sure the compound volatilizes only slowly above 150°; it is readily soluble in chloroform, rather less soluble in carbon tetrachloride, alcohol, carbon disulfide, benzene and sparingly soluble in ligroin. It is insoluble in and unaffected by dilute acids or bases and aqueous oxidizing agents such as ceric sulfate. On treatment with nitric acid, 6 N or stronger or with bromine water, the compound is decomposed with evolution of carbon monoxide. There is no evidence for the formation of any complex cyclopentadienyl ions. The molecular weight was determined by cryoscopy using benzene as solvent; a value of 455 ± 20 was obtained, the calculated value being 461.0. The measured molar susceptibility was $\chi_{mol}^{298°K.} = -210 \pm 5 \times 10^{-6}$ c.g.s.u.

Tungsten cyclopentadienyl carbonyl is also a purple-red crystalline substance having a m.p. 240–242° with decomposition. *Anal.* Calcd.: C, 28.86; H, 1.50; W, 55.25. Found: C, 28.94; H, 1.68; W, 55.23. The compound is readily soluble in chloroform, but rather less soluble than its molybdenum analog in other organic solvents, and is insoluble in ligroin. It is unaffected by dilute acids, bases and aqueous oxidizing agents except 6 N nitric acid or bromine, which cause decomposition. The molecular weight by cryoscopy in benzene was 650 ± 20 (calculated 666.0). The compound is diamagnetic, $\chi_{mol}^{298°K.} = -220 \pm 5 \times 10^{-6}$ c.g.s.u.

The low solubility of both the molybdenum and tungsten cyclopentadienyl carbonyls in carbon disulfide or carbon tetrachloride allows only the infrared C–O frequencies to be observed using these solvents; solutions 1 mg./ml. concentration in carbon tetrachloride were used for high resolution in the C–O region with a Perkin–Elmer single beam instrument. The spectra over the 650–4000 cm.$^{-1}$ region were obtained using 1 inch diameter wafers formed under 40,000 lb. pressure from 1.5 g. of potassium iodide and a few mg. of the compound intimately ground together.

Analyses of molybdenum were made by the lead molybdate method (ref. 10, p. 589) and of tungsten by the cinchonine-tungstic oxide procedure (ref. 10, p. 1011); in both cases, organic material was first destroyed by oxidation with perchloric acid.

CAMBRIDGE, MASS.

Steric Effects and the Stability of Complex Compounds. II. The Chelating Tendencies of N,N'-Dialkylethylenediamines with Copper(II) and Nickel(II) Ions[1]

BY FRED BASOLO AND R. KENT MURMANN[2]

The stepwise formation constants for RHNCH₂CH₂NHR (R = methyl, ethyl, *n*-propyl or *n*-butyl), with copper(II) and nickel(II) ions have been determined at 0° and 25°. The results show an appreciable steric effect in the case of the N,N'-dialkylethylenediamines compared to the N-alkylethylenediamines and unsubstituted ethylenediamine. N,N'-Diisopropylethylenediamine did not form normal complexes with copper(II) and nickel(II) ions.

While correlation of the stepwise formation constants of a metalammine with the base strength of the amine is usually good, there are several examples of irregularities that have been attributed to steric factors.[3] The magnitude of this effect has been determined in the case of N-alkylethylenediamines[4] and was found to increase with increasing alkyl size. This paper is the second in a series of investigations to determine the effect of steric hindrance on the stability of complex compounds.

Reported here are the results obtained on the chelating tendencies of N,N'-dialkylethylenediamines with copper(II) and nickel(II) ions in 0.50 M potassium nitrate as measured by the Bjerrum titration technique.[5] Since the N,N'-dialkylethylenediamines have approximately the same base strength,[6] any large difference in the formation constants of the chelate may be attributed to steric hindrance. Copper(II) and nickel(II) ions were chosen in order to study the effect of steric hindrance in complexes having a planar configuration as well as octahedral.

Experimental

Calculation of Formation Constants.—The concentration formation constants for equilibria of the type [MA$_{(n-1)}$] + A ⇌ [MA$_n$] are designated by the expression $K_n = $ [MA$_n$]/ [MA$_{(n-1)}$] [A].

These constants may be found by measuring the pH of solutions containing known amounts of the metal ion plus hydrogen ion and a large amount of a non-complexing electrolyte. The maximum value of $\bar{n}$ for systems investigated here was 3 and the modified development previously reported[4] was applied. This method of calculation is valid only if the pH is higher than 4.5 as was the case in all of the titrations reported here. Each of the constants was measured at two temperatures, 0° and 25°. However, it has been observed since paper I in this series[4] that values of enthalpy and entropy derived from equilibrium data measured at only two temperatures can be greatly in error, therefore these values are not presented. Each titration was conducted at least twice, the formation constants for the two determinations not varying by more than ±0.02 log K unit.

Reagents.—The amines N,N'-diMeen, N,N'-diEten, N,N'-di-*n*-Pren and N,N'-di-*n*-Buen[7] were prepared by the method of Schneider.[8] N,N'-Di-*i*-Pren was obtained by a modification of the procedure of Zienty[9] using ethylene dibromide and isopropylamine. The preparation and properties of the amines used in this investigation have been described in a previous note.[6]

Standard Solutions.—The amines were diluted with distilled water until approximately 5 M and then standard-

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

(2) 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.

(3) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

(4) F. Basolo and R. K. Murmann, THIS JOURNAL, **74**, 5243 (1952).

(5) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(6) F. Basolo, R. K. Murmann and Y. T. Chen, THIS JOURNAL, **75**, 1478 (1953).

(7) The diamines discussed here are designated as follows: N,N'-diMeen = N,N'-dimethylethylenediamine, N,N'-diEten = N,N'-diethylethylenediamine, N,N'-di-*n*-Pren = N,N'-di-*n*-propylethylenediamine, N,N'-di-*n*-Buen = N,N'-di-*n*-butylethylenediamine, and N,N'-di-*i*-Pren = N,N'-di-*i*-propylethylenediamine.

(8) P. Schneider, *Ber.*, **28**, 3074 (1895).

(9) F. B. Zienty, THIS JOURNAL, **68**, 1388 (1946).

ized with standard hydrochloric acid by conductometric and pH titration. Both methods gave the same result. The molarity of the amine solutions thus prepared was known with an accuracy of 2 parts per thousand (p.p.t.).

The copper standard solution, approximately 0.1 M nitric acid, 0.05 M copper nitrate and 0.50 M potassium nitrate, was standardized: the copper by electrodeposition, the nitric acid by titration against standard base. The primary standard for all acid–base titrations was a sample of potassium acid phthalate obtained from the Bureau of Standards. The molarities of the copper solutions were known to 2 p.p.t. and that of the nitric acid 1 p.p.t.

The nickel nitrate standard solution was prepared in the same manner as the copper solution and the concentration of the nickel determined either by electrodeposition or by precipitation with dimethylglyoxime. The nickel molarity was known to 2 p.p.t. and the nitric acid concentration to 1 p.p.t.

All chemicals used were of analytical reagent grade and the potassium nitrate was recrystallized before use. Measurements of pH were made with a Beckman pH meter, model G, equipped with a model 1190–90 glass electrode. A saturated calomel electrode model E was used in conjunction with the glass electrode. The solutions were maintained at a constant temperature by means of a constant temperature bath at 25 ± 0.1°, and by means of an intimate mixture of ice and water at 0 ± 0.1°.

Calorimetric Measurements.—All heat measurements were made with a Dewar-type calorimeter equipped with a Beckmann thermometer and a light weight stirrer. The calorimetric constant of 6.8 cal./deg. was determined by measurements on the reaction $BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2NaCl$. The heat of neutralization of sodium hydroxide with hydrochloric acid measured with this calorimeter checked literature values to within 1%. The heat evolved was measured upon the addition of a concentrated solution of either $Ni(NO_3)_2$ or $Cu(NO_3)_2$ to a dilute solution containing an excess of diamine and 0.50 M KNO_3. The heat of dilution of the metal salt, the heat of dilution of the diamine–KNO_3 solution, and the heat capacity of the complex–amine solution were taken into account in the calculation of the enthalpies of the reaction.

Results

The $p[A]$ and the $\bar{n}$ values were calculated for each point in the titration and a graph of $\bar{n}$ vs. $p[A]$ was made for each amine. With copper(II) ion a nearly constant value of $\bar{n} = 2$ was obtained toward the end of the titration indicating a maximum coördination number of four. On the other hand, nickel(II) showed a maximum of $\bar{n}$ equal to three with N,N'-diMeen and N,N'-diEten. However, with N,N'-di-n-Pren the curve leveled off at $\bar{n} = 2$ and thereafter rose slowly to a value of $\bar{n} = 2.2$ at the end of the titration, which showed the stability of the tris compound to be low. N,N'-Di-n-Buen leveled off at $\bar{n} = 1$ and slowly rose to a value of 1.4 at the end of the titration indicating the small stability of the bis-(N,N'-di-n-Buen)-nickel(II). N,N'-di-i-Pren behaved differently and gave a precipitate when added to both metal ion solutions. Nickel solutions gave $Ni(OH)_2$ while copper solutions precipitated a substance whose formula is believed to be bis-N,N'-di-i-Pren-μ-dihydroxodicopper(II) nitrate.[10] Therefore we were unable to determine formation constants in water with this ligand.

Table I contains the stepwise formation constants for copper(II) and nickel(II) chelates and the ratios $\log K_{me}^{+2}$(av.)/$\log K_{AH}^+$ and $\log K_1/K_2$ which may be related to the steric effect. Ethylenediamine, though not measured in this investigation, is included for comparison.[4] Figures 1 and 2 graphi-

(10) M. Calvin and A. E. Martell, "Chemistry of Metal Chelate Compounds," Prentice–Hall, Inc., New York, N. Y., 1952, p. 170.

cally represent the formation constants for nickel and copper chelates, respectively. The heats of reaction of ethylenediamine and N,N'-diethylethylenediamine with nickel(II) and copper(II), respectively, as determined by calorimetric measurements are shown in Table II. During the investigation several solid compounds were isolated by crystallization from water solutions containing an excess of amine. Their constitution and analyses are given in Table III.

TABLE I
FORMATION CONSTANTS OF NICKEL(II) AND COPPER(II) IONS WITH N,N'-DIALKYLETHYLENEDIAMINES

	en	N,N'-DiMeen	N,N'-DiEten	N,N'-Di-n-Pren	N,N'-Di-n-Buen
Nickel(II), 0°					
$\log K_1$	7.92	7.87	7.42	5.87	6.03
$\log K_2$	6.77	5.28	4.76	3.0	...
$\log K_3$	5.36	2.5	2	...	...
$\log K_T$	20.05	15.65	14.18	8.87	6.03
$\log K_1/K_2$	1.15	2.59	2.76	2.85	...
$\dfrac{\log K_{Ni}^{+2} \text{ (ave.)}}{\log K_{AH}^+}$	0.62	0.60	0.55	0.41	0.28
25°					
$\log K_1$	7.60	7.11	5.62	5.52	5.42
$\log K_2$	6.48	4.73	3.3	2.5	...
$\log K_3$	5.03	1.5	...	...	...
$\log K_T$	19.11	13.34	8.92	8.02	5.42
$\log K_1/K_2$	1.12	2.38	2.32	3.0	...
$\dfrac{\log K_{Ni}^{+2} \text{ (ave.)}}{\log K_{AH}^+}$	0.63	0.58	0.43	0.34	0.27
Copper(II), 0°					
$\log K_1$	11.34	11.22	10.84	9.39	9.44
$\log K_2$	9.95	8.31	7.85	6.15	6.54
$\log K_T$	21.29	19.53	18.69	15.54	15.98
$\log K_1/K_2$	1.39	2.91	2.99	3.24	2.90
$\dfrac{\log K_{Cu}^{+2} \text{ (ave.)}}{\log K_{AH}^+}$	0.99	0.90	0.84	0.71	0.73
25°					
$\log K_1$	10.76	10.47	9.30	8.79	8.67
$\log K_2$	9.37	7.63	6.32	5.55	4.84
$\log K_T$	20.13	18.10	15.62	14.34	13.51
$\log K_1/K_2$	1.39	2.84	3.02	3.24	3.83
$\dfrac{\log K_{Cu}^{+2} \text{ (ave.)}}{\log K_{AH}^+}$	1.04	0.88	0.74	0.70	0.65

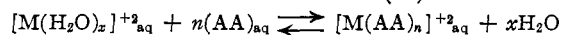## Discussion

A decrease in magnitude in the ratio $\log K_{me}^{+2}$(ave.)/$\log K_{AH}^+$ in a series of closely related complex compounds has been shown to be an indication of steric hindrance.[3,4] Furthermore, an increase in the difference between successive formation constants may be attributed to the greater steric hindrance afforded by coördinated amine molecules (K_2) as compared with coördinated water molecules (K_1). The data obtained (Table I) give strong evidence of a steric effect in the N,N'-dialkylethylenediamine series. The copper(II) complex with ethylenediamine gives a value of about 1.4 for $\log K_1/K_2$, which is significantly lower than that obtained for the N-alkylethylenediamines,[4] 1.7, and considerably lower than the average value of 3 obtained with the N,N'-dialkylethylenedia-

TABLE II

THERMODYNAMIC DATA (0°)

$$[M(H_2O)_x]^{+2}{}_{aq} + n(AA)_{aq} \rightleftharpoons [M(AA)_n]^{+2}{}_{aq} + xH_2O$$

		Nickel			Copper			
Amine	n	ΔF^0	ΔH^0	ΔS^0	n	ΔF^0	ΔH^0	ΔS^0
Ethylenediamine	3	−25.1	−24.9[a]	+1	2	−26.6	−24.6[a]	+7
	2	−18.1	−16.3	+7[b]				
N-Methylethylenediamine[b]	2	−17.2	−17.0	+1	2	−25.3	−23.0	+8
N,N'-Diethylethylenediamine	2	−15.3	−7.8	+27	2	−23.3	−17.5	+21

[a] The values obtained calorimetrically are in accord with values calculated from potentiometric data by Calvin and Bailes[11] and McIntyre,[12] but do not agree with that of Irving[13] and of Basolo and Murmann.[4]   [b] G. H. McIntyre, Jr., Ph.D. Thesis, Pennsylvania State College, 1953.

TABLE III

COMPLEX COMPOUNDS ISOLATED FROM AQUEOUS SOLUTION

	Calculated			Found		
Formula	C	H	N	C	H	N
[Cu(N,N'-diMeen)₂]Br₂	24.05	6.21	14.04	24.35	6.20	14.30
[Ni(N,N'-diMeen)₂(H₂O)₂]Br₂	22.32	6.51	13.00	22.10	6.32	12.87
[Cu(N,N'-di-n-Pren)₂](NO₃)₂	40.40	8.41	17.66	40.24	8.97	17.41
[Ni(N,N'-di-n-Pren)₂(H₂O)₂](NO₃)₂	37.81	8.76	16.56	37.97	8.72	16.83
[Ni(N,N'-diEten)₂(H₂O)₂](NO₃)₂	31.92	7.99	18.62	32.19	8.05	...
[Cu(N,N'-di-n-Buen)₂](NO₃)₂	45.20	9.04	15.81	45.73	9.13	15.69

mines. The same trends occur among the nickel(II) complexes, with the approximate values of 1.1, 1.5 and 3, respectively. Thus it would appear that the interaction of a coördinated amine with coördinated waters is dependent on the extent of alkyl substitution. It is also apparent from these results that the steric hindrance between two amines attached to the same metal ion is greater than that between one amine and water molecules. Furthermore, the values of the expression $\log K_{me}{}^{+2}$ (ave.)/$\log K_{AH}{}^+$ for copper(II) and nickel(II) ions show a gradual decrease in this series. Similarly, the ratio $\log K_{me}{}^{+2}$(ave.)/$\log K_{AH}{}^+$ decreases and the difference between successive formation constants

increases with increasing size of alkyl groups in this series of N,N'-dialkylethylenediamines. Thus the results obtained clearly indicate the marked effect of alkyl size and number of alkyl groups in the tendency of analogous ethylenediamines to coördinate.

Figures 1 and 2 show a gradual decrease in stability from methyl to the n-propyl derivative, but this is followed by a slight increase in $\log K_1$ at N,N'-di-n-Buen. A leveling off in stability at this point was also noted in the N-alkylethylenediamine series, and may be attributed to the ability of the long chain to become coiled around the central metal ion, shielding it from interaction with the solvent.
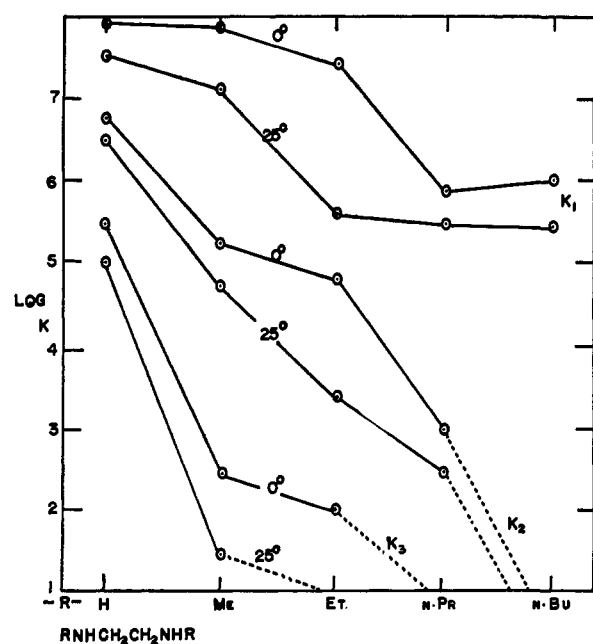

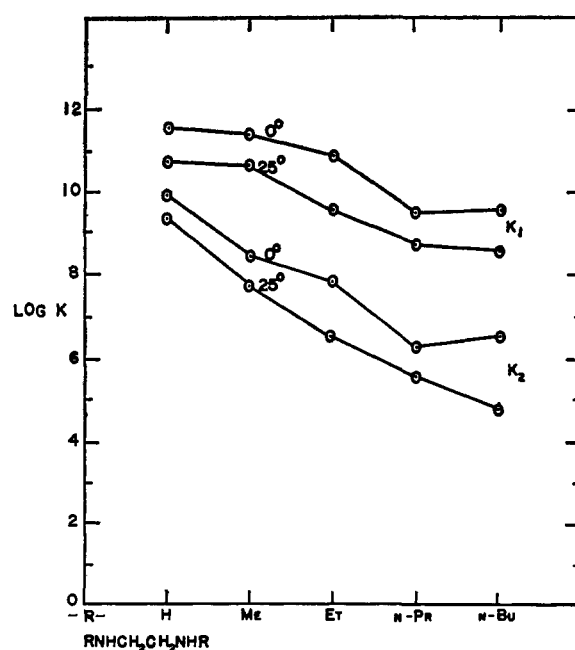Fig. 1.—Formation constants of nickel(II) with N,N'-dialkylethylenediamines.

Fig. 2.—Formation constants of copper(II) with N,N'-dialkylethylenediamines.

(11) M. Calvin and R. Bailes, THIS JOURNAL, 68, 953 (1946).

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

(13) H. Irving, unpublished results, taken from a summary paper of a talk given in 1951 on "The Stability of Coördination Compounds in Aqueous Solution and Varying Strength of the Metal-Ligand Bond,"

Molecular models indicate increased strain in the formation of $[M(AA)_2]^{+2}$ as compared to $[M(AA)]^{+2}$ complex ions. This is readily apparent experimentally in Figs. 1 and 2. Furthermore the $[Ni(AA)_3]^2$ complexes were formed only by the methyl and ethyl derivatives and, since they are not too stable, these values are only semi-quantitative.

That the N,N'-di-n-Pren chelates are considerably more stable than those of the corresponding branched chain isomer (N,N'-di-i-Pren) was demonstrated by the fact that in aqueous solution nickel(II) yielded only the hydroxide and copper(II) formed an entirely different species[10] (A). However, a cold alcoholic solution containing copper ion and an excess of amine yielded large deep-purple crystals of the normal type (B). Since in water solution, metal hydroxide precipitation is always in competition with the formation of metalammines, one would expect precipitation of the hydroxide only when the stability of the complex is too low to keep the concentration of the metal ion below a value which would exceed the solubility product.

$[(N,N'-di-i-Pren)Cu \langle{}^{O}_{O}\rangle Cu(N,N'-di-i-Pren)](NO_3)_2$ (A)
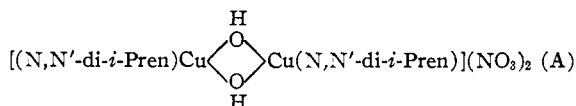
Anal. Calcd. for $Cu_2C_{16}H_{42}N_6O_8$: Cu, 22.27; N, 14.66. Found: Cu, 22.53; N, 14.79.

$[Cu(N,N'-di-i-Pren)_2](NO_3)_2$ (B)
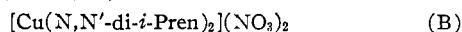
Anal. Calcd. for $CuC_{16}H_{40}N_6O_6$: Cu, 13.37; N, 17.66. Found: Cu, 13.23; N, 17.39.

The increased steric effect in branched chain compared to normal alkyl substituents was also observed with the N-alkylethylenediamines,[4] but as expected is much more pronounced in the N,N'-dialkylethylenediamine series.

Finally it should be repeated that values of enthalpy and entropy calculated from titration data can be given only qualitative significance. It was therefore decided to determine the heats of reaction by direct calorimetric measurements. Direct heat measurements were made on the systems copper(II) and nickel(II) ions with ethylenediamine and N,N'-diethylethylenediamine. The values of ΔH^0 from calorimetric data and those of ΔF^0 obtained from the formation constants together with the values of ΔS^0 calculated from these quantities are shown in Table II.

The values of ΔH^0 for the N,N'-diethylethylenediamine complexes are observed to be significantly lower than those of the corresponding unsubstituted ethylenediamine complexes. If ΔH^0 is considered to be a measure of bond strength, it is evident that there is a strong steric hindrance operating in the formation of the metalammine.

Calvin and Bailes[11] have shown that the conversion of $[Ni(NH_3)_6]^{+2}$ into $[Ni(en)_3]^{+2}$ involved an increase in entropy of 24 cal./deg. The greater portion of this increase in entropy they attributed to the fact that the reaction is accompanied by an increase in the number of particles. This results from ammonia being monodentate, whereas ethylenediamine is bidentate. It therefore follows that the replacement of one bidentate by another bidentate will occur with the same number of particles on the right side of the reaction as there are on the left. In such a case if the bidentate groups involved are sufficiently similar that there is little change in the second coördination sphere one would anticipate only a small difference in entropy. Consistent with this assumption are the recent results obtained by McIntrye[12] on the system

$$[M(en)_2]^{+2}{}_{aq} + 2(Meen)_{aq} = [M(Meen)_2]^{+2}{}_{aq} + 2(en)_{aq}$$
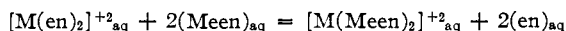
which gave ΔS^0 values of -6 and $+1$ for nickel(II) and copper(II) complexes, respectively. It is to be expected that this difference in entropy will become larger as the extent of substitution on the ethylenediamine increases. The results obtained with N,N'-diethylethylenediamine of $+20$ and $+14$ cal./deg. for ΔS lend support to this supposition. Furthermore, it would appear that the increase in entropy is at least largely due to an increase in randomness of the system resulting from a release of water molecules from the second coördination sphere of N,N'-dialkylethylenediamine complexes. Since the hydration of the substituted ethylenediamine is probably comparable to that of ethylenediamine, the large entropy values may be attributed to differences in the hydrophilic character of the metalammine complexes.

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