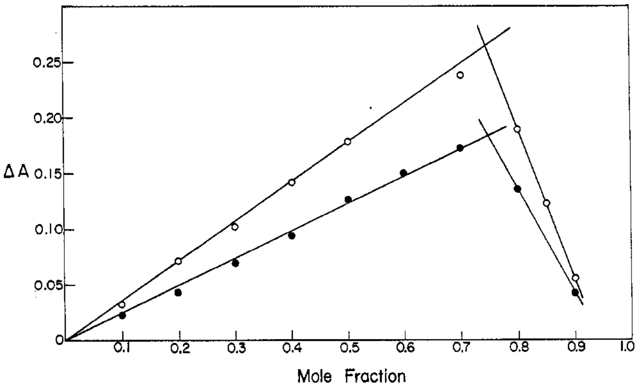

Figure 1.—Difference between absorbance expected assuming no complex formation and that observed *vs.* mole fraction of nickel tetraglycine in solutions with total concentrations of 4.00 $\times 10^{-3}$ *M* (filled circles) and 6.00 $\times 10^{-3}$ *M* (open circles) and varying concentration ratios of NiG^{2-} and trien. Measurements were made in a 1.00-cm cell.

As noted above the mixed complexes formed from NiG^{2-} and the polydentate amines all yield spectra with the same absorption maximum, 412 mμ, as NiG^{2-}

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[7] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 46.

but with lesser molar extinction coefficients when based on nickel content. Since the mixed complexes are formed with favorable equilibrium constants, their molar extinction coefficients may be estimated from results of the numerous continuous variation and molar ratio method studies and from plots of other data derived from considerations of the stoichiometries of the reactions[1] in solutions of pH about 10.5. Following the simplest formula of each mixed complex is the value of its molar extinction coefficient at 412 mμ; NiGen, 145; $(NiG)_2$dien, 322; $(NiG)_3$trien, 420; $(NiG)_3$EDTA, 430; and $(NiG)_5$tetren, 850. Based on content of nickel ion, the molar extinction coefficients are 145, 161, 140, 143, and 170, respectively. Absorptions calculated by use of these values for a solution containing differing amounts of NiG^{2-} and polydentate amine yield absorptions in close agreement with those observed experimentally.

In order to provide additional information about the requirements for maintenance of a yellow color in mixed complexes, some experiments with triglycine were conducted. Addition of 3 equiv of base to a solution containing equimolar amounts of nickel ion and triglycine yields a yellow solution with an absorption maximum at 432 mμ and a molar extinction coefficient of 240. No significant change in spectra occurs upon the addition of 1 mole of ethylamine. Upon the addition of 1 mole of en, however, the molar extinction coefficient decreases to 139 with the wavelength of maximum absorption unchanged. Thus, as with the tetraglycine complex, addition of en induces no change in wavelength of maximum absorption, but the drop in absorption intensity is more than 50% greater in the triglycine case. Though the nickel glycylglycine complex has undergone amide hydrogen ionization, it is not yellow[2] and addition of en does not induce a yellow color.

The experiments just described have established that NiG^{2-} reacts rapidly with trien to form a mixed complex $(NiG)_2$trien. The charge on the complex is as yet undetermined, and some experiments were performed to measure the proton balance upon mixed complex formation. When a solution of NiG^{2-} at pH 10.1–10.8 is mixed with one containing one-third as much trien at the same initial pH, an instantaneous increase in pH is observed. In order to return the combined solution to the pH of the original ones, 1.1–1.2 equiv of acid per mole of trien had to be added. The same number of equivalents of acid could also be added to either initial solution at pH 10.80 before mixing to yield the initial pH after mixing. Evidently for every three molecules of NiG^{2-} and one of basic trien about one proton is added to form a mixed complex of −5 net charge with an over-all but not detailed composition indicated by $[(NiG)_3Htrien]^{5-}$.

Similar proton balance experiments were also performed on the dien and tetren systems where the mixed complexes contain 2 and 5 parts of NiG per molecule of polydentate amine, respectively. Mixing of a solution containing NiG^{2-} with one containing half as much dien at an identical pH near 11.1 required the addition of just 0.5 equiv of acid per mole of dien to reduce the pH to the initial value, suggesting that the formula of the mixed complex might be $[(NiG)_4H(dien)_2]^{7-}$. A solution of tetren when mixed with one containing 5 times as much NiG^{2-} near pH 11.1 required 1.0 equiv of acid per mole of tetren to regain the pH of the initial solutions in accord with the formula $[(NiG)_5Htetren]^{9-}$.

Compared to the rapid first-order formation of the mixed complexes from NiG^{2-} and polydentate amine, their decomposition to yield octahedral nickel–amine complex and tetraglycine is slow and complex. Decomposition, when it occurred at all in NiGen, was much slower than the other mixed complexes, possibly reflecting the relative lower formation constants for en complexes of Ni(II), and was not subjected to quantitative study. All reactions were followed at 25.0°, at 0.5 ionic strength, and at 412 mμ where the octahedral nickel ion complexes of the polydentate amines all exhibit molar extinction coefficients of less than 5.

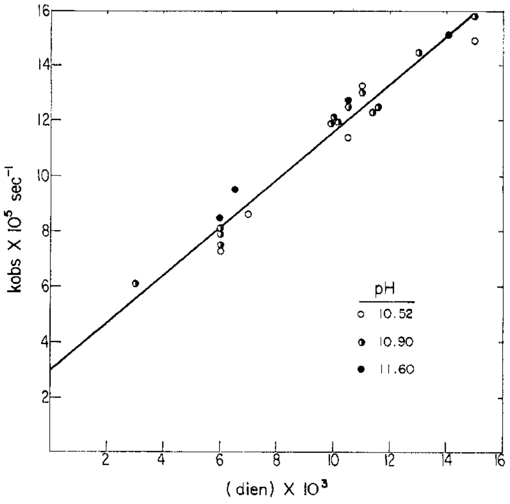

Figure 2.—Observed first-order rate constants for decomposition of $(NiG)_2$dien mixed complex *vs.* molar concentration of free dien at three pH values in 0.08 or 0.12 M triethylamine buffer.

The decomposition of $(NiG)_2$dien in the presence of excess dien was followed at pH values of 10.52, 10.90, and 11.60 in the presence of 0.08 or 0.12 M triethylamine buffer. Concentrations of NiG^{2-} were varied from 2 to 4×10^{-3} M and those of dien from 3 to 15×10^{-3} M. Observed first-order rate constants k_{obsd} for mixed complex decomposition were obtained from log $(A - A_\infty)$ *vs.* time plots and were found to be independent of triethylamine concentration and pH. As shown in Figure 2 for the results obtained at three pH values a plot of k_{obsd} *vs.* free dien concentration that is not tied up in original mixed complex yields a single straight line conforming to the equation

$$k_{obsd} = k_1 + k_2(\text{dien}) \qquad (1)$$

For the straight line shown in Figure 2, $k_1 = 3.0 \times 10^{-5}$ sec^{-1} and $k_2 = 8.6 \times 10^{-3}$ M^{-1} sec^{-1}. In carbonate buffers from pH 10.0 to 10.5 the rate is first order in complex and independent of free dien concentration, but dependent upon a fractional power of the hydrogen ion concentration and somewhat dependent upon buffer concentration. Results in the carbonate buffer system are not reported further here.

The decomposition of $(NiG)_3$trien in the presence of excess trien was found to be independent of pH from pH 10.0 to 11.5 in solutions containing borate, carbonate, triethylamine, or sodium hydroxide buffers. Concentrations of NiG^{2-} were varied from 4 to 6 $\times 10^{-3}$ M. Observed first-order rate constants appear nearly independent of trien concentration from 4 to 16 $\times 10^{-3}$ M. This apparent relative concentration independence compared to the dien system may be reflected in the higher value of $k_1 = 12 \times 10^{-5}$ sec^{-1} for the trien system. A less extensive study of the decomposition of $(NiG)_3$EDTA in the presence of excess EDTA in carbonate buffers yields $k_1 = 7 \times 10^{-5}$ sec^{-1}.

The decomposition of $(NiG)_4$tetren in the presence of excess tetren was found to be independent of pH from pH 10.5 to 11.6 and independent of 0.08 or 0.12 M triethylamine buffer. Concentrations of NiG^{2-} were varied from 2 to 4 $\times 10^{-3}$ M and tetren from 4 to 16 $\times 10^{-3}$ M. When the observed first-order rate constants at three pH values are plotted according to eq 1, a straight line is not obtained but rather a curve that is concave upward. As shown in Figure 3, a single straight line is obtained when the data are plotted according to $k_{\text{obsd}} = k_1 + k_3(\text{tetren})^2$, where (tetren) represents the excess concentration of tetren above that found in the original mixed complex. From the line drawn in Figure 3, $k_1 = 4.5 \times 10^{-5}$ sec^{-1} and $k_3 = 0.28$ M^{-2} sec^{-1}.

Several other combinations of reacting species were investigated briefly. Addition of 1,10-phenanthroline to a solution containing NiG^{2-} causes first-order disappearance of the yellow color at a measurable rate without apparent formation of intermediate mixed complexes. Nickel ion complexes formed with one molecule of triglycine,[2] two molecules of glycinamide,[2] or one molecule of glycylhistidine[8] are also planar. The reaction of any of these three complexes with trien is complete in less than 1 min.

The double-exchange reaction of $Ni(trien)^{2+}$ with CuG^{2-} to yield NiG^{2-} and $Cu(trien)^{2+}$ was studied in both directions at pH 10.3 in carbonate buffers. Though the reaction is first order with respect to nickel complexes and zero order with respect to cupric complexes in both directions and independent of buffer concentration, the kinetics are complicated by the appearance of two-step reactions and fractional order dependencies on hydrogen ion concentration. The rate of the reverse reaction is somewhat faster than the slow decomposition step in the reaction of NiG^{2-} with free trien.

Discussion

From pH 10.5 to 13 square-planar, yellow, diamagnetic nickel(II) tetraglycine, NiG^{2-}, combines with any of five polydentate amines in an initial rapid reaction that is zero order in polydentate amine, hydrogen ion, and buffer concentrations and first order in nickel complex concentration with a rate constant of 0.037 sec^{-1}. The zero-order dependency on all reagents except nickel complex and the identical first-order rate constant obtained with five different polydentate amines assures that this first reaction is a process involving the dissociation or rearrangement of at least one ligand atom in the nickel tetraglycine complex or its displacement by water. Dissociation and exchange reactions of other square-planar nickel complexes of amines have received study.[9] Octahedral nickel ion interactions with polydentate amines are more rapid than the rates reported here.[10]

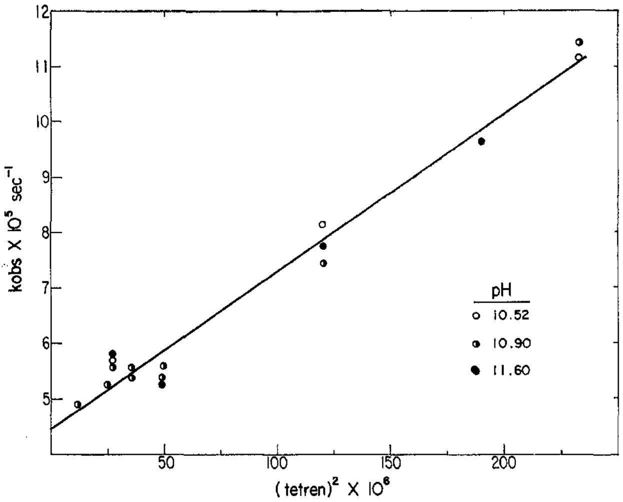

Figure 3.—Observed first-order rate constants for decomposition of $(NiG)_5$tetren mixed complex *vs.* square of molar concentration of free tetren at three pH values in 0.08 or 0.12 M triethylamine buffer.

Though the rate of the rapid first reaction is independent of the concentration and nature of polydentate amine, the composition of the mixed complexes formed depends critically on the amine. The simplest formulas for the products of the initial rapid reaction are NiGen, $(NiG)_2$dien, $(NiG)_3$trien, $(NiG)_3$EDTA, and $(NiG)_5$-tetren. All five mixed complexes absorb maximally at the same wavelength as NiG^{2-} but with molar extinction coefficients based on nickel content of 13–28% less. Because addition of ethylamine to NiG^{2-} yields no change in spectra, an amine with ability to chelate seems essential for an absorption decrease. Five-coordinate nickel complexes with nitrogen donors are high spin and exhibit quite different spectra than the mixed complexes reported here.[11] The nonintegral number of equivalents of hydrogen ion obtained in the case of dien in the proton-balance studies of mixed complex formation suggests that their formulas may be more complicated than depicted above. Though nickel

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(11) M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966); M. Ciampolini and N. Nardi, *ibid.*, **5**, 41 (1966); M. Ciampolini and G. P. Speroni, *ibid.*, **5**, 45 (1966).

(triglycine)$^-$ is diamagnetic in solution,[3] solid nickel triglycine chloride exhibits an unusual magnetic moment of 1.4 BM.[4] A relatively unstable mixed complex is indicated in the reaction of square-planar, diamagnetic Ni(CN)$_4^{2-}$ with a large excess of EDTA.[12] This paper reports the occurrence of complicated mixed complexes of NiG^{2-}; their detailed structural elucidation awaits further study.

The mixed complexes formed from NiG^{2-} and polydentate amine undergo, in the presence of excess amine, slower decomposition reactions to yield octahedral nickel complexes of the amines and tetraglycine. In general the decomposition reactions appear to be independent of buffer concentration and pH from pH 10.5 to 11.5. They exhibit a first-order dependence on mixed complex and a zero- and first-order dependence on excess polydentate amine.

The metal ion exchange reaction to EDTA from square-planar complexes of Ni(II) with aliphatic amine oximes[13] and cysteine[14] have been studied. No buildup of mixed-complex intermediates is reported. Two ligand molecules are required to produce the square-planar complexes in both studies while one tetraglycine molecule wraps around the plane of the nickel ion. EDTA was present in much greater excess than were the polydentate amines of this study. Conversions of square-planar nickel to the octahedral EDTA complexes followed a rate law of the form of eq 1. Neglecting the initial rapid reaction to form mixed complexes described above for the tetraglycine complex, rate constants for EDTA reactions with the nickel complexes of cysteine appear more rapid than those of amine oximes or tetraglycine which seem comparable.

Considering the multiplicity of functional groups on both reactants, NiG^{2-} and polydentate amines, it is not surprising that the two reactions possess rates so that they are measurable by conventional techniques. Indeed, in cases as complicated as that reported here, a pertinent question is whether three or more measurable reactions would be recognized if they did occur.

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

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Reaction of *trans*-[Ni(PR$_3$)$_2$X$_2$] Complexes with Phosphines and Amines. Formation of Stable Five-Coordinate Intermediates

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Tertiary phosphines PR$_3$ do not yield five-coordinated adducts by reaction with the planar complexes *trans*-Ni(PR$_3$)$_2$X$_2$ (PR$_3$ = P(C$_2$H$_5$)$_3$, P(C$_2$H$_5$)$_2$C$_6$H$_5$ and X = Cl, Br, NCO, NCS; PR$_3$ = P(C$_2$H$_5$)$_2$Cy, PC$_2$H$_5$Cy$_2$, PCy$_3$ (Cy = cyclohexyl) and X = Cl, Br, NCS; PR$_3$ = PC$_2$H$_5$(C$_6$H$_5$)$_2$ and X = NCS). However, P(C$_2$H$_5$)$_3$ and P(C$_2$H$_5$)$_2$C$_6$H$_5$ immediately replace PCy$_3$ and PC$_2$H$_5$Cy$_2$ in the reactions with the halide complexes. Since the reverse reactions are also observable, the result of these reactions is actually the exchange of the coordinated by the free phosphine. However, the reactions of the complexes *trans*-Ni(PR$_3$)$_2$(CN)$_2$ with the corresponding phosphines give in solution the stable five-coordinated intermediates as shown by the visible spectra. The compound Ni(P(C$_2$H$_5$)$_2$C$_6$H$_5$)$_3$(CN)$_2$ has also been isolated in the solid state. The five-coordinate compounds are discussed in terms of the binding properties of the ligands, the kinetic behavior toward the substitution, and their thermodynamic stability. With ethyl- and *n*-butylamine only substitution reactions occur.

Introduction

Whereas there are a number of five-coordinate complexes of nickel(II) with polydentate ligands,[1] little is known about the complexes with monodentate ligands in which coordination number and geometry are essentially determined by the tendency of the metal ion to attain a particular type of coordination.

Recent work on the stability of five-coordinated low-spin complexes of cobalt(II) has shown that the tris(phosphine) compounds Co(PR$_3$)$_3$X$_2$ (R = alkyl, aryl) are thermodynamically unstable when X = Cl, Br, NCO but are easily formed by addition of PR$_3$ to the four-coordinated Co(PR$_3$)$_2$X$_2$ when X = NCS.[2,3] This behavior has been attributed to the ability of NCS$^-$ to give better covalent bonds and it has been suggested that other "good" ligands such as NO$_2^-$ and CN$^-$ should promote stabilization of the five-coordinated compounds.[4]

As an extension of our work on the cobalt(II) complexes[2,3] we have now investigated the similar compounds of nickel(II). In complexes of the type M(PR$_3$)$_2$X$_2$ the behavior of nickel(II) apparently parallels

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