

plane as the C_2N_2Ni chelate ring would place excessive strain on the required planar nature of the C_2N_2Ni chelate ring. The low-energy shoulder at $\sim 17,000\text{ cm}^{-1}$ and the maximum at $\sim 21,000\text{ cm}^{-1}$ in the electronic absorption spectra of these five-coordinate, square-pyramidal complexes are assigned to transitions of d-orbital character $z^2 \rightarrow x^2 - y^2$ and $xy \rightarrow x^2 - y^2$, respectively.

The cis arrangement of donor atoms in the basal plane of the square-pyramidal structure yields complexes whose electronic absorption spectra are quite similar in energy position and contour to those of the $Ni\{CH_3As(CH_2CH_2CH_2AsMe_2)_2\}Br_2^{25,26}$ (Figure 5) and $Ni\{CH_3N(CH_2CH_2PPh_2)_2\}Br_2^{27,28}$ complexes which are known to possess unsymmetrical square-pyramidal structures. This observation gives additional support to the assigned square-pyramidal structure. The dia-

(25) G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc., London*, 415 (1961).

(26) G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 4433 (1961).

(27) L. Sacconi and R. Morassi, *ibid.*, A, 2997 (1968).

(28) P. L. Orioli and L. Sacconi, *Chem. Commun.*, 1310 (1968).

magnetic, five-coordinate nickel(II) complexes of the *o*-phenylene-bridged bidentate ligands $Ph_2P(o-C_6H_4AsPh_2)$, $Ph_2P(o-C_6H_4SCH_3)$, and $Ph_2P(o-C_6H_4SeCH_3)$ have been assigned square-pyramidal structures on the basis of their electronic absorption spectra.^{29,30} A comparison of the electronic absorption spectrum of the $[Ni\{Ph_2P(o-C_6H_4AsPh_2)\}_2Br]^+$ cation with that of the $[Ni(C_{32}H_{34}N_2P_2)Br]^+$ cation illustrates that the absorption maxima appear at similar energies (Figure 5). The lack of splitting in the absorption bands of the square-pyramidal nickel(II) complexes with the bidentate ligands suggests that these complexes have a trans arrangement of identical donor groups in the basal plane of the square pyramid rather than a cis arrangement of identical donor atoms.

The fact that monomeric complexes of the types $[Ni(C_{32}H_{34}N_2P_2)X]ClO_4 \cdot 0.5ROH$ ($X = Cl, Br, I$ where $R = C_2H_5$ and $X = Cl, Br$ where $R = C_4H_9$) can be prepared demonstrates that two diphenylphosphino groups can occupy cis positions in the basal plane of a square-pyramidal nickel(II) complex.

(29) T. D. DuBois and D. W. Meek, *Inorg. Chem.*, **6**, 1395 (1967).

(30) M. O. Workman, G. Dyer, and D. W. Meek, *ibid.*, **6**, 1543 (1967).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF HAWAII, HONOLULU, HAWAII 96822

Magnetic Titrations. Nickel(II) Complexes of C-Substituted Ethylenediamines

By G. RICHARD GRAYBILL,¹ JAY W. WRATHALL, AND JUDSON L. IHRIG*

Received June 28, 1971

The Quincke method of magnetic susceptibility measurement has been adapted for use in magnetic titrations. The technique has been employed to study the complex formation reactions of nickel(II) with ethylenediamine, 1,2-propanediamine, 2-methyl-1,2-propanediamine, and 2,3-dimethyl-2,3-butanediamine in 40% aqueous methanol solution. It was found that ethylenediamine and 1,2-propanediamine react with nickel(II) to give paramagnetic tris complexes, with no indication of intermediate diamagnetic species. 2-Methyl-1,2-propanediamine gives a paramagnetic tris complex with excess ligand but forms a diamagnetic intermediate species during the magnetic titration at a 2:1 ligand:metal ratio. 2,3-Dimethyl-2,3-butanediamine reacts with nickel(II) to give a diamagnetic bis complex with no indication of further interaction, even at large ligand:metal ratios. Increasing C-substitution of ethylenediamines causes an increase in the relative tendency to form stable diamagnetic bis complexes with nickel(II). This is due principally to steric interactions. The reaction of nickel(II) with *meso*-1,2-diphenylethylenediamine in 50% aqueous dioxane was also studied. A paramagnetic mono complex and a diamagnetic bis complex were formed during the course of the magnetic titration in this system.

Introduction

Nickel(II) complexes of ethylenediamines have been the subject of a number of investigations,²⁻⁸ since the bonding characteristics and even the structure of the complexes are very sensitive to structural variations of the ligand. Ethylenediamine itself and other derivatives which are not highly substituted form blue, paramagnetic complexes, whereas highly substituted ligands form yellow, diamagnetic complexes.

Basolo and collaborators have determined stepwise formation constants for the nickel(II) complexes of

several ethylenediamines,³⁻⁵ including ethylenediamine (en), 1,2-propanediamine (pn), 2-methyl-1,2-propanediamine (*i*-bn), 2,3-dimethyl-2,3-butanediamine (tetraMeen), and *meso*-1,2-diphenylethylenediamine (*ms*-stien). They found that en, pn, and *i*-bn form mono, bis, and tris complexes but that tetraMeen and *ms*-stien do not go beyond the bis complex. Furthermore, the order of stability constants was found to be anomalous for the tetraMeen complex, with K_2 being greater than K_1 . In the same study the solid compounds $Ni(\text{tetraMeen})_2Cl_2$ and $Ni(i\text{-bn})_2Cl_2$ were isolated and found to be diamagnetic. It was concluded that the tendency to form yellow, diamagnetic compounds increases with increasing methyl substitution.

Wilkins⁷ has studied the kinetics of the dissociation of the mono and bis nickel(II) complexes of all five of these diamines in aqueous acid. Although Basolo found no correlation between *C*-methyl and *C*-phenyl

(1) From the Ph.D. thesis of G. R. G., University of Hawaii, 1970.

(2) I. Lifschitz, J. G. Bos, and K. M. Dijkema, *Z. Anorg. Allg. Chem.*, **242**, 97 (1937).

(3) F. Basolo and R. K. Murmann, *J. Amer. Chem. Soc.*, **74**, 5243 (1952).

(4) F. Basolo and R. K. Murmann, *ibid.*, **76**, 211 (1954).

(5) F. Basolo, Y. T. Chem, and R. K. Murmann, *ibid.*, **76**, 956 (1954).

(6) H. Irving and J. M. M. Griffiths, *J. Chem. Soc.*, 213 (1954).

(7) R. G. Wilkins, *ibid.*, 4521 (1957); *Accounts Chem. Res.*, **3**, 408 (1970).

(8) D. L. Leussing, *Inorg. Chem.*, **2**, 77 (1963).

substitution and the stability constants, Wilkins reported that the dissociation rate is decreased by *C*-methyl substitution and increased by *C*-phenyl substitution.

The factors influencing the nature of the complexes formed and the anomalous stability constants of the tetraMeen-nickel(II) system have been discussed by a number of investigators.⁵⁻⁸ Several explanations have been proposed to interpret the observations. One difficulty in explaining the data is that none of the studies thus far has given specific information about the nature of intermediate complexes formed during the course of the metal-ligand titrations. Magnetic studies in solution should be an ideal method for studying the course of complex formation reactions, since the planar complexes are diamagnetic whereas the octahedral complexes and free metal are paramagnetic. Thus, appreciable formation of a planar species should result in lowering the total susceptibility of the solution.

Although the magnetic susceptibilities of nickel(II) and of some nickel(II) complexes have been determined in solution, complex formation reactions have not been followed in this way. This is probably due to experimental difficulties which would be involved in following sequential magnetic susceptibility changes with the commonly used Gouy method.

In this study a greatly simplified magnetic titration technique is used to follow complex formation in these nickel(II)-diamine systems.

Experimental Section

Materials.—Nickel(II) solutions were prepared with reagent grade $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Baker) and standardized gravimetrically with dimethylglyoxime.

Ethylenediamine (Baker reagent grade), 1,2-propanediamine (Baker 95%), and 2-methyl-1,2-propanediamine (Aldrich) were converted to the dihydrochlorides and purified by recrystallization from alcohol-water. *Anal.* Calcd for $\text{C}_3\text{H}_{10}\text{Cl}_2\text{N}_2$ ($\text{en} \cdot 2\text{HCl}$): Cl, 53.30. Found: Cl, 53.30. Calcd for $\text{C}_4\text{H}_{12}\text{Cl}_2\text{N}_2$ ($\text{pn} \cdot 2\text{HCl}$): Cl, 48.22. Found: Cl, 48.11. Calcd for $\text{C}_4\text{H}_{14}\text{Cl}_2\text{N}_2$ ($i\text{-bn} \cdot 2\text{HCl}$): Cl, 44.02. Found: Cl, 43.99.

The dihydrochloride of 2,3-dimethyl-2,3-butanediamine was prepared by the method of Sayre⁹ and purified by recrystallization from alcohol-water. *Anal.* Calcd for $\text{C}_6\text{H}_{18}\text{Cl}_2\text{N}_2$ ($\text{tetraMeen} \cdot 2\text{HCl}$): Cl, 37.48. Found: Cl, 37.28, 37.44.

meso-1,2-Diphenylethylenediamine was prepared by the method of Trippett¹⁰ and purified by recrystallization as the dihydrochloride. *Anal.* Calcd for $\text{C}_{14}\text{H}_{18}\text{Cl}_2\text{N}_2$ ($\text{ms-stien} \cdot 2\text{HCl}$): Cl, 24.86. Found: Cl, 24.84.

Water-methanol solutions were prepared using triply distilled water and spectroscopic grade methanol (Baker). The solvent for dioxane solutions was purified as follows. Reagent grade *p*-dioxane (Baker) was passed through an 18-in. column of acid-washed alumina, refluxed for 24 hr with sodium, and distilled. The fraction boiling at 100.5–101° was collected and stored in the dark over acid-washed alumina. Just before use the solvent was passed through an 18-in. column of Linde Type 5A 1/8-in. molecular sieves.

All titrations were carried out under a nitrogen atmosphere which was saturated with solvent.

Apparatus and Procedure.—Magnetic titrations were carried out with a modified Quincke apparatus which is described in detail elsewhere.¹¹ The Quincke method of magnetic susceptibility measurement consists, essentially, of a U tube, one side of which is a capillary placed in a magnetic field normal to it. Influence of the field causes a displacement of the meniscus of a solution in the tube, depending upon the susceptibility of the solution. The method is conveniently adapted to a titration

system. A simplified schematic diagram of the apparatus used is shown in Figure 1.

Titrations were carried out in the following manner. The solution to be titrated was placed in the mixing bulb under nitrogen. The solution was then allowed to flow into the capillary tube and the meniscus was centered in the magnetic field. Adjustment of the meniscus was carried out by regulating the gas pressure. After centering of the meniscus, the capillary system was isolated by closing the stopcocks to the mixing bulb and the nitrogen. The effect of a magnetic field on the height of the capillary was then determined with the measuring microscope. After the reading was taken, titrant was added to the mixing bulb and the solution in the capillary was returned to the bulb through the use of gas pressure. Mixing was achieved by bubbling nitrogen through the solution. The next point could then be determined by repeating the above process. The time required was about 5 min per point.

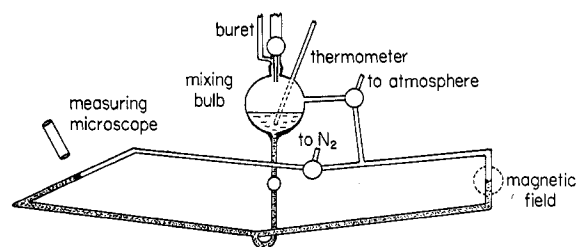


Figure 1.—The Quincke magnetic titration apparatus.

All of the titrations were carried out in both directions; *i.e.*, metal was titrated with ligand and ligand was titrated with metal. The results were identical, within experimental error, in both directions.

In all cases, except the Ni(II)-*ms-stien* system, 0.1 *M* Ni(II) and 0.1 *M* ligand solutions were used in the titrations. In the Ni(II)-*ms-stien* case, the metal and ligand solution concentrations were both 0.01 *M*.

Results

Calculations.—Details of the calculations are reported elsewhere.¹¹ The magnetic data are reported as the average molar susceptibility of the metal ion and as the average μ_{eff} of the metal ion.

In the Quincke method, the quantity measured is the linear displacement of a solution contained in a cylindrical tube when a magnetic field is applied. This displacement, designated Δl , is influenced by all components of the solution—metal-containing species, ligand, and solvent. Δl , must, then, first be corrected so that it reflects only the susceptibility of the metal. This is done by use of the equation

$$\overline{\Delta l}_m = \frac{\Delta l_t w_t - \Delta l_s^0 w_s^0 - \Delta l_l^0 w_l}{w_m}$$

where $\overline{\Delta l}_m$ is the displacement caused by the metal-containing species; Δl_t , Δl_s^0 , and Δl_l^0 are the total displacement, the displacement due to solvent, and that due to free ligand, respectively. The displacements due to solvent and ligand are calculated from known values of their susceptibility. w_t , w_s^0 , w_l , and w_m are the total weight, the weight of the solvent, weight of ligand, and weight of metal, respectively.

The average molar susceptibility of the metal can then be calculated by use of the equation

$$\overline{\chi}_{\text{Mn}}^{25} = \overline{\Delta l}_m \left(\frac{CMT}{298} \right)$$

where *C* is an apparatus constant, *M* is the molecular weight of metal, and *T* is the temperature. μ_{eff} is, of course, equal to $2.828 \sqrt{\chi_{\text{Mn}} T}$ BM.

(9) R. Sayre, *J. Amer. Chem. Soc.*, **77**, 6689 (1955).

(10) S. Trippett, *J. Chem. Soc.*, 4407 (1957).

(11) G. R. Graybill, J. W. Wrathall, and J. L. Ihrig, *Chem. Instrum.*, **3**, 71 (1971).

For some complexation reactions, information about the stability constants can be obtained. If two, and only two, complex species of different spin states are present in solution in significant quantities, the concentrations of each may be estimated, with reasonable accuracy, using the relationships

$$c_2 = c_T \left(\frac{\chi_{\text{measd}} - \chi_1}{\Delta\chi} \right)$$

$$c_1 = c_T - c_2$$

where c_1 and c_2 are the concentrations of the species with the lowest and highest spin states, respectively, c_T is the total concentration of complex species, χ_{measd} is the measured susceptibility, χ is the susceptibility of the species of the low-spin state, and $\Delta\chi$ is the difference in the susceptibilities of the two species in different spin states.

Magnetic Titrations.—Figure 2 shows the results of

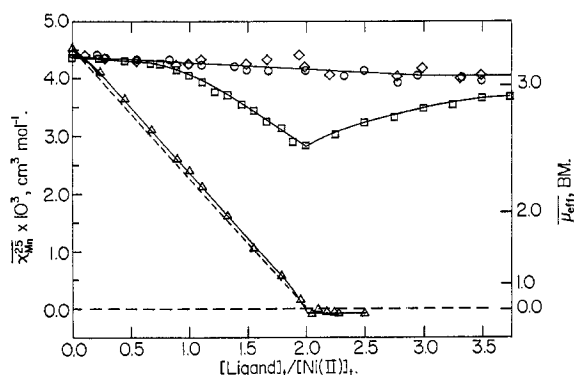


Figure 2.—Collection of plots of magnetic titrations of NiCl_2 with diamine ligands: \diamond , en; \circ , pn; \square , *i*-bn; Δ , tetraMeen.

magnetic titrations of nickel(II) with en, pn, *i*-bn, and tetraMeen in 40% aqueous methanol solutions. Each curve represents the combined results of several titrations. Although not shown on this combined graph, the titrations of the first three systems were carried out to ligand:metal ratios of ca. 7:1. The dashed line represents the form the titration curve would take if the only complex species were a spin-paired complex.

Nickel(II)-Ethylenediamine and Nickel(II)-1,2-Diaminopropane Titrations.—It is obvious from the plots of the titrations that the Ni(II)-en and Ni(II)-pn systems do not form measurable quantities of diamagnetic complex during the titrations of metal with ligand. Since the plots are almost identical within experimental error, they will be considered together. In both cases there is a definite drop in susceptibility from 4.43×10^{-3} ml/mol ($\mu_{\text{eff}} = 3.25$ BM) to about 4.00×10^{-3} ml/mol ($\mu_{\text{eff}} = 3.09$ BM). This change must be caused by partial quenching of the orbital contribution to the magnetic moment. There are slight breaks in the titration curves at close to a 3:1 ligand:metal ratio (difficult to observe on the scale of Figure 2) which indicates that quenching is not complete until the tris complex has formed. The Ni(II)-pn titration curve shown in Figure 3 illustrates this break more clearly. The values of 3.10 and 3.11 BM which have been reported for the moment of Ni(en)_3^{2+} in aqueous solution^{12,13} agree well with the results presented here.

(12) F. H. Field and W. C. Vosburgh, *J. Amer. Chem. Soc.*, **71**, 2398 (1949).

(13) C. D. Russell, G. R. Cooper, and W. C. Vosburgh, *ibid.*, **65**, 1301 (1943).

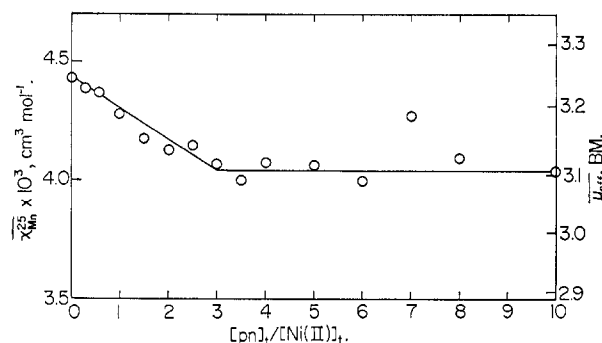


Figure 3.—Magnetic titration of NiCl_2 with 1,2-diaminopropane in 40% methanol.

Nickel(II)-2-Methyl-1,2-propanediamine Titrations.—The Ni(II)-i-bn system is a case in which diamagnetic bis complex is formed at a 2:1 ligand:metal ratio and then is converted to the paramagnetic tris complex as more ligand is added. In aqueous solution at 25° Basolo reported the following formation constants: $\log K_1 = 6.77$, $\log K_2 = 5.40$, $\log K_3 = 2.25$.⁵ For these relative stabilities each metal complex will have the major effect on the average susceptibility at that point in the titration curve where the ligand to metal ratio represents the stoichiometry of the complex. In Figure 4, Basolo's data are used to plot hypothetical

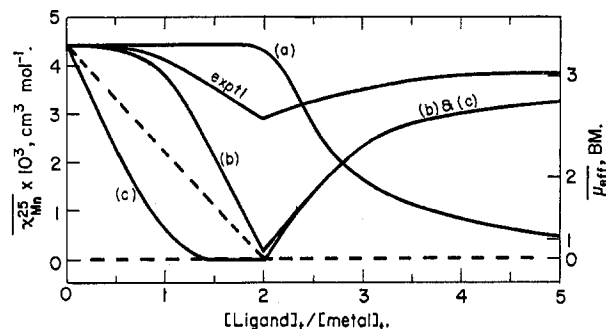


Figure 4.—Experimental and calculated magnetic titration curves for Ni(II)-i-bn : (a) ML , ML_2 paramagnetic; ML_3 diamagnetic; (b) ML , ML_3 paramagnetic; ML_2 diamagnetic; (c) ML , ML_2 diamagnetic; ML_3 paramagnetic. (a), (b), and (c) apply to aqueous solution; the experimental curve applies to 40% methanol solution.

curves for several possible assignments of spin states for the three complex species. It is seen that the symmetry of the experimental titration curve for the Ni(II)-i-bn system agrees with that expected if Ni(i-bn)_2^{2+} and Ni(i-bn)_3^{2+} are paramagnetic and Ni(i-bn)_2^{2+} is diamagnetic. The position of the curve, however, indicates that the amount of diamagnetic complex formed is not as large as the amount of bis complex predicted by the formation constant data.

Nickel(II)-2,3-Dimethyl-2,3-diaminobutane Titrations.—The Ni(II)-tetraMeen system is a case in which a bis complex is formed at a 2:1 ligand:metal ratio. Further addition of ligand, however, does not yield a higher complex. Stability constant data indicate an anomalous order, $K_2 > K_1$, which further demonstrates the increased stability of $\text{Ni(tetraMeen)}_2^{2+}$ compared to the bis complexes of less substituted 1,2-diamines. The values of stability constants in aqueous solution are reported as $\log \beta_2 = 14.56$ and 14.68, while the upper limit of $\log K_2$ is set at 6.^{5,8} These values indicate that the mono complex should not be observed in a titration. In 40% meth-

anol a slight, but reproducible, positive deviation from the straight line is observed, indicating that a significant amount of paramagnetic mono complex is present. This indicates that the K_2/K_1 ratio is smaller in 40% methanol than in water. The value of $\log(K_2/K_1)$, calculated in the present study, is 1.48 ± 0.29 . The bis complex is still more stable but the ratio of stabilities has decreased by at least an order of magnitude.

Nickel(II)-1,2-Diphenylethylenediamine Titrations.

—Because of the low solubility of reaction products in 40% methanol, the Ni(II)-*ms*-stien system was titrated in 50% aqueous dioxane. Even in this solvent the maximum concentrations obtainable were of the order of 0.01 mol/l. The results of these titrations are shown in Figure 5. The precision is as good as can be

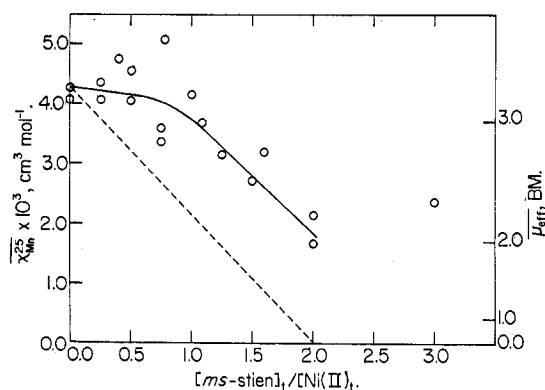


Figure 5.—Magnetic titrations of NiCl₂ with *ms*-stien in 50% dioxane.

expected at these concentrations. The shape of the first segment of the titration curve is fairly well defined and indicates that a paramagnetic mono complex and a diamagnetic bis complex are formed and that K_1 is greater than K_2 . These conclusions agree with Basolo's equilibrium study and with the report that solid Ni(*ms*-stien)₂Cl₂ is diamagnetic. No other reference to magnetic measurements of these complexes in solution has been found.

Discussion

The magnetic titrations show conclusively that *en* and *pn* have little tendency to form diamagnetic complexes in 40% methanol at any stoichiometric ratio of ligand to metal. *i*-*bn* forms some diamagnetic bis complex at a 2:1 ligand:metal ratio but further addition of ligand results in reaction of the diamagnetic bis compound to form the tris complex. *tetra*Meen quantitatively forms the diamagnetic bis complex at any ligand:metal ratio above 2:1. No sign of formation of the tris complex was observed.

The course of the titrations of Ni(II) with various 1,2-diamines proceeds as follows. The paramagnetic solvated Ni(II) ion first adds one diamine ligand to form, in all cases, a paramagnetic mono complex ion. C-Substitution of the ligand has no effect on the spin-state of the mono complexes. However, C-substitution does appear to decrease the stability constants of the mono complexes.⁵ This is probably attributable to a sterically induced decrease in solvation energy of the complex as substitution in the ligand increases.⁸

As the titrations proceed with addition of ligand to the paramagnetic mono complexes, bis complexes are formed. The magnetic properties and structures of these bis complexes differ greatly as C-substitution of

the ligand is increased. The bis complexes of *en* and *pn* are paramagnetic and no change in susceptibility is observed in the magnetic titration curves. The structure of these paramagnetic bis complexes is very probably octahedral, with solvent occupying the two remaining positions. *tetra*Meen, however, gives a diamagnetic bis complex and the susceptibility of the solution at a 2:1 ligand:metal ratio falls to close to 0. The geometry of this diamagnetic bis complex is square planar. Solvent would be excluded from the remaining positions by steric hindrance. The bis complex of *i*-*bn* appears to be an intermediate case. The susceptibility falls to a minimum at a 2:1 ligand:metal ratio but does not approach the expected susceptibility value of close to 0.

Either of two explanations would account for these results. One possibility is that the ratio of equilibrium constants for the system differs significantly between 40% methanol and completely aqueous solutions. Another explanation—which we favor—is that an equilibrium exists in solution between the para- and diamagnetic forms of the bis complex. This interesting type of equilibrium has recently been observed in other systems.¹⁴

Stability constant data indicate that formation of diamagnetic bis complexes by the highly C-substituted ligands results in enhanced stability of the complex. *tetra*Meen actually gives a $K_1:K_2$ ratio of less than 1, and although K_1 is smaller for Ni(II)-*tetra*Meen than for Ni(II)-*en*, the overall constant, β_2 , is greater for Ni(II)-*tetra*Meen than for Ni(II)-*en*.^{5,8} This enhanced stability can be attributed to the square-planar geometry of the complex which results in a closer approach of the donor atoms to the metal than would be the case if the complex were octahedral.⁸

Further addition of ligand to the bis complexes of *en*, *pn*, and *i*-*bn* results in formation of octahedral paramagnetic tris complexes. The stability of the tris complexes, as indicated by the aqueous stability constants, decreases with increasing C-substitution. Basolo reported $\log K_3$ values of 5.03, 4.27, and 2.25 for the Ni(II)-*en*, Ni(II)-*pn*, and Ni(II)-*i*-*bn* systems, respectively.⁵ This decrease in stability can be attributed to steric hindrance which increases as substitution increases. The Ni(II)-*tetra*Meen system shows no tendency to form the tris complex. Addition of ligand to the diamagnetic bis complex causes no change in the susceptibility of the solution. Steric hindrance completely prevents any tris complex formation in this case.

Since the magnetic properties of Ni(II)-*ms*-stien complexes are of considerable interest, our results for this system have been reported here. Because the anion of these so-called Lifschitz complexes has such a marked effect on the magnetic properties of their crystalline forms, further solution studies of magnetic properties with anions other than chloride would be of considerable interest.

Acknowledgments.—This work was supported in part by the University of Hawaii Research Council. G. R. G. gratefully acknowledges receipt of a NASA traineeship during the period of this work. We are indebted to Dr. R. E. Cramer for helpful discussions.

(14) R. G. Wilkins, R. Yelin, D. W. Margerum, and D. C. Weatherburn, *J. Amer. Chem. Soc.*, **91**, 4326 (1969).