based on differences of 50 cm^{-1} or less. We have reported that Dq varies by 80 cm^{-1} when the value is calculated from mull and solution spectra.[19]

In view of the dominance of σ effects in this series, it is of interest to reexamine the Dq results in Tables III and IV. As the donor properties of the in-plane group increase, as is manifested by our σ order, the metal–chlorine interaction decreases as evidenced by a decrease in Dq^z for chloride. We in effect have a "ligand inductive effect" by the xy ligands decreasing the metal formal charge and decreasing the metal–halogen interaction. Thus the Dq for Cl^- is greater in the pyridine complex than in $Ni(Temp\ a)Cl_2$. The values for Dq in the O_h complexes indicate az and S-dmeen interact more strongly with nickel than with pyridine, and in accordance with the ligand inductive effect the Dq of Cl^- is greater in the pyridine complex than in the others. The same trend is observed for the bromo complexes. Consistent with this model we also find that Dq for pyridine is larger in $Ni(py)_4(BF_4)_2$ or $Ni(py)_4(ClO_4)_2$ than in $Ni(py)_4Cl_2$ or $Ni(py)_4Br_2$ as would be expected from the poorer donor strength of BF_4^- or ClO_4^- than of Cl^- or Br^-. Again, we are reluctant to interpret differences in these parameters which are less than 50 cm^{-1} because of lattice effects. Large differences are expected when comparing complexes with one type of in-plane ligands and two axial ligands that are widely different. When four xy ligands are changed and the axial ligands held constant, the differences in ligand donor strengths need not be as large to change Dq^z as the differences need be in the above case ($Ni(L)_4X_2$) when only two ligands are changed.

In conclusion: (1) the Dq of ligands toward nickel does not remain constant as previously thought but often varies in a predictable way with the inductive property of the ligands; (2) when attempting to calculate spectrochemical parameters, all configuration interaction *and* all off-diagonal matrix elements must be considered; and (3) it is impossible to base assignments of spectra on the signs of $\delta\pi$ and $\delta\sigma$, if configuration interaction has not been taken into consideration.

Acknowledgment.—The authors acknowledge the financial support of the research by The National Science Foundation through Grant GP-5498.

[19] In a previous article we incorrectly reported the position of the $^3B_{1g} \rightarrow {}^3B_{2g}$ transition of $Ni(py)_4Cl_2$ in solution as being 1400 cm^{-1} different from that in the solid. In solution the bands broaden and are very close. When properly resolved with a Du Pont curve resolver, the difference is only 800 cm^{-1}.

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Effect of Steric Hindrance in the 1,1,7,7-Tetraethyldiethylenetriamine Complexes of Copper(II)

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The proton stability constants of 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien) are slightly lower than those of dien with log K values of 9.66, 8.62, and 3.55 for Et_4dien compared to 9.94, 9.13, and 4.34 for dien. On the other hand the stability constant for Cu(II)–Et_4dien (log K_1 = 10.1) is very much less than for Cu(II)–dien (log K_1 = 16.0). The ethyl groups severely hinder coordination of ligands to the out-of-plane positions of copper. The 10^6-fold decrease in the stability constant is attributed primarily to blocking the coordination of water in these axial positions. The log (stability constant) of $[Cu(Et_4dien)OH]^+$ is 6.0 compared to 4.9 for $[Cu(dien)OH]^+$, which is consistent with increased binding of coordinated water in the fourth planar position due to reduced coordination of water in the axial positions. All Et_4dien constants are at 25.0° and 0.1 M ionic strength.

Introduction

Diethylenetriamine (dien) is a well-known ligand which forms quite stable complexes with the transition metals.[1,2] The coordination properties of this tridentate ligand are altered significantly when two ethyl groups are placed on each terminal nitrogen to give 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien).[3] The square-planar complex, $[Pd(Et_4dien)Cl]^+$, has been observed to undergo halide substitution with a kinetic expression similar to that of octahedral complexes.[4,5] It has been called a pseudo-octahedral complex because the ethyl groups, which extend above and below the square-planar configuration, do not permit the normal square-planar substitution mechanism.

Four-, five-, and six-coordinate complexes containing Et_4dien are reported with nickel(II), cobalt(II), and rhodium(III), respectively.[6] Steric crowding of the ethyl groups has been shown to be an important factor in changing the coordination number of nickel

[1] J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 985 (1950).

[2] H. B. Jonassen, G. G. Hurst, R. B. LeBlanc, and A. W. Meibohm, *J. Phys. Chem.*, **56**, 16 (1952).

[3] Et_4dien also is named and sold as N,N-bis(β-diethylaminoethyl)-amine.

[4] F. Basolo and W. H. Baddley, *J. Am. Chem. Soc.*, **86**, 2075 (1964).

[5] W. H. Baddley and F. Basolo, *ibid.*, **88**, 2944 (1966).

[6] Z. Dori and H. B. Gray, *ibid.*, **88**, 1394 (1966).

and cobalt[6,7] and in the apparent stability of the halide complexes of Ni(Et$_4$dien)X$^+$. Relief of steric strain is considered the principal determinant of the molecular geometry of the Co(Et$_4$dien)Cl$_2$ complex.[7]

In the present study the stability constant of the copper(II) complex of Et$_4$dien is measured in order to determine quantitatively the effect which steric hindrance has on the ability of the ligand to form complexes in aqueous solution.

Experimental Section

Et$_4$dien was prepared as the trihydrochloride salt by dissolving the amine (Ames Laboratories, Inc., Milford, Conn.) in absolute ethanol and saturating with HCl gas in an ice bath. Et$_4$dien·3HNO$_3$ also was prepared from the amine using concentrated HNO$_3$ and precipitating the solid with ethanol and ether. The salts were recrystallized from absolute ethanol. Aqueous solutions of the salts were standardized by NaOH titration.

Acid constants of the chloride salt in 0.10 *M* KCl and of the nitrate salt in 0.10 *M* KNO$_3$ were measured by potentiometric titration. In each of seven titrations 25 ml of 1.4×10^{-4} *M* Et$_4$dien·3HCl was titrated with 0.1 *M* NaOH driven from a calibrated 2.5-ml syringe (Radiometer Titrigraph). Two additional titrations were carried out manually using 0.51 mmol of Et$_4$dien·3HNO$_3$ in 50 ml in a closed titration assembly with a Beckman Research Model 1016 pH meter. A nitrogen atmosphere was maintained and reagents were prepared from CO$_2$-free water. The temperature was 25.0 ± 0.1°.

The pH readings with the Beckman meter were calibrated in terms of the hydrogen ion concentration by titrating (1) 0.0100 *M* HCl + 0.090 *M* KNO$_3$ and (2) 0.0140 *M* HC$_2$H$_3$O$_2$ with 0.1733 *M* NaOH. The hydrogen ion concentration was calculated assuming complete dissociation of HCl and using $\log([\mathrm{H}^+][\mathrm{C_2H_3O_2}^-]/[\mathrm{HC_2H_3O_2}]) = -4.545$ under these conditions.[8] The titrations also gave a calibration at pH 11–12 using the added hydroxide ion concentration and $K_w = 10^{-13.79}$. In the acid region the deviation between meter readings and calculated $-\log [\mathrm{H}^+]$ was negligible. At high pH readings there was a total deviation of 0.040 unit which was applied as a linear correction from pH 7 to 12.

The Radiometer meter was standardized using National Bureau of Standards buffers and $-\log [\mathrm{H}^+]$ was calculated by subtracting 0.10 from the observed pH value.[9]

Copper stability constants with Et$_4$dien were determined spectrophotometrically and potentiometrically. When chloride ion was present above 0.01 *M* it interfered slightly, presumably owing to [Cu(Et$_4$dien)Cl]$^+$. However, the latter species was a minor component of the system even in 0.1 *M* Cl$^-$. Nevertheless, chloride ion was removed from Et$_4$dien·3HCl with AgClO$_4$ to avoid any possible interference and 0.1 *M* NaClO$_4$ was used for constant ionic strength. The constants also were determined using Et$_4$dien·3HNO$_3$ in 0.10 *M* KNO$_3$. The stability constants obtained by the spectrophotometric method used 8–18 data points between pH values of 4.9 and 6.0. The constants were calculated with a computer program proposed by Conrow, *et al.*,[10] with slight modifications to convert it to FORTRAN IV.[11]

The potentiometric data were obtained using the closed titration assembly and the calibrated Beckman meter. A computer program calculated a stability constant for each datum point. The reported value remained constant for nine or ten points for a = 1.3–2.7 (pH 4.9–6.0).

Results

Acid Stability Constants.—The pH titration curve of the H$_3$Et$_4$dien^{3+} salts has a sharp break (pH 4–8) at 1 equiv of base and an inflection (pH 10–11) at 3 equiv of base. The acid stability constant of H$_3$Et$_4$dien^{3+} ($K_3 = [\mathrm{H_3Et_4dien^{3+}}]/[\mathrm{H_2Et_4dien^{2+}}][\mathrm{H^+}]$) is well separated from those of H$_2$Et$_4$dien^{2+} (K_2) and HEt$_4$dien$^+$ (K_1). The value for K_3 was calculated by a graphical method[12] based on eq 1 where $x = C_b + [\mathrm{H}^+]$, C_a is the stoichiometric concentration of acid, and C_b is the stoichiometric concentration of added base. A plot of $x[\mathrm{H}^+]$ against x gave a straight line with a slope of $-1/K_3$.

$$K_3[\mathrm{H}^+] = \frac{C_a - x}{x} \tag{1}$$

The constants K_1 and K_2 are close together so a variation of Schwarzenbach's graphical method was used.[13] The resulting expression was

$$\frac{[\mathrm{H}^+]^2((a-1)C_a[\mathrm{H}^+] - K_w)}{(3-a)C_a[\mathrm{H}^+] + K_w} = K_1K_2 - \frac{[\mathrm{H}^+][(2-a)C_a[\mathrm{H}^+] + K_w]}{(3-a)C_a[\mathrm{H}^+] + K_w}K_2 \tag{2}$$

where C_a is the stoichiometric concentration of added base and a is the number of moles of base added per mole of Et$_4$dien. A linear-least-squares computer program was used to calculate K_1 and K_2 using data from $a = 1.3$ to $a = 2.7$.

Table I summarizes the constants and standard deviations determined from nine different titration curves. The same results were obtained for the NaClO$_4$ and KNO$_3$ solutions. Constants for dien are included for comparison.

TABLE I

PROTON STABILITY CONSTANTS AT 25° AND μ = 0.10

	Log K_1	Log K_2	Log K_3
Et$_4$dien (exptl)	9.66 ± 0.06	8.62 ± 0.05	3.55 ± 0.02
dien (ref 1)[a]	9.94	9.13	4.34

[a] At 20.0° and μ = 0.1. The same values are reported for 25°: L. G. Sillén and A. E. Martell, "Stability Constants of Metal Ion Complexes," The Chemical Society, London, 1964, p 422.

Copper–Et$_4$dien.—Unlike dien only one molecule of Et$_4$dien adds to copper(II) and the bis complex is not observed. With millimolar concentrations of copper and Et$_4$dien a blue complex of Cu(Et$_4$dien)$^{2+}$ forms at about pH 6. As the pH is increased, the color first intensifies and then changes to purple by pH 8. Figure 1 gives the absorption spectrum of Cu(Et$_4$dien)$^{2+}$ in curve 1 and shows the changes above pH 7 due to the formation of [Cu(Et$_4$dien)OH]$^+$ in curves 2–5. Figure 2 shows the pH dependence of the absorbance at 700 mμ. The absorbance increases from pH 4 to 6.6 as copper replaces hydrogen ion to give the first complex. The absorbance drops from pH 6.6 to 10 as Cu(Et$_4$dien)$^{2+}$ is converted to [Cu(Et$_4$dien)OH]$^+$.

All data for the stability constant, $K_1 = [\mathrm{Cu(Et_4dien)^{2+}}]/[\mathrm{Cu^{2+}}][\mathrm{Et_4dien}]$, were taken from below pH

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(7) Z. Dori, R. Eisenberg, and H. B. Gray, *Inorg. Chem.*, **6**, 483 (1967).

(8) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, p 676.

(9) R. G. Bates, "Determination of pH," John Wiley and Sons, Inc., New York, N. Y., 1964, p 74.

(10) K. Conrow, G. D. Johnson, and R. E. Bowen, *J. Am. Chem. Soc.*, **86**, 1025 (1964).

(11) N. E. Jackobs, Ph.D. Thesis, Purdue University, 1967.

(12) J. C. Gage, *Analyst*, **82**, 219 (1957).

(13) A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p 91.

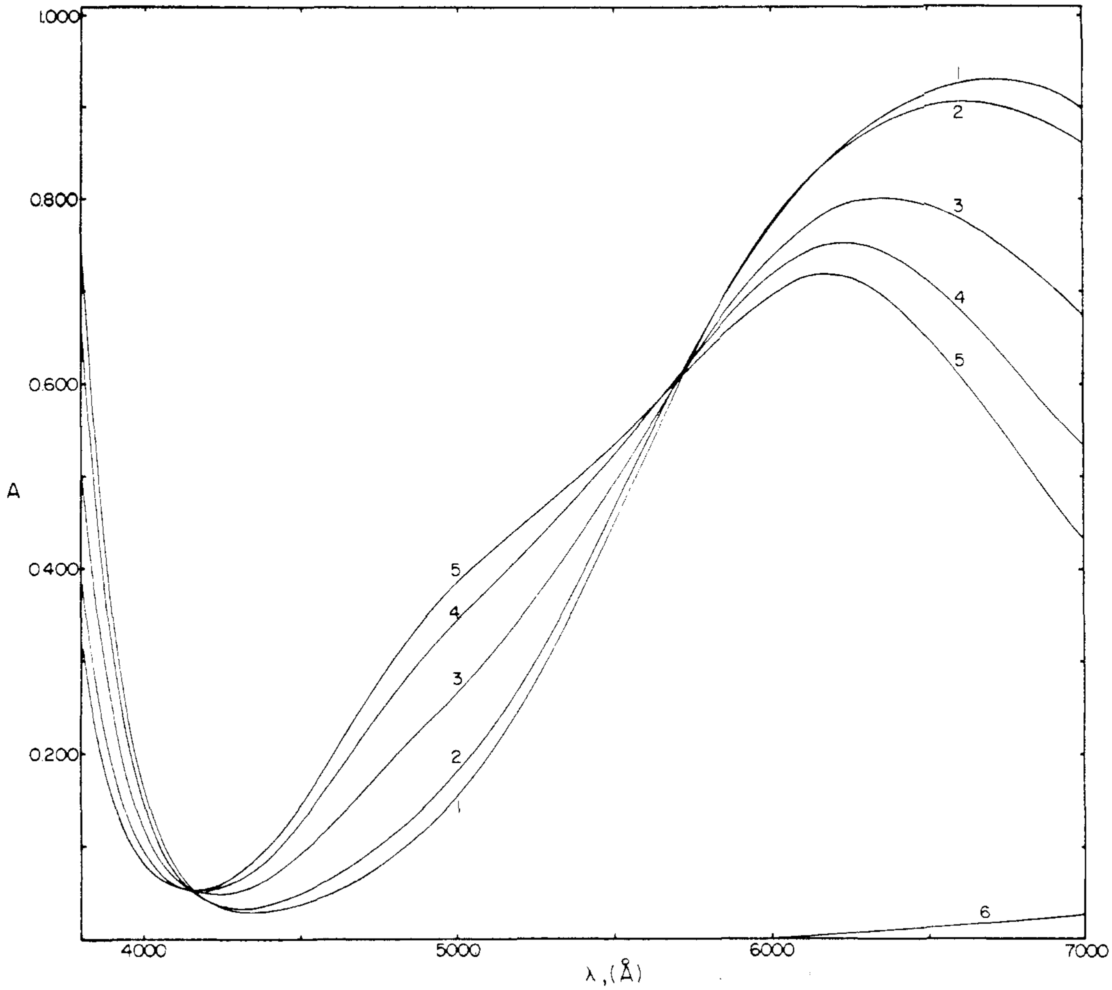


Figure 1.—Absorption spectra of the Cu–Et$_4$dien complex at pH values of (1) 6.59, (2) 7.04, (3) 7.89, (4) 8.45, and (5) 10.22. [Cu-(ClO$_4$)$_2$] = [Et$_4$dien·3HNO$_3$] = 3.73×10^{-4} *M*, [NaClO$_4$] = 0.10 *M*, 0.050 *M* borate buffer, 5-cm cell, 25°. Curve 6 is the spectrum of 3.73×10^{-4} *M* Cu(ClO$_4$)$_2$ in 0.1 *M* NaClO$_4$, 5-cm cell.

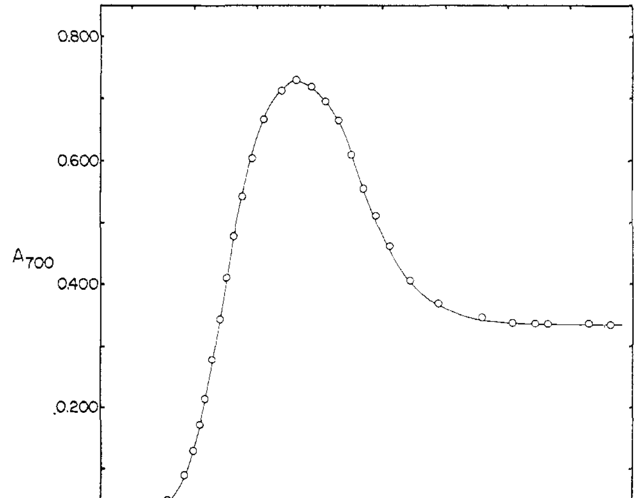


Figure 2.—The absorbance of the Cu–Et$_4$dien solutions changes with change in $-\log$ [H$^+$] due to the formation of [Cu(Et$_4$-dien)]$^{2+}$ (pH 4.5–6.5) and [Cu(Et$_4$dien)OH]$^+$ (pH 6.5–8.5). [Cu(ClO$_4$)$_2$] = [Et$_4$dien·3HNO$_3$] = 3.00×10^{-3} *M*, [KNO$_3$] = 0.10 *M*, λ 700 mμ, 25°, 1-cm cell.

6.0 under conditions specified in Table II. The values of both K_1 and the molar absorptivity of the complex, ε, were computed by the program used.[11] The potentiometric and spectrophotometric values were in good agreement and the average value of log K_1 was 10.11 with a standard deviation of 0.06 for seven determinations. The acid constants given in Table I were used in these calculations so that log K_1 = 10.1 ± 0.1 is a reasonable statement of the value.

Graphical treatment of the data in which the ε of Cu(Et$_4$dien)$^{2+}$ was determined with excess Et$_4$dien present at pH 6.5 gave K_1 values in good agreement with those in Table II.

Stability of [Cu(Et$_4$dien)OH]$^+$.—As shown in Figures 1 and 2 another copper complex is formed as the pH increases. The spectrophotometric changes are consistent with a hydroxide complex and the isosbestic points shown in Figure 1 indicate that two species are present. The value of the constant K_{OH} = [Cu(Et$_4$-dien)OH$^+$]/[CuEt$_4$dien^{2+}][OH$^-$] was determined from

$$\frac{[\mathrm{Cu}]_T b}{A_T - A} = \frac{1}{\Delta\epsilon} + \frac{1}{K_{\mathrm{OH}}\Delta\epsilon}\,\frac{1}{[\mathrm{OH}^-]} \qquad (3)$$

TABLE II

STABILITY CONSTANT OF $Cu(Et_4dien)^{2+}$ AT 25° AND $\mu = 0.10$

$10^3[Cu^{2+}]$, *M*	$10^3[Et_4dien]$, *M*	Method[a]	ϵ (λ, mμ)	Log K_1
1.02	1.66	S	313 (650)	10.18
1.02	1.91	S	252 (650)	10.05
0.614	1.91	S	248 (650)	10.03
4.06	4.12	S	272 (700)	10.06
3.00	3.00	S[b]	272 (700)	10.14
4.06	4.12	P	. . .	10.15
3.00	3.00	P[b]	. . .	10.14
			Av	10.11 ± 0.06

[a] S = spectrophotometric, P = potentiometric. [b] KNO_3; the other solutions used $NaClO_4$ for ionic strength control.

where A_T is $[Cu]_T b\epsilon_{CuL}$, $\Delta\epsilon$ is $\epsilon_{CuL} - \epsilon_{CuLOH}$, and A is the observed absorbance. Figure 3 is a plot of eq 3 for a variety of experimental conditions. At 700 mμ the values for ϵ_{CuL} and ϵ_{CuLOH} are 272 (Table II) and 140 (excess OH^-), respectively. The slope in Figure 3 gives a K_{OH} value of $10^{6.04}$. The $[Cu]_T$ was varied fourfold and the Cu:Et$_4$dien ratio varied from 1:1 to 1:5 at lower pH values up to 1:100 at high pH values.

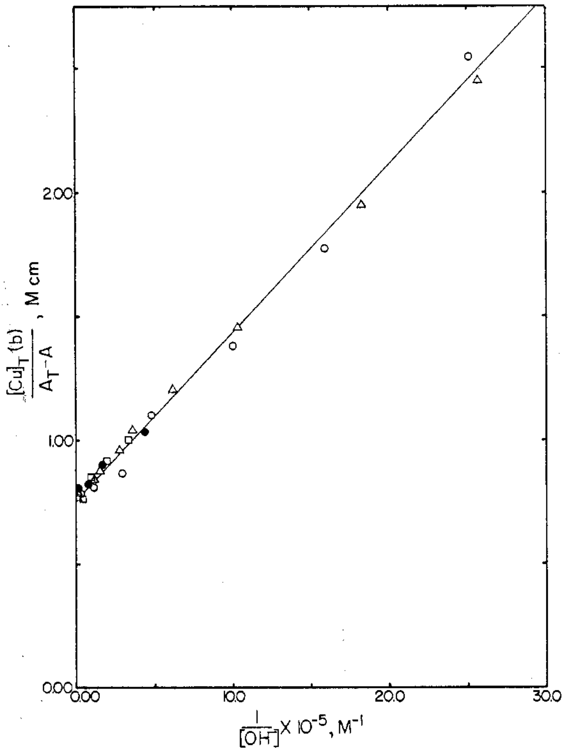
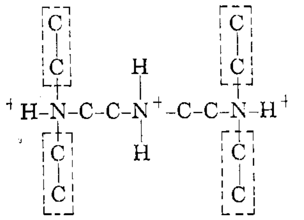


Figure 3.—A plot of eq 3 to determine the stability constant K_{OH} of the hydroxide complex of Cu–Et$_4$dien (λ 700 mμ, 25°): ○, 3.00×10^{-3} *M* $Cu(ClO_4)_2$, 3.00×10^{-3} *M* Et$_4$dien, $\mu = 0.10$ (KNO_3); △, 0.373×10^{-3} *M* $Cu(ClO_4)_2$, 3.73×10^{-3} *M* Et$_4$dien, $\mu = 0.10$ ($NaClO_4$); ●, 0.406×10^{-3} *M* $Cu(ClO_4)_2$, 40.6×10^{-3} *M* Et$_4$dien, $\mu = 0.10$ ($NaClO_4$), 0.05 *M* borate buffer; □, 0.487×10^{-3} *M* $Cu(ClO_4)_2$, 4.87×10^{-3} *M* Et$_4$dien, $\mu = 0.10$ ($NaClO_4$), 0.05 *M* borate buffer.

Discussion

Effect of N-Ethyl Groups on the Proton Stability Constants.—The fact that $H(Et_4dien)^+$ and $H_2(Et_4dien)^{2+}$ have lower acid stability constants than $Hdien^+$ and H_2dien^{2+} is not too surprising. Replacement of hydrogen by alkyl groups in ammonia causes the acid stability constants to increase first and then to decrease; thus log K_H values for ammonia, methylamine, dimethylamine, and trimethylamine are 9.25, 10.62, 10.77, and 9.80, respectively. This trend has been explained by the competition between an inductive effect which makes the nitrogen more basic and a steric effect which causes decreased solvation and makes the ion more acidic.[14] The Δ log K_1 value for $H(Et_4dien)^+$ and $Hdien^+$ of -0.28 can be explained in this manner. However, this does not explain the Δ log K_2 value of -0.51 or the Δ log K_3 value of -0.79. The Δ log K_3 value is interesting because the third proton must go on the central nitrogen atom which has exactly the same atoms bonded to it in dien and Et$_4$dien


$$^{+}H-N-C-C-N^{+}-C-C-N-H^{+}$$

Log K_3 = 3.55 with and 4.34 without the four ethyl groups.

The disruption of the ionic solvation by the ethyl groups may be a contributing factor to Δ log K_3 but we believe the primary effect is due to a decrease in the effective dielectric constant between the centers of positive charge. Thus, the coulombic repulsion of the terminal charges for the center proton is increased because the lines of force pass through a greater volume of hydrocarbon of low dielectric constant.

Effect of N-Ethyl Groups on the Copper Stability Constants.—There is a decrease of 6.0 log *K* units in the stability of Cu–Et$_4$dien compared to Cu–dien. Despite the large difference in the K_1 values all three nitrogens of Et$_4$dien must be coordinated to the copper. If all three nitrogens were not coordinated, a different pH dependence would be expected owing to the formation of a protonated complex. Neither the potentiometric nor the spectrophotometric data gave any indication of a complex with only two nitrogens bound to the copper. Further, if only two nitrogens were coordinated because of steric hindrance, then clearly the complex that results should be significantly less stable than Cu–en (log K_1 = 10.55) rather than being of nearly equal stability. Thus, for the copper complex of N,N-diethylethylenediamine[15] log K_1 equals 8.17 and the presence of two ethyl groups on one nitrogen causes the value of log K_1 to decrease by 2.38. Finally, other Et$_4$dien complexes[4-7] are known to be tridentate, and, although the four ethyl groups block the addition of a second ligand and interfere with the axial coordination positions, there is no difficulty in coordinating all three nitrogens.

Copper tends to form square-planar complexes because of the Jahn–Teller effect and axial groups are

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[14] J. F. King in "Technique of Organic Chemistry," Vol. II, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Part I, p 34.

[15] H. Irving and J. M. M. Griffiths, *J. Chem. Soc.*, 213 (1954).

usually considered to be weakly bound. However, this study suggests that the out-of-plane water molecules are quite important in copper complexes and that by blocking axial water coordination in Cu–Et_4dien the stability of the complex is diminished 1,000,000-fold.

Several explanations of the effect of the four N-ethyl groups should be considered. The possibility that additional alkyl groups in general cause poorer solvation of the complex and lower stabilities can be discarded because $\log \beta_2 = 21.87$ for the C-tetramethylethylenediamine–copper complex[16] compared to $\log \beta_2 = 20.13$ for ethylenediamine. The eight additional methyl groups are roughly equivalent to four additional ethyl groups in regard to the size of the complex. Obviously it is the position as well as size of the alkyl groups which is important as shown by the studies of N-alkylethylenediamine–copper complexes. Thus, N,N,N′,N′-tetramethyl[17] has $\log K_1 = 7.20$, N,N′-diethyl[18] has $\log K_1 = 9.30$ and $\log \beta_2 = 15.62$, and N,N-diethyl[15] has $\log K_1 = 8.17$ and $\log \beta_2 = 13.72$.

Therefore, (1) the alkyl groups sterically hinder axial coordination by water, (2) the axial waters are coordinated forcing the alkyl groups into strong mutual repulsion, or (3) the alkyl groups block coordination from water in the second coordination sphere.[18] All of the explanations have as a common feature a very strong interaction between water and the copper complex which adds significantly to the stability of the complex. Other studies of Et_4dien complexes[4–7] indicate that accommodation of the four ethyl groups around metal ions is not difficult when there is a coordination number of four but steric crowding occurs with additional coordination or with a large ligand in the fourth position. Hence, in the N-alkyl–copper complexes it is the steric interaction with water rather than the steric hindrance between the alkyl groups which is important. Little is known about interactions in the second coordination sphere. However, the large increase of $\Delta S°$, attributed to the release of water molecules from the second coordination sphere, and the more positive $\Delta H°$ reported[19] for $Cu(N,N'\text{-}Et_2en)_2^{2+}$ compared to $Cu(en)_2^{2+}$ also is consistent with the loss of axial waters in the first coordination sphere.

Kinetic studies with the Pd–Et_4dien complex[4,5] and our own studies with the Cu–Et_4dien complex indicate that the axial positions are not readily available for substitution reactions.

The log (stability constants) of $[Cu(Et_4dien)OH]^+$ and $[Cu(dien)OH]^+$ are 6.0 and 4.9, respectively. The increased stability of the hydroxide complex in the case of Et_4dien is consistent with the absence of water coordination in the axial positions. Coodinated water in the fourth in-plane site would be bound more strongly to the copper and therefore would be more acidic. The absence of axial coordination thus tends to strengthen the planar bonding but weakens the over-all stability of the copper complex.

Acknowledgment.—This investigation was supported by PHS Research Grant No. 12152 from the National Institute of General Medical Sciences.

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(16) F. Basolo, Y. T. Chen, and R. K. Murmann, *J. Am. Chem. Soc.*, **76**, 956 (1954).

(17) R. L. Gustafson and A. E. Martell, *ibid.*, **81**, 525 (1959).

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