

The Stabilities of Complexes formed by Some Bivalent Transition Metals with N-Alkyl-substituted Ethylenediamines.

By H. IRVING and J. M. M. GRIFFITHS.

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The acid dissociation constants of *NN'*-dimethyl-, *NN*-dimethyl-, and *NN*-diethyl-ethylenediamine, together with the stability constants of the complexes formed by these diamines with nickel, copper, and zinc ions, have been determined in 0.1M-potassium chloride at 25°. Here, as with mono-*N*-alkyl-ethylenediamines, increasing substitution reduces the stabilities of the metal complexes relative to those of the corresponding proton complexes. The results can be interpreted in terms of steric hindrance to coordination and this also accounts for the preferential formation of basic or polynuclear complexes when metals react with more highly substituted ligands. A spectrophotometric study of the system cupric ions-*NN'*-dimethylethylenediamine confirms the existence of only 1:1 and 1:2 complexes, whose absorption characteristics have been measured and compared with those of the corresponding ethylenediamine complexes.

ALTHOUGH *N*-methylethylenediamine, the symmetrical *NN'*-diethylethylenediamine ("dimen"), and the unsymmetrical *NN*-diethylethylenediamine resemble ethylenediamine itself in giving deep violet solutions with cupric salts from which crystalline perchlorates of complex ions of type (I) or (II) ($R = H$ or alkyl) can be separated, Pfeiffer and Glaser (*J. pr. Chem.*, 1938, **151**, 134) found that the tri-*N*-alkyl-substituted derivatives gave binuclear complexes with OH bridges of type (III; $R = R' = \text{alkyl}$) while *NN'*-diethyl-*N*-phenylethylenediamine gave only a greenish precipitate which quickly darkened and formed a resin. These results, and abortive attempts to prepare ammine complexes of Cr^{3+} and Co^{3+} from *N*-alkyl-substituted ethylenediamines were explained in terms of steric hindrance.

Now the replacement of hydrogen atoms in ammonia by alkyl groups always has a

Excellent agreement is obtained for values of pK_{BH^+} by the two methods but more weight ought perhaps to be given to values of $pK_{BH_2^{++}}$ obtained by titration, since shortage of diamine made it necessary to use smaller volumes when studying the pH of the more acid mixtures by the "separate solutions" procedure. An error in $pK_{BH_2^{++}}$ will introduce an equivalent error in computing $\log K_1$ and $\log K_2$ (see p. 216) in addition to any experimental errors incurred.

Table 1 summarises our measurements at 25°, together with data from various sources for other amines.

Values of pK_{BH^+} refer to the addition of the first proton to the diamine. While a single alkyl group produces a small increase in basic strength, there is a marked decrease on introduction of a second on the same nitrogen atom, the effect being more marked with methyl than with ethyl groups. A second alkyl group placed symmetrically has only a slight effect. In these respects ethylenediamine may be compared with ethylamine where similar changes of basic strength are produced by alkylation, the values of pK_{BH^+} being respectively 10.66 for ethylamine, 11.0 for diethylamine, and 10.72 for triethylamine. The addition of a second proton at the nitrogen atom separated from the 'onium ion by a chain of two carbon atoms ought not to be too greatly influenced by the number and nature of the alkyl substituents there. Values of $pK_{BH_2^{++}}$ show this to be true for single methyl or ethyl substituents; but two alkyl groups cause a definite base-weakening effect which is especially marked with two methyl groups placed unsymmetrically as in $NH_2 \cdot CH_2 \cdot CH_2 \cdot NMe_2$. Correction for the statistical effect (Bjerrum, *op. cit.*) would alter the apparent acid dissociation constants of ethylenediamine to 9.88 and 7.77 and those of

TABLE 1. Acid dissociation constants at 25° of N-alkyl-substituted ethylenediamines of the type, $NRR' \cdot CH_2 \cdot CH_2 \cdot NHR''$.

R	R'	R''	pK_{BH^+}	$pK_{BH_2^{++}}$	Δ	Refs.	R	R'	R''	pK_{BH^+}	$pK_{BH_2^{++}}$	Δ	Refs.
H	H	H	10.18	7.47	2.71	a, b	Et	H	H	10.56	7.63	2.93	a
			10.17	7.44	2.73	c, d				10.36	7.42	2.94	c
Me	H	H	10.40	7.56	2.84	a	Et	Et	H	10.02	7.07	2.95	e
			10.32	7.42	2.90	c	Me	H	Me	10.16	7.40	2.76	e
Me	Me	H	9.53	6.63	2.90	e	Pr ⁱ	H	H	10.62	7.70	2.92	a

^a Basolo and Murmann, *J. Amer. Chem. Soc.*, 1952, **74**, 2373. Measurements with a glass electrode in a medium 0.5M with respect to potassium nitrate and 0.05M with respect to barium nitrate. ^b Everett and Pinsent (*Proc. Roy. Soc.*, 1952, **215**, A, 417) report very precise data covering a wide range of ionic strengths, amine concentrations, and temperatures, from which thermodynamic constants are calculated. ^c Keller and Edwards, *J. Amer. Chem. Soc.*, 1952, **74**, 2931. Measurements with the hydrogen electrode in M-potassium chloride containing 0.1M-barium chloride. ^d Additional values for ethylene diamine are quoted by Bjerrum (*loc. cit.* and *op. cit.*). ^e Present authors.

the other symmetrical base, *NN'*-dimethylethylenediamine, to 9.86 and 7.70. The corrections appropriate to the unsymmetrical diamines cannot be calculated with any confidence, but they will certainly be small. The effect of these corrections will be to emphasise the effects of alkyl substitution on basic strength already noted.

The Stability Constants of Copper-Diamine Complexes.—The stability of complexes formed between cupric ions and symmetrical *NN'*-dimethylethylenediamine ("dimen") was studied by measuring the pH of mixtures containing known total concentrations of ligand, C_B , of acid, C_H , and of metal, C_M ; a constant ionic strength was maintained by making each solution 0.1M with respect to potassium chloride. Knowing K_{BH^+} and $K_{BH_2^{++}}$ from previous measurements it is possible to calculate the concentration, $[B]$, of ligand which is complexed neither to proton nor to metal from the equation:

$$[B] = \alpha(C_H - [H^+])/\bar{n}_B \quad \dots \quad (3)$$

$$\text{where} \quad \alpha = K_{BH^+}K_{BH_2^{++}}/(K_{BH^+}K_{BH_2^{++}} + K_{BH_2^{++}}[H^+] + [H^+]^2) \quad \dots \quad (4a)$$

$$\text{and} \quad \bar{n}_B = (K_{BH_2^{++}}[H^+] + 2[H^+]^2)/(K_{BH^+}K_{BH_2^{++}} + K_{BH_2^{++}}[H^+] + [H^+]^2) \quad \dots \quad (4b)$$

The ligand number, or degree of formation of the complex, is then given by

$$\bar{n} = \{C_B - (C_H - [H^+])/\bar{n}_B\}C_M \quad \dots \quad (5)$$

Fig. 1 (open circles) shows the formation curve, *viz.*, the plot of \bar{n} against pB , for the system cupric ions—"dimen." From this it is apparent that the highest complex formed has a molar ratio Cu^{++} : "dimen" of 1 : 2, while its perceptibly wave-like character shows that the first molecule of ligand becomes chelated with appreciably greater ease than the second (Bjerrum, *op. cit.*). Fig. 1 (solid circles) presents data obtained by titrating an acid solution of 0.05M-copper sulphate with 1.503M—"dimen" in 0.1M-potassium chloride. The formation curve is scarcely distinguishable from the former and calculations of the stability constants (cf. Irving and Rossotti, *J.*, 1953, 3397)

$$K_1 = [CuB^{++}]/[Cu^{++}][B], \text{ and } K_2 = [CuB_2^{++}]/[CuB^{++}][B]$$

where B represents the diamine used gave the following results :

	$\log K_1$	$\log K_2$	$\log K_1/K_2$
Using separate solutions	9.66	6.68	2.98
By titration procedure	9.69	6.71	2.99

To economise in amine, the titration procedure was used in all the following measurements.

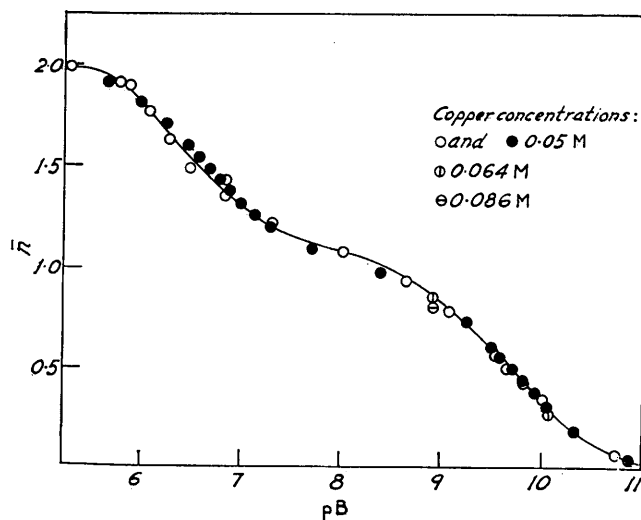


FIG. 1. Formation curve for 0.05M-copper and NN'-dimethylethylenediamine at 25°. Open circles refer to separate solutions; black circles refer to the titration method.

The possibility of binuclear complexes (*e.g.*, III) being formed is not excluded by Fig. 1. However, titrations with 0.064M- and 0.086M-cupric solutions in addition to those with 0.05M-solution gave substantially the same formation curves (cf. Fig. 1.; only a few of the experimental points are shown) so that this possibility may be excluded.

TABLE 2. Stability constants at 25° of cupric complexes of diamines of the type $NRR' \cdot CH_2 \cdot CH_2 \cdot NHR''$.

R	R'	R''	$\log K_1$	$\log K_2$	$\log K_1/K_2$	pK_{BH^+}	$\frac{1}{2} \log K_1 K_2 / pK_{BH^+}$	Refs.
H	H	H	10.73	9.30	1.43	10.18	0.98	a
			10.76	9.37	1.39	10.18	0.99	b
Me	H	H	10.55	8.56	1.99	10.40	0.92	b
Et	H	H	10.19	8.38	1.81	10.56	0.88	b
Pr ^a	H	H	9.07	7.45	1.62	10.62	0.78	b, c
Me	H	Me	9.69	6.65	3.04	10.16	0.80	d
Me	Me	H	9.23	6.73	2.50	9.53	0.73	d
Et	Et	H	8.17	5.55	2.60	10.02	0.68	d

^a Bjerrum and Nielsen, *Acta Chem. Scand.*, 1948, 2, 297. Copper amalgam, and glass electrode measurements in M-potassium nitrate. ^b Basolo and Murmann, *J. Amer. Chem. Soc.*, 1952, 74, 5243. Glass electrode with 0.5M-potassium nitrate, 0.1M-nitric acid, and 0.05M-copper nitrate. ^c Data for R = Pr^a and Bu^a by the same authors show closely similar trends. ^d Present authors.

Table 2 summarises measurements with several diamines from which it will be obvious that although *N*-methylethylenediamine is a stronger base than ethylenediamine

(cf. Table 1) it does not form a stronger complex with cupric ions; that this is due to steric factors is confirmed by the perceptibly greater difficulty with which the second molecule of diamine is chelated. In cupric complexes a square planar configuration is to be expected, and although *cis-trans*-isomerism is possible with unsymmetrical diamines the effect of steric factors, which can readily be demonstrated with the aid of models, will be to favour the *trans*-configuration.

Despite the increase in basicity when ethyl replaces methyl in a mono-*N*-alkyl-substituted ethylenediamine (Table 1) there is a decrease in the stability of both 1 : 1 and 1 : 2 metal complexes. This effect is even more marked with the bulky *isopropyl* group. Disubstitution produces a further decrease in the stability of 1 : 1 complexes which is quite definite in the case of the symmetrical "dimen," great for the unsymmetrical $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$, and still greater for the diethyl analogue. With these disubstituted amines the steric hindrance which opposes complex formation is especially noticeable in the attachment of the second molecule of ligand—as would again be expected from an

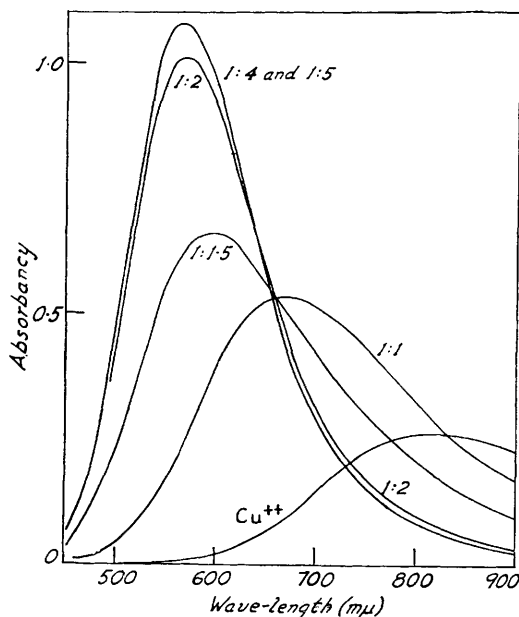


FIG. 2. The absorption spectra of cupric ion and *NN'*-dimethylethylenediamine complexes. The molar ratio $[\text{Cu}^{++}] : [\text{ligand}]$ is shown on the graph.

examination of scale models. The magnitude of the effect is clearly shown both by the increase in the ratio $\log K_1/K_2$ (Table 2) which serves to compare the change in free energy on attachment of the first and the second ligand molecule (with concomitant replacement of solvated water), and by the trend in the values shown in the penultimate column of Table 2 which show how the average free energy of complex formation with cupric ions decreases in comparison with the free-energy change in complex formation with a proton.

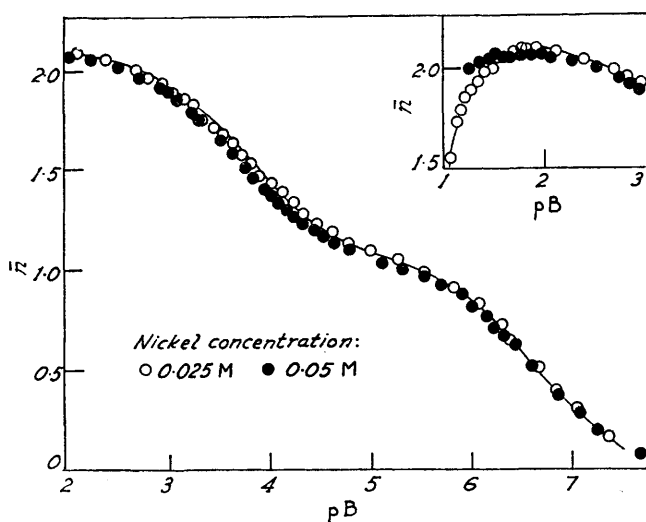
Fig. 2 shows the absorption spectra of mixtures of copper sulphate and "dimen" in molecular proportions varying from 1 : 1 to 1 : 5. The isobestic point at 660 $m\mu$, and the fact that further increase in ligand concentration produced no change in the absorption spectrum demonstrates that the only complexes present are $\text{Cu}(\text{dimen})^{++}$ and $\text{Cu}(\text{dimen})_2^{++}$. Knowing the stability constants for the system it is possible to calculate the parameters of the absorption spectrum of each individual complex (Bjerrum, *op. cit.*). These are given in Table 3 with corresponding values for the copper-ethylenediamine system interpolated from data by Bjerrum and Nielsen (*Acta Chem. Scand.*, 1948, 2, 297). The large increase in molecular extinction coefficient caused by symmetrical *N*-methylation is of the same order as that observed when a tridentate polyamine replaces ethylenediamine, for from data given by Crumpler (*Analyt. Chem.*, 1947, 19, 325) in a study of potential reagents for the absorptiometric determination of copper we calculate ϵ_{max} for the highest complexes

formed by ammonia, ethylenediamine, diethylenetriamine, triethylenetetramine, and tetraethylenepentamine as 41, 58, 102, 121, and 140 at λ_{max} . 635, 570, 710, 590, and 650 $\text{m}\mu$, respectively.

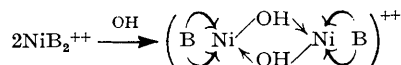
TABLE 3. *Molecular extinction coefficients of copper-diamine complexes.*

λ ($\text{m}\mu$)	Cu^{++}	Cu(en)^{++}	Cu(en)_2^{++}	Cu(dimen)^{++}	Cu(dimen)_2^{++}
450	0	~0.1	(~8)	0.2	6.4
475	0	1.4	25.2	—	—
500	0.03	2.3	44.3	2.8	46.3
525	0.1	4.5	47	4.0	77.5
550	0.25	11.7	63.0	11.3	103
575	0.5	20.5	56	20.6	107
600	1.0	28	45	36.5	96
625	1.2	31	34	—	—
650	3.1	37.5	22.9	54.0	58.0
700	7.2	—	—	54.3	29.2
750	11.1	—	—	44.8	15.0
800	12.8	—	—	32.8	8.1
850	12.5	—	—	23.2	4.2
900	11.1	—	—	16.4	2.2

Nickel Complexes.—Bivalent nickel usually forms four-co-ordinate square coplanar, or six-co-ordinate octahedral complexes with neutral ligands such as ammonia, ethylenedi-

FIG. 3. *Formation curve for nickel and NN'-dimethylethylenediamine at 25°.*

amine, or dipyridyl. Measurements with 0.025M-nickel sulphate and *NN'*-dimethylethylenediamine gave a formation curve (Fig. 3) which indicated the addition of two molecules of ligand in discrete stages; but when the concentration of diamine was very considerably increased the ligand number rose to just above two and then decreased (Fig. 3, inset). This might be due to the displacement of diamine by hydroxyl ions at high alkalinities (in this case $\text{pH} > 9$) leading to the formation of a mononuclear hydroxy-complex $\text{NiB}_2^{++} \xrightarrow{\text{OH}} \text{NiB(OH)}^+$, or of a binuclear complex of type (III), thus:



Both reactions would cause a decrease in \bar{n} . But since, until pB became large, there was no significant change in the course of the formation curve when measurements were repeated at twice the nickel concentration, and since at high ligand concentrations there was then no comparable decrease in \bar{n} after the maximum value of 2 had been reached (Fig. 3 and inset, black circles) it would appear that mononuclear complexes were responsible for the effect first noted.

Data in Table 4 support the generalisation that complexes of nickel are invariably less stable than those of copper with the same ligand (Irving and Williams, *Nature*, 1948, **162**, 764; *Analyst*, 1952, **77**, 813; *J.*, 1953, 3192), and afford further evidence of steric hindrance

TABLE 4. Stability constants at 25° of nickel complexes of diamines of the type $\text{NRR}'\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NHR}''$.

R	R'	R''	$\log K_1$	$\log K_2$	$\log K_1/K_2$	$\text{p}K_{\text{BH}^+}$	$\frac{1}{2} \log K_1K_2/\text{p}K_{\text{BH}^+}$	Refs.
H	H	H	7.60	6.48	1.12	10.18	0.69	a, b, c
Me	H	H	7.36	5.74	1.62	10.40	0.63	a, d
Et	H	H	6.78	5.30	1.48	10.56	0.58	a, e
Pr ⁱ	H	H	5.17	3.47	1.70	10.62	0.41	a, f
Me	H	Me	6.65	3.85	2.80	10.16	0.52	g

^a Basolo and Murmann, *loc. cit.* ^b For values by other authors and at different temperatures see Irving and Williams, *J.*, 1953, 3192. ^c $\log K_3 = 5.03$. ^d $\log K_3 = 2.01$. ^e $\log K_3 = 2.00$. ^f $\log K_3$ not measurable. ^g Present authors.

to co-ordination caused by *N*-alkylation. Indeed it proved impossible to obtain stability constants for complexes of nickel with unsymmetrical dialkylethylenediamines owing to the precipitation of basic salts early in the titration.

Although the general trend in values is the same for both copper and nickel complexes Tables 2 and 4 show that with nickel there are smaller differences in free energy (as measured by $2.303 \log K_1/K_2$) in attaching successive molecules of ligand. The stability order $\text{Cu} > \text{Ni}$ is again reflected in comparisons of the relative magnitudes of $\frac{1}{2} \log K_1K_2/\text{p}K_{\text{BH}^+}$ for the two metals for any given ligand.

Zinc complexes.—It should be possible to test whether the enhanced values of $\log K_1/K_2$ which we have correlated with increasing *N*-alkylation are consequent upon steric hindrance by comparing the behaviour of nickel complexes with those of zinc where, as a consequence of the preferred tetrahedral arrangement of bonds, the chelation of the second molecule of diamine will be in a plane at right-angles to the first so that steric effects should be appreciably smaller. Unfortunately zinc always forms weaker complexes than does copper (Irving and Williams, *loc. cit.*) and to reach corresponding values of \bar{n} along the formation curves a higher concentration of amine and a correspondingly higher pH are necessary. Precipitation of zinc hydroxide (or of a basic complex) took place at pH 6.2 during titrations with "dimen" when \bar{n} had only just exceeded 0.5, and even when a ten-fold excess of diamine salt was introduced as a buffer it proved impossible to study the system further. The tentative value of $\log K_1 = 5.4$ is, as expected, lower than that for the corresponding ethylenediamine complex (5.92). Since the whole formation curve is traceable with the unsubstituted diamine, to give $\log K_2 = 5.15$ and $\log K_3 = 1.86$ (Bjerrum and Andersen, *Kgl. Danske Videnskab. Selsk.*, 1945, **22**, 1773) it appears that $\log K_2$ in the "dimen" system must have been appreciably lower than $\log K_1$, as a result of steric hindrance. We were unable to obtain any significant results for complexes of zinc with *NN*-dimethyl- or -diethyl-ethylenediamine owing to the premature precipitation of basic materials.

Discussion.—From extensive studies of the stability of complexes formed between bases of the type $\text{NRR}'\text{R}''$ and (Lewis) acids such as trimethylboron, Brown and his co-workers (*loc. cit.*) have found that the comparatively small free-energy changes for these reactions which may be formulated



represent the difference between numerically large and opposing values of ΔH and $T\Delta S$, entropy values of 40 cal. per degree being not uncommon. Structural factors were shown to affect complex stability in two ways. Face-to-face interference, dependent on the steric requirements of both components, was termed *F*-strain. Steric effects localised at the back, away from the entering molecule, were described as *B*-strain (*J. Amer. Chem. Soc.*, 1944, **66**, 441).

While an obvious parallel exists between these reactions and the formation of a metal complex in solution where an electron donor (an ion or dipolar ligand) co-ordinates to a metal ion (a Lewis acid), the formal similarity between equation (6) and that commonly

used to define a stability constant, *viz.*, $ML_{n-1} + L \rightleftharpoons ML_n$, can be misleading. In aqueous solution each species is more or less hydrated and we should strictly write



If L is monodentate it does not necessarily and invariably follow that it will only displace one molecule of water. Neither is it certain that $n - 1 + p = n + q = N$, the maximum co-ordination number of the cation. The significant hydration numbers may well be considerably greater than N and will certainly depend on the concentration and nature of the reacting species and on the concentration and nature of the salt "background." They are likely to be greater for cationic than for anionic species, *e.g.*, $[FeCl_n]^{3-n}$ when $n < 3$ or $n > 3$ (cf. Gamlen and Jordan, *J.*, 1953, 1435). But while changes in hydration number will play a special part in questions of the energetics of reaction—particularly in entropy changes—we are here concerned with emphasising the effect of hydration in connection with the steric factors which must operate when ammonia or an alkylamine is co-ordinated to a hydrated cation.

Consider, *e.g.*, a cupric ion with four water molecules disposed round it at the corners of a square, with two others further removed at the apices of a tetragonal bipyramid with the cation in the centre. Despite its greater deformability—a factor which would favour replacement of water by ammonia—the co-ordination of the bulkier molecule will be opposed by some *F*-strain. Both *F*-strain and *B*-strain will increase as ammonia is replaced successively by a primary, a secondary, or a tertiary aliphatic amine, and will thereby modify and reduce the increased bond-strength due to any increasing donor character of the ligand. When ethylenediamine co-ordinates to copper it is easy to see from a model that the hydrogen atoms attached to the nitrogen atoms of the diamine are constrained by the almost planar chelate ring to positions which interfere less with remaining co-ordinated molecules (*e.g.*, of water in the plane which includes the copper atom) than would hydrogen atoms belonging to ammonia molecules co-ordinated at the same place. *F*-Strain is reduced by this smaller "interference volume." For this reason, among others, the free-energy change on chelation of one molecule of ethylenediamine to copper (14.4 kcal.) is greater than that for co-ordination of two molecules of ammonia (10.4 kcal.; further discussion will appear in a later paper). But the effect is still more marked in chelation of a second molecule of ethylenediamine to Cu^{++} , aq. for which the free-energy change (12.3 kcal.) is proportionately greater than that (6.8 kcal.) for co-ordination of a further pair of ammonia molecules. A comparable effect appears when *F*-strain due to a secondary or tertiary aliphatic amine is reduced by "tying back" the carbon atoms attached to the nitrogen atom through the formation of a reduced ring. Thus among complexes of trimethylboron the stability order is quinuclidine > triethylamine (Brown and Sei Sujishi, *J. Amer. Chem. Soc.*, 1948, 70, 2878) and diethylamine < dimethylamine < piperidine < pyrrolidine < trimethyleneimine for which the values of ΔF_{100} are +147, -2850, -2864, -4190, and -5960, respectively (Brown and Gerstein, *ibid.*, 1950, 72, 2926). Similar decreases in *F*-strain probably suffice to explain why the ratio $\log K_{Ag^+}/pK_{BH^+}$ is smaller for triethylamine than for hexamethylenetetramine (Bjerrum, *op. cit.*). It is unnecessary to labour the respective contributions of *F*-strain and *B*-strain towards the steric hindrance opposing complex formation shown by the data of Tables 2, 3, and 4. One striking difference between complexes of copper and nickel ought, however, to be emphasised. In the former, four water molecules are attached coplanarly while co-ordination at right angles is comparatively weak. In the case of nickel there is no reason to doubt the full octahedral symmetry of co-ordinated water molecules in the first hydration sphere, so that replacement of water by groups occupying a larger "interference volume" will result in an appreciably greater *F*-strain, which will increase with the co-ordination of further molecules even more rapidly than in the case of copper.

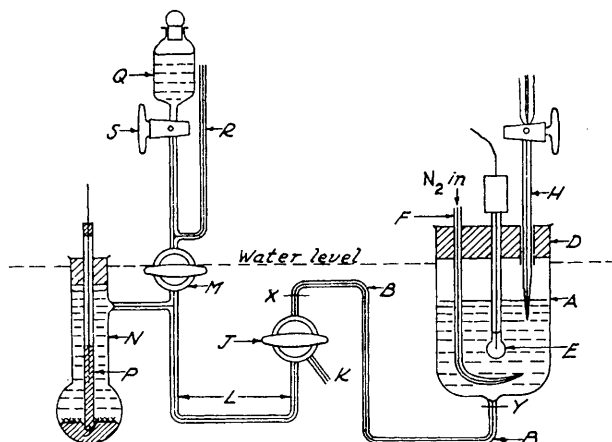
With increasing *N*-substitution the values of the successive stability constants of metal complexes decrease, so that in order to achieve any specified degree of complex formation (as measured by the appropriate value of \bar{n}) the magnitude of [L] must be continually increased. This may be achieved by increasing C_L , the total concentration of ligand, or by the addition of alkali to liberate a greater fraction of that already present from its

proton complexes. In either event, more particularly in the latter case, the pH will rise and the probability of forming mixed metal-ligand-hydroxide complexes increases. As their concentration rises concomitantly with increase of pH, condensation of these hydroxy-complexes to form binuclear ions with OH bridges of the type (III), or polynuclear ions of still greater complexity, will be favoured. In the limit, basic salts (often of indefinite composition) or even the metal hydroxide itself will be precipitated. This invariably occurred in our preliminary studies of amines of the type $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHR}$ (R = alkyl or 1-piperidyl) and of the type $\text{NH}_2 \cdot \text{CHR} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHR}'$ (R = alkyl, R' = alkyl or 1-piperidyl) where the increased chain length was an additional factor favouring instability (Irving, Williams, Ferrett, and Williams, in the press).

EXPERIMENTAL

Materials.—*NN'*-Dimethylethylenediamine (Messrs. Light and Co.) was refluxed over freshly fused, powdered barium oxide and fractionated in an all-Pyrex apparatus, the fraction of b. p. 117–119°/760 mm. being collected directly in a weight-burette fitted with a soda-lime guard tube. Solutions in 0.1M-potassium chloride were prepared by weight, and the purity determined by titration against standard hydrochloric acid was 98.2%. After similar treatment *NN*-dimethylethylenediamine, b. p. 106–107°/760 mm., had purity of 96.5% and *NN*-

FIG. 4. Titration apparatus (not to scale).



diethylethylenediamine, b. p. 143.5°/760 mm., was 97.8% pure. Carbonate-free sodium hydroxide was standardised against hydrochloric acid. All solutions used were made up with "AnalaR" potassium chloride to a constant concentration of 0.1M.

For titration experiments (see below) solutions of the diamines were prepared by adding known weights of freshly distilled diamine to a suitable volume of 0.1M-potassium chloride in boiled-out water contained in the reservoir of a specially constructed micro-burette, Sofnolite guard-tubes being fitted to prevent intrusion of carbon dioxide. After thorough admixture the amine solution was standardised against hydrochloric acid (methyl-red), itself prepared from freshly distilled constant-boiling hydrochloric acid and standardised (bromocresol-green) against weighed portions of pure borax which was preserved over a solution saturated with respect to both sodium chloride and sucrose (cf. Hurley, *Ind. Eng. Chem., Anal. Ed.*, 1936, 8, 220; 1937, 9, 237).

The Titration Apparatus.—Liquid to be titrated was contained in a vessel A (Fig. 4) which carried a Doran Universal glass electrode and communicated with the saturated calomel electrode N and a reservoir of saturated potassium chloride Q through the three-way tap J. Titrant was admitted through a micro-burette with an extended tip dipping just below the surface, and mixing was rapidly effected by a micro-stirrer (not shown) or by a fine stream of nitrogen freed from carbon dioxide and equilibrated with water vapour by passage through a sample of the solution to be titrated. The whole was kept in a thermostat at $25 \pm 0.05^\circ$. With the apparatus to the left of J completely filled with saturated potassium chloride and that to the right with the solution to be titrated, a reproducible cylindrical liquid-liquid boundary could be set up at X by closing S and manipulating M and J in such a way as to

permit the saturated potassium chloride in the capillary *R* to fall slowly from the upper to the lower of two etched marks. In later experiments the portion of tubing labelled *B* was eliminated and *X* and *Y* became coincident. In this way the development of a diffuse liquid-liquid boundary between *Y* and the solution in *A* during titration, which sometimes affected the steadiness of calibration of the glass electrode, was avoided. In the final experiments the inclusion of a disc of coarse sintered glass at *Y* was found of great advantage. Solutions in *A* could be withdrawn through *K* by applying slight suction without the necessity of removing the apparatus from the thermostat. Before and after each set of measurements the glass electrode was calibrated against a Cambridge pH-meter; 0.05M-potassium hydrogen phthalate in 0.1M-potassium chloride, and 0.05M-sodium borate in 0.1M-potassium chloride, being used and assumed to have pH values at 25° of 3.93 and 9.11 respectively (Hamer and Acree, *J. Res. Nat. Bur. Stand.*, 1944, **32**, 215; Manov, DeLollis, Lindvall, and Acree, *ibid.*, 1946, **36**, 543).

Determination of Acid Dissociation Constants.—(a) *By using separate solutions* (all of which were made 0.1M with respect to potassium chloride). Various volumes of 0.368M-*NN'*-dimethylethylenediamine were mixed with 6.25 ml. of 0.392M-hydrochloric acid and 6.25 ml. of 0.20M-magnesium sulphate (to correspond in ionic strength with the metal sulphate to be used in later determinations) and made up to 25 ml. with 0.1M-potassium chloride. The pH of each solution was measured in turn and pK_{BH^+} and $pK_{BH_2^{++}}$ were calculated as described above (page 214). The results are in Table 5.

(b) *Titration method.* 60 ml. of 0.1682M-hydrochloric acid, and 25 ml. of 0.20M-magnesium sulphate were made up to 100 ml. with 0.1M-potassium chloride. Portions of 50 ml. were titrated in the apparatus depicted in Fig. 4 with a 1.503M-solution of diamine in 0.1M-potassium chloride. The measurements made at the lower alkaline range are in Table 6. The averages given are from these, and similar measurements at pH 9.9–10.1.

TABLE 5.

No.	Amine (ml.)	pH	n_B	pK (calc.)	No.	Amine (ml.)	pH	\bar{n}_B	pK (calc.)
1	11.00	9.90	0.6053	10.08	7	8.50	7.14	1.566	7.26
2	12.50	10.03	0.5326	10.085	8	9.00	7.245	1.479	7.21
3	12.00	9.97	0.5550	10.06	9	9.00	7.265	1.479	7.23
4	12.00	9.98	0.5550	10.07	10	9.60	7.465	1.387	7.27
5	12.00	9.965	0.5550	10.06	11	9.60	7.48	1.387	7.285
6	8.50	7.12	1.566	7.24					

Averages: $pK_{BH^+} = 10.07$; $pK_{BH_2^{++}} = 7.25$.

TABLE 6.

Amine (ml.)	pH	\bar{n}_B	$pK_{BH_2^{++}}$	Amine (ml.)	pH	\bar{n}_B	$pK_{BH_2^{++}}$
2.00	7.03	1.646	7.29	2.22	7.375	1.483	7.35
2.10	7.18	1.567	7.30	2.26	7.425	1.456	7.35
2.14	7.235	1.538	7.30	2.30	7.46	1.431	7.34
2.18	7.31	1.508	7.33	2.40	7.54	1.372	7.32

Averages: $pK_{BH_2^{++}} = 7.32$; $pK_{BH^+} = 10.05$.

TABLE 7.

Soln.	Amine (ml.)	pH	\bar{n}	pB	Soln.	Amine (ml.)	pH	\bar{n}	pB
1	7.00	3.89	0.0498	10.87	10	16.0	5.91	1.355	6.84
2	9.00	4.32	0.344	10.01	11	16.5	5.90	1.429	6.86
3	10.00	4.50	0.491	9.65	12	17.0	6.09	1.492	6.48
4	12.00	4.785	0.785	9.08	13	18.0	6.19	1.632	6.29
5	13.00	5.00	0.931	8.65	14	19.0	6.30	1.768	6.07
6	14.00	5.32	1.076	8.01	15	20.0	6.40	1.903	5.88
7	15.00	5.67	1.216	7.31	16	21.0	6.70	1.998	5.30
8	9.50	4.41	0.418	9.83	17	23.0	7.58	2.017	3.79
9	10.5	4.56	0.565	9.53	18	25.0	8.02	1.982	3.18

The acid dissociation constants of *NN*-dimethyl- and -diethyl-ethylenediamine were measured in the same way; the average values are reported in Table 1.

Determination of the Stability Constants of Metal Complexes.—(a) *By using separate solutions.* Known volumes of *NN'*-dimethylethylenediamine solution (0.368M) were mixed severally with 12.5 ml. of 0.2M-copper sulphate and 12.5 ml. of 0.392M-hydrochloric acid. All these solutions had been made up in 0.1M-potassium chloride and the total volume was made up to 50 ml. with this solution. The pH of each solution was measured in the titration apparatus (Fig. 4) and values of \bar{n} and pB were calculated as described on page 215. Some typical results are in

Table 7. Additional measurements (see Fig. 1) were made with different concentrations of copper.

(b) *Titration method.* A mixture of 60.00 ml. of 0.1682M-hydrochloric acid, 25.00 ml. of 0.20M-copper sulphate, 3.00 ml. of 1.503M-*NN'*-dimethylethylenediamine, and 12 ml. of 0.1M-potassium chloride was titrated with 1.503M-diamine solution. All solutions were made up in 0.1M-potassium chloride. Steady potentials were reached within 0.5 min. of a fresh addition of amine. The pH readings and calculated values of \bar{n} and pB are given in Table 8.

TABLE 8.

Total vol. of amine (ml.)	pH	\bar{n}	pB	Total vol. of amine (ml.)	pH	\bar{n}	pB
3.52	3.875	0.048	10.89	7.00	5.465	1.088	7.73
4.00	4.145	0.192	10.35	7.40	5.675	1.202	7.31
4.40	4.285	0.313	10.07	7.60	5.75	1.259	7.16
4.60	4.345	0.373	9.95	7.80	5.82	1.319	7.03
4.80	4.405	0.433	9.84	8.00	5.88	1.376	6.91
5.00	4.46	0.493	9.73	8.20	5.935	1.432	6.80
5.20	4.52	0.553	9.61	8.40	5.985	1.491	6.70
5.40	4.565	0.614	9.52	8.60	6.04	1.547	6.59
5.80	4.69	0.733	9.27	8.80	6.095	1.604	6.49
6.20	4.855	0.853	8.94	9.20	6.205	1.716	6.27
6.60	5.12	0.971	8.41	9.60	6.34	1.821	6.01
				10.00	6.515	1.918	5.67

Similar titrations were carried out with nickel at concentrations of 0.05 and 0.025M. The formation curves are reproduced in Fig. 3. Data for other systems are summarised in Table 9, computed values of stability constants being given in Tables 2, 3, and 4.

TABLE 9.

<i>n</i>	pB	\bar{n}	pB	\bar{n}	pB	\bar{n}	pB	\bar{n}	pB	\bar{n}	pB
<i>0.05M-Zinc sulphate and NN'-dimethylethylenediamine.</i>											
0.053	12.09	0.364	5.80	0.600	5.15	0.780	4.72	0.882	4.41	0.910	4.09
0.167	11.63	0.394	5.67	0.619	5.09	0.790	4.67	0.899	4.37	0.925	4.06
0.215	8.39	0.422	5.59	0.676	4.97	0.824	4.63	0.899	4.32	0.920	4.02
0.246	7.29	0.452	5.49	0.699	4.92	0.827	4.57	0.907	4.24	0.918	3.86
0.269	6.69	0.485	5.42	0.715	4.86	0.851	4.54	0.915	4.20	0.909	3.70
0.290	6.33	0.513	5.35	0.749	4.82	0.859	4.49	0.909	4.16	0.887	3.46
0.311	6.10	0.545	5.28	0.769	4.77	0.868	4.44	0.908	4.12	0.836	3.26
0.333	5.93	0.566	5.20								
<i>0.05M-Copper sulphate and NN-dimethylethylenediamine.</i>											
0.020	10.41	0.447	9.30	0.873	8.29	1.289	7.15	1.609	6.50	1.857	5.33
0.104	10.06	0.533	9.17	0.957	7.98	1.371	6.99	1.688	6.29	1.879	4.97
0.191	9.82	0.618	8.99	1.040	7.72	1.453	6.83	1.759	6.04	1.890	4.65
0.274	9.64	0.703	8.81	1.123	7.50	1.534	6.68	1.817	5.71	1.896	4.38
0.362	9.46	0.789	8.57	1.206	7.30						
<i>0.05M-Copper sulphate and NN-diethylethylenediamine.</i>											
0.129	9.05	0.569	8.07	0.994	6.92	1.377	5.81	1.718	5.08	1.931	4.35
0.192	8.84	0.631	7.95	1.050	6.67	1.429	5.69	1.762	4.99	1.964	4.17
0.255	8.67	0.693	7.83	1.104	6.46	1.482	5.60	1.801	4.87	1.974	4.03
0.317	8.52	0.755	7.694	1.160	6.30	1.531	5.49	1.839	4.77	1.993	3.69
0.380	8.40	0.817	7.55	1.216	6.17	1.577	5.38	1.871	4.65	1.998	3.29
0.443	8.28	0.878	7.38	1.270	6.033	1.629	5.29	1.896	4.53	1.998	2.79
0.506	8.17	0.937	7.15	1.323	5.909	1.677	5.19				

Spectrophotometric Measurements.—Solutions of 0.01M-copper sulphate containing varying amounts of *NN'*-dimethylethylenediamine were examined in 1.005-mm. Corex cells in a compartment kept in a thermostat at $25^\circ \pm 0.1^\circ$ and attached to a Model DU Beckman spectrophotometer. Typical absorption spectra are shown in Fig. 2. The formation of 1:1 and 1:2 complexes was confirmed by Job's method of continuous variations (*Ann. Chim.*, 1928, 9, 113) as modified by Vosburgh and Cooper (*J. Amer. Chem. Soc.*, 1941, 63, 437).

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