

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Steric Effects and the Stability of Complex Compounds. IV. The Chelating Tendencies of C-Substituted Ethylenediamines with Copper(II) and Nickel(II) Ions^{1,2}BY FRED BASOLO, YUN TI CHEN AND R. KENT MURMANN³

RECEIVED AUGUST 28, 1953

The effect of steric hindrance on the chelating tendencies of diamines with copper(II) and nickel(II) ions has been investigated using C-substituted ethylenediamines. The stepwise formation constants of these two ions with $H_2NCR_2CR_2NH_2$ ($R = H, CH_3$ or C_6H_5) have been determined at 0 and 25°. The chelating tendency of *rac*-butylenediamine is less than that of *meso*-butylenediamine as is likewise true of *rac*-stilbenediamine compared to *meso*-stilbenediamine. Tetramethylethylenediamine, like *meso*-stilbenediamine, forms a yellow diamagnetic complex with nickel(II) of the type $[Ni(AA)_2]X_2$. Several other diamagnetic nickel(II) complexes have been isolated as the iodide salts.

The effect of steric hindrance on the chelating tendencies of N-substituted ethylenediamines has recently been reported.⁴ Carlson, McReynolds and Verhoek⁵ report that the chelating tendency of propylenediamine is the same as that of ethylenediamine. It would appear that this should be the case because one methyl group on a carbon atom of ethylenediamine is not expected to alter greatly the coordinating ability of the diamine. However, it is of interest to determine if additional substitutions may not in fact have some effect on the chelating tendency of the bidentate molecule. This paper reports the results of such a study using *dl*-bn, *m*-bn, *i*-bn, *dl*-stien, *m*-stien and TetraMeen⁶ with copper(II) and nickel(II) ions. The stepwise formation constants have been determined for these complex ions at 0 and 25° in water, except for the water-insoluble complexes of *dl*-stien and *m*-stien in which case a 50–50 dioxane–water mixture was used.

Experimental

Calculation of Formation Constants.—The stepwise formation constants were calculated by the method previously described.^{3b} In the investigation of *dl*-stien and *m*-stien, lower concentrations of metal ion were employed and it was found more convenient to evaluate the formation constants by the method of Calvin and Melchior.⁷ The dissociation constants reported earlier⁸ were used in these calculations of the formation constants.

Reagents.—Except for TriMeen the syntheses of the diamines used have already been described.³ Attempts to prepare sufficient quantities of TriMeen for these studies were not successful. However, it was possible to reduce 2-methyl-2-amino-3-ketoximebutane and isolate a small amount of the diamine and its nickel(II) complex from this reaction mixture.

(1) This investigation was supported by a grant-in-aid from the National Institutes of Health, Grant No. G-3239.

(2) Presented in part at the Los Angeles Meeting of the American Chemical Society, March, 1953.

(3) Abstracted in part from a thesis by R. Kent Murmann presented to the graduate faculty of Northwestern University, in partial fulfillment of the requirements for the Ph. D. degree, 1954.

(4) (a) H. Irving, Paper No. 4, "A Discussion on Coordination Chemistry," Butterwick Research Laboratories, I.C.I., Sept., 21–22, 1950; (b) F. Basolo and R. K. Murmann, *THIS JOURNAL*, **74**, 5243 (1952); (c) **75**, 211 (1953).

(5) G. A. Carlson, J. P. McReynolds and F. H. Verhoek, *ibid.*, **67**, 1334 (1945).

(6) The diamines are designated as follows: en = ethylenediamine; pn = propylenediamine; *dl*-bn = *rac*-2,3-diaminobutane; *m*-bn = *meso*-2,3-diaminobutane; *i*-bn = 2-methyl-1,2-diaminopropane; TetraMeen = 2,3-dimethyl-2,3-diaminobutane; *dl*-stien = *rac*-1,2-diphenylethylenediamine; *m*-stien = *meso*-1,2-diphenylethylenediamine; TriMeen = 2-methyl-2,3-diaminobutane.

(7) M. Calvin and N. C. Melchior, *THIS JOURNAL*, **70**, 3270 (1948).

(8) F. Basolo, R. Kent Murmann and Yun Ti Chen, *ibid.*, **75**, 1478 (1953).

Nitrosyl chloride⁹ was added slowly to an excess of trimethylethylene¹⁰ at –20°. The white crystals of 1-chloro-1-methyl-2-nitrosobutane were removed on a filter and added to a saturated solution of ammonia in alcohol at 0°. The temperature was then raised and the mixture refluxed for 6 hr. with continuous addition of ammonia. After removal of the solvent at reduced pressures the residue was extracted first with hot benzene and then with *sec*-butyl alcohol. The benzene solution yielded the desired product, 2-methyl-2-amino-3-ketoximebutane (12%); m.p. 98.0–98.5°. *Anal.* Calcd. for $C_5H_{12}N_2O$: C, 51.65; N, 24.15; H, 10.34. Found: C, 51.48; N, 24.42; H, 10.11. An additional yield of 62% of the hydrochloride (m.p. 192–194°) was obtained from the *sec*-butyl alcohol solution.

Attempts to prepare the desired diamine by a catalytic (PtO_2) hydrogenation of the ketoxime hydrochloride and by electrolytic reduction were not successful. Reduction with tin(II) chloride in concentrated hydrochloric acid gave almost a quantitative yield of 2,2,3,5,5,6-hexamethyl-2,5-dihydropyrazine¹¹ (m.p. 64–65°). It was finally possible to isolate only 1.5 g. of the diamine (b.p. 138–142°) and 2.2 g. of $[Ni(TriMeen)_2]I_2$ from the reduction of 100 g. of 2-methyl-2-amino-3-ketoximebutane hydrochloride with sodium amalgam and alcohol.

Dioxane was purified by the method of Weissburger and Proskauer.¹² The other chemicals were all of reagent grade.

Standard Solutions.—Aqueous solutions of the diamines, except *dl*-stien and *m*-stien, were standardized by titration with standard acid. The dioxane–water (50% by volume) solutions of *dl*-stien and *m*-stien of approximately 0.5 M concentration were standardized by conductometric titration with standard perchloric acid. Standard aqueous solutions of copper(II) nitrate and nickel(II) nitrate were prepared which contained approximately 0.05 M metal ion, 0.1 M nitric acid and 0.5 M potassium nitrate. A 50% dioxane–water solution of approximately 0.05 M copper perchlorate was standardized by electrodeposition. A 100-cc. portion of this standard solution was diluted with an approximate amount of standard perchloric acid solution to result in a mixture containing 0.005 M copper(II) ion and 0.025 M perchloric acid. Similarly a standard 50% dioxane–water solution of 0.005 M nickel(II) perchlorate and 0.025 M perchloric acid was prepared. This choice of perchlorate as the anion in the dioxane–water solutions was made as the perchlorate complexes were somewhat more soluble than the nitrate salts. Furthermore, no supporting electrolyte was used in these mixed solvents.

Titrations.—The apparatus and procedures employed were the same as described in paper I of this series.^{4b} However, it was necessary to prepare a calibration curve to correct for changes in the activity coefficient of the hydrogen ion in the dioxane–water solutions. The results indicated that the actual pH meter readings were correct within experimental error below a pH of 9, which for the systems reported here was well outside the range of complex formation.

Continuous Variation Studies.—The method of Vosburgh and Cooper¹³ was applied to solutions of nickel(II) ions and

(9) G. H. Coleman, G. A. Lillis and G. E. Goheen, "Inorganic Syntheses," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1939, p. 55.

(10) A. Michael and F. Zeidler, *Ann.*, **385**, 259 (1911).

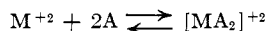
(11) S. Gabriel, *Ber.*, **44**, 64 (1911).

(12) A. Weissburger and F. S. Proskauer, "Organic Solvents," Oxford Press, 1935, p. 139.

(13) W. C. Vosburgh and G. H. Cooper, *THIS JOURNAL*, **63**, 437 (1941).

TetraMeen. The absorption spectra and optical density measurements at selected wave lengths were made with a Beckman DU spectrophotometer on solutions of from 10^{-3} to 10^{-2} molar concentration.

Absorption Spectrum and Formation Constant of [Ni(TetraMeen)₂]⁺².—The absorption spectrum of an aqueous solution of [Ni(TetraMeen)₂](NO₃)₂ was determined and observed to obey Beer's law upon dilution. However, when an excess of acid is added to the yellow solution the complex dissociates at a measurable rate (half-life of approximately 142 sec. at 25°). Therefore, several solutions of the complex containing varying amounts of acid were thermostated at 15, 25 and 39° until equilibrium was reached, at which time both the pH and optical density of the solutions were measured. These data were used to calculate the total formation constant of the complex for the reaction¹⁴



where

$$K = \frac{[MA_2^{+2}]}{[M^{+2}][A]^2} \quad (1)$$

Since it was shown (Figs. 1 and 2) that the concentration of [MA]⁺² must indeed be very small, it follows that

$$C_M = [M^{+2}] + [MA_2^{+2}] \quad (2)$$

$$C_A = [A] + [AH^+] + [AH_2^{+2}] + 2[MA_2^{+2}] \quad (3)$$

and

$$C_H = [H^+] + [AH^+] + 2[AH_2^{+2}] \quad (4)$$

From the dissociation constants of the diamine

$$k_{AH_2^{+2}} = \frac{[AH^+][H^+]}{[AH_2^{+2}]} \quad (5)$$

$$k_{AH^+} = \frac{[A][H^+]}{[AH^+]} \quad (6)$$

together with equations 2, 3 and 4 it follows that

$$[A] = \frac{k_{AH_2^{+2}} \times k_{AH^+} (C_H - [H^+])}{(k_{AH_2^{+2}} \times [H^+]) + 2[H^+]^2} \quad (7)$$

and

$$[MA_2^{+2}] = \frac{1}{2} \left\{ C_A - \left(\frac{(k_{AH_2^{+2}} \times k_{AH^+}) + (k_{AH_2^{+2}} \times [H^+]) + [H^+]^2}{[H^+]} \right) \left(\frac{C_H - [H^+]}{k_{AH_2^{+2}} + 2[H^+]} \right) \right\} \quad (8)$$

Therefore substituting equations 2, 7 and 8 into 1, the formation constant of the complex is calculated. The concentration of [MA₂]⁺² can also be obtained directly from the spectrophotometric data since

$$[MA_2^{+2}] = \frac{\log(I_0/I)}{\epsilon}$$

The molecular extinction coefficient, ϵ , is obtained from the optical density of solutions containing known amounts of nickel(II) and an excess of the diamine.

Yellow, Diamagnetic Complexes of Nickel(II).—The addition of excess TetraMeen to a nickel(II) solution yielded a compound which could be isolated either as the insoluble iodide or the slightly soluble chloride. *Anal.* Calcd. for NiC₁₂H₃₂N₄Cl₂: Ni, 16.24; C, 39.8; H, 8.85; N, 15.5; Cl, 19.63. Found: Ni, 16.35; C, 39.6; H, 8.64; N, 15.4; Cl, 19.68. Conversion to the more soluble [Ni(TetraMeen)₂](NO₃)₂ was accomplished by grinding the iodide with slightly less than the calculated amount of concentrated aqueous silver nitrate and extracting the reaction mixture with water at 80°. Recrystallization from an ethanol-water mixture produced the pure nitrate which has an absorption band at 434 m μ with a molecular extinction coefficient, ϵ , of 63.8.

A yellow solution was formed when solutions of nickel(II) and TriMeen were mixed at a pH of 9. The yellow iodide, [Ni(TriMeen)₂]₂ was precipitated upon the addition of excess potassium iodide and was recrystallized from ethanol-water. *Anal.* Calcd. for NiC₁₀H₂₈N₄I₂: Ni, 11.37; C, 23.55; H, 5.41; N, 10.82; I, 49.08. Found: Ni, 11.32; C,

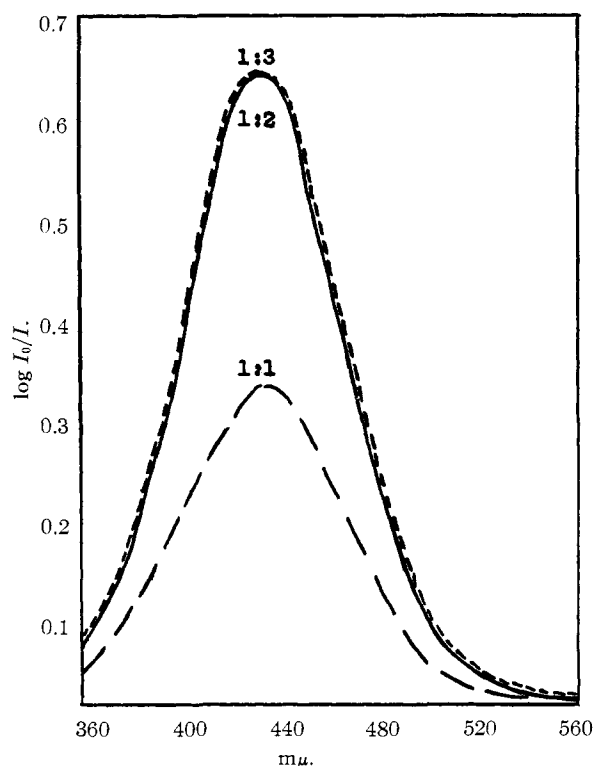


Fig. 1.—Absorption spectra of solutions containing different mole ratios of Ni⁺²:TetraMeen. Concentration of Ni(NO₃)₂ kept the same at 0.01 M whereas that of TetraMeen was changed to give the mole ratios designated. Measurements were made at room temperature with a Beckman Du spectrophotometer using 1-cm. quartz cells.

23.88; H, 5.47; N, 10.80; I, 49.1. (ϵ at 440 m μ is 54.7.)

Essentially the same procedure was used for the preparation of the compounds [Ni(*dl*-bn)₂]₂, [Ni(*m*-bn)₂]₂ and [Ni(*i*-bn)₂]₂. An aqueous solution containing one equivalent of nickel(II) nitrate and two equivalents of diamine dichloride was adjusted to a pH of 9 by the addition of potassium hydroxide and then saturated with potassium iodide. Upon standing overnight yellow crystals deposited which were recrystallized from acetone. *Anal.* Calcd. for NiC₈H₂₄N₄I₂: C, 19.62; H, 4.91; N, 11.45. Found for [Ni(*m*-bn)₂]₂: C, 20.43; H, 4.93; N, 11.53. Found for [Ni(*i*-bn)₂]₂: C, 19.68; H, 4.92; N, 11.49. (ϵ at 448 m μ is 21.8.) The complex [Ni(*dl*-bn)₂]₂

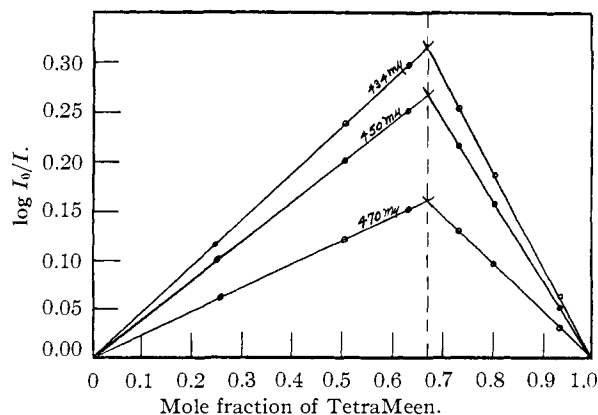


Fig. 2.—Continuous variations studies on the system Ni⁺²-TetraMeen.

(14) Symbols used are the same as those in reference 4h.

was instead recrystallized from a concentrated aqueous solution of potassium iodide. *Anal.* Found: C, 20.00; H, 5.09; N, 11.56.

Calorimetric Measurements.—These measurements of heats of reaction for the formation of $[\text{Cu}(\text{TetraMeen})_2]^{+2}$ and $[\text{Ni}(\text{TetraMeen})_2]^{+2}$ salts were made in a Dewar-type calorimeter by the procedure described previously.¹⁰

Results

The formation constants for copper(II) and nickel(II) complexes are shown in Table I and II, respectively. The data on the stilbenediamine compounds were obtained in 50% dioxane-water solution and these are not comparable to the values obtained in aqueous systems.

TABLE I
FORMATION CONSTANTS OF COPPER(II) WITH C-SUBSTITUTED ETHYLENEDIAMINES

	0°C.			25°C.		
	log K_1	log K_2	log K_T	log K_1	log K_2	log K_T
en	11.34	9.95	21.29	10.76	9.37	20.13
pn	11.65	10.12	21.77	10.78	9.28	20.06
<i>dl</i> -bn	12.22	10.65	22.87	11.39	9.82	21.21
<i>m</i> -bn	11.50	10.05	21.55	10.72	9.34	20.06
<i>i</i> -bn	11.31	9.88	21.19	10.53	9.05	19.58
TetraMeen	12.22	10.88	23.10	11.63	10.24	21.87
<i>dl</i> -Stien	11.03	10.20	21.23	10.07	9.11	19.18
<i>m</i> -Stien	9.30	8.20	17.50	8.46	7.50	15.96

TABLE II
FORMATION CONSTANTS OF NICKEL(II) WITH C-SUBSTITUTED ETHYLENEDIAMINES

	0°C.			25°C.				
	log K_1	log K_2	log K_T	log K_1	log K_2	log K_T		
en	7.92	6.77	5.36	20.05	7.60	6.48	5.03	19.11
pn	8.05	6.80	4.92	19.77	7.43	6.19	4.27	17.89
<i>dl</i> -bn	8.30	7.09	5.00	20.39	7.71	6.48	4.31	18.50
<i>m</i> -bn	7.37	6.16	3.21	16.74	7.04	5.70	2.89	15.63
<i>i</i> -bn	7.27	5.94	2.77	15.98	6.77	5.40	2.25	14.42
TetraMeen								14.68 ^a
<i>dl</i> -stien	7.98	7.98	4.94	19.61	7.37	6.09	4.38	17.84
<i>m</i> -stien	4.97	3.72		8.69	4.70	3.52		8.22

^a Value of log K_1 and log K_2 obtained from spectrophotometric data and pH measurements. This value at 15° is 14.87 and at 39° it is 14.32.

The absorption spectra for solutions containing different ratios of nickel(II) and TetraMeen were determined between 360 and 800 μ . In all of these solutions only one absorption band was found and that at 434 μ . The absorption at this wave length of a solution containing equivalent amounts of nickel(II) and TetraMeen is, within experimental error, exactly half that of one containing the same amount of nickel(II) and two equivalents of diamine (Fig. 1). It would therefore appear that either virtually all the diamine is being used to form $[\text{Ni}(\text{TetraMeen})_2]^{+2}$ or that $[\text{Ni}(\text{TetraMeen})(\text{H}_2\text{O})_4]^{+2}$ has the same absorption spectra as the bis complex. The latter possibility does not appear very probable since the absorption of the mono complex may be expected to more closely resemble that of $[\text{Ni-en}(\text{H}_2\text{O})_4]^{+2}$. That the complex in solution is in fact the ion $[\text{Ni}(\text{TetraMeen})_2]^{+2}$ is supported by the results of a continuous variation study shown in Fig. 2. Similar studies with copper(II) and TetraMeen reveal that both the mono and bis complexes are formed in appreciable concentrations as is also true of nickel(II) with *m*-stien and with TriMeen.

Calorimetric data obtained for the reactions of nickel(II) and copper(II) ions with TetraMeen are shown in Table III. Likewise included for comparison in this table are the thermodynamic data for the analogous reactions with ethylenediamine. Magnetic susceptibilities of some yellow-orange complexes are given in Table IV.

TABLE III
THERMODYNAMIC DATA

Amine	ΔF°	Nickel ΔH°	ΔS°	ΔF°	Copper ΔH°	ΔS°
en	-18.6 ^a	-16.3 ^a	+7	-26.6	-24.6 ^a	+7
TetraMeen	-20.0	-14.1	+20	-29.9	-24.4	+19

^a G. H. McIntyre, Jr., Ph.D. Thesis (1953), Pennsylvania State College.

TABLE IV
MAGNETIC SUSCEPTIBILITY OF SOME $[\text{Ni}(\text{AA})_2]\text{X}_2$ COMPLEXES^a

Complex	Color	χ_s
$[\text{Ni}(\text{TetraMeen})_2]\text{Cl}_2$	Yellow	-0.615×10^{-6}
$[\text{Ni}(m\text{-bn})_2]\text{I}_2$	Yellow	$-.428 \times 10^{-6}$
$[\text{Ni}(i\text{-bn})_2]\text{I}_2$	Orange	$-.205 \times 10^{-6}$
$[\text{Ni}(dl\text{-bn})_2]\text{I}_2$	Yellow	$-.306 \times 10^{-6}$
$[\text{Ni}(\text{TriMeen})_2]\text{I}_2$	Yellow

^a Magnetic measurements were made using the Gouy method by Mr. Steve Adler.

Discussion

The results of this study show that generally C-substitution on ethylenediamine has only a relatively small effect on its coordination tendency toward copper(II) and nickel(II) ions. However, it is of interest that the complexes of *dl*-bn are more stable than those of *m*-bn which is also true of *dl*-stien compared to *m*-stien. These results on *dl*-stien and *m*-stien are in accord with the qualitative observations of Lifschitz, Bos and Kijkema.¹⁵ A consideration of molecular models shows that the five-membered chelate of the racemic bases are free of internal strain as the methyl or phenyl groups have ample room being on opposite sides of the ring. However, the *meso* bases form rings with the substitution on the same side and there would appear to be considerable internal strain resulting from crowding of the adjacent groups.

In order to test this hypothesis the chelating tendencies of TetraMeen and *i*-bn were determined. It should be noted that the resulting five-membered chelate ring of TetraMeen has adjacent methyl groups on both sides of the ring, whereas with *i*-bn the two methyl groups are on the same carbon. Since the complexes of TetraMeen are more stable while those of *i*-bn are less stable than those of either *dl*-bn or *m*-bn, it may appear as if any strain within the chelate ring in these systems must be playing a minor role. It is of interest, however, that these results closely parallel the findings of Kuhn¹⁶ on the intra-

(15) I. Lifschitz, J. G. Bos and K. M. Kijkema, *Z. anorg. allgem. Chem.*, **242**, 97 (1939); I. Lifschitz and J. G. Bos, *Rev. trav. chim.*, **59**, 407 (1940); I. Lifschitz and K. M. Kijkema, *ibid.*, **60**, 581 (1941).

(16) L. P. Kuhn, *This Journal*, **74**, 2492 (1952).

molecular hydrogen bonding in alcohols. This process of hydrogen bonding involves the formation of a ring and is somewhat analogous to the chelation which occurs during the coordination of diamines with metal ions. Kuhn reports that the extent of hydrogen bonding in *d*-butane-2,3-diol and also in tetramethylethylene glycol is greater than that in *meso*-butane-2,3-diol.

An interesting observation was made during the titrations of nickel(II) salt solutions with alkylethylenediamines. The color of the solutions in the *pH* region or maximum concentration of the bis complex, changed from the typical violet-blue of tetramminenickel(II) ion through greenish-yellow to a bright yellow as the extent of C-substitution on the diamine increased. Except for solutions containing either TetraMeen or *m*-stien which remained bright yellow, the addition of excess diamine produced the characteristic violet color of hexamminenickel(II) ion. In other words, nickel(II) does not appear to coordinate with more than two molecules of either TetraMeen or *m*-stien. In fact a sample of $[\text{Ni}(\text{TetraMeen})_2](\text{NO}_3)_2$ has remained unchanged in anhydrous TetraMeen at room temperature for one month. A consideration of molecular models show that coordination of a third molecule of TetraMeen would involve considerable steric hindrance.

Several of these yellow salts have been isolated and found to be diamagnetic (Table IV). It therefore appears that they are of the dsp^2 -type and thus have a planar configuration. It is of interest to speculate as to why this tendency toward the formation of a planar complex should be enhanced by the increased C-substitution on ethylenediamine. One possible interpretation is that the increased alkyl substitution renders the bis complex more hydrophobic such that the coordinated water molecules in the complex $[\text{Ni}(\text{AA})_2(\text{H}_2\text{O})_2]^{+2}$ are repelled to yield the tetravalent ion $[\text{Ni}(\text{AA})_2]^{+2}$. This assumption receives some support from the fact that even the ethylenediamine complex $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{+2}$ has been shown¹⁷ to produce an orange diamagnetic salt of the ion $[\text{Ni}(\text{en})_2]^{+2}$ upon removal of the coordinated water.

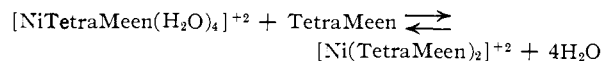
That the formation constant K_2 is appreciably larger than K_1 for the stepwise formation of $[\text{Ni}(\text{TetraMeen})_2]^{+2}$ is not without precedent. For example, K_3 is larger than either K_1 or K_2 for the formation of tris-(1,10-phenanthroline)-ion(II).¹⁸ It has been suggested⁴³ that unusual behaviors of this type may result from sudden changes in bond type or orbital hybridization. For example the

(17) H. Glaser and P. Pfeiffer, *J. prakt. Chem.*, **153**, 300 (1939); C. M. Harris, *Proc. Roy. Soc. N. S. Wales*, **85**, 142 (1953).

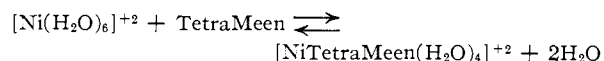
(18) T. S. Lee, I. M. Kolthoff and D. L. Leussing, *THIS JOURNAL*, **70**, 2348, 3596 (1948); **72**, 2173 (1950).

mono and bis iron(II) complexes may be primarily ionic (sp^3d^2) and on coordination of a third molecule of 1,10-phenanthroline from the covalent d^2sp^3 tris complex. In an analogous fashion one may suggest that the nickel(II) complex $[\text{NiTetraMeen}(\text{H}_2\text{O})_4]^{+2} - sp^3d^2$ changes to the more covalent bond structure $[\text{Ni}(\text{TetraMeen})_2]^{+2} - dsp^2$.

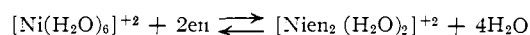
An alternative explanation¹⁹ to account for the large value of K_2 as compared to K_1 is that a greater increase in entropy is associated with the second step



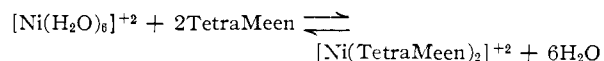
than the first step



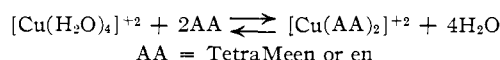
The greater increase in entropy may be expected to result from the release of four molecules of water in the second step as compared to only two for the first step. Consistent with this view is the fact that an entropy increase of +7 cal./deg. was observed for the reaction



Whereas a value of +20 cal./deg. was obtained (Table III) for



It is believed that the greater increase in entropy for the TetraMeen reaction compared to that of the ethylenediamine (en) reaction can in part at least be attributed to the release of two more molecules of water. However, approximately the same difference in entropy was observed for the analogous reactions of copper(II). Since the coordination number of copper(II) is generally believed to be four, it should follow that in both of these reactions



four molecules of water are released. It would therefore appear that either the amount of water released does not make a major contribution to the changes in entropy or that in aqueous solution there are in fact six molecules of water associated with the copper(II) ion. The latter reason would seem to be the more plausible one as there have been several reports of hexacoordinated copper(II) complexes.²⁰

EVANSTON, ILLINOIS

(19) M. Calvin, private communication.
(20) P. Pfeiffer and K. Pimmer, *Z. anorg. Chem.*, **48**, 98 (1905); F. Rosenblatt, *ibid.*, **204**, 351 (1932); J. M. Jaeger and J. H. VanDyk, *Proc. Koninkl. Akad. Amsterdam*, **37**, 395 (1934).