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Copper(II) Complexes of Diamino Diamide and Diamino Diamine in Aqueous Solution

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In order to study the difference on the equilibrium, spectral properties of copper(II) complexes of diamino diamide and diamino diamine, new tetradentate ligands, 4,7-dimethyl-4,7-diazadecanediamide (4,7-N,N′-Me_2-L-2,2,2) and 1,10-diamino-4,7-dimethyl-4,7-diazadecane (4,7-N,N′-Me_2-3,2,3-tet), have been synthesized. Synthetic procedures for these new ligands are described. Their protonation constants have been determined potentiometrically in 0.10 M KCl at 25.0 °C. The formation of their copper(II) complexes have been investigated quantitatively by the potentiometric technique and by the measurement of their electronic spectra.

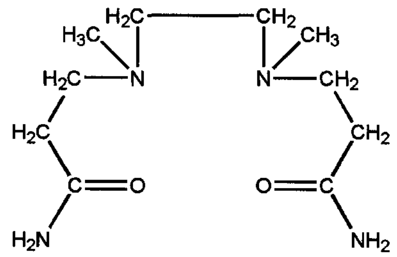
INTRODUCTION

Metal-containing polymer has become more and more popular for use in gas separation. Sakai et al.[1] prepared Nafion-silver microcomposite membranes having a significantly improved O_2/N_2 selectivity ratio because of the affinity between oxygen and silver. Lai and coworkers[2,3] reported that gas permeability of polycarbonate (PU)-dimethyl formamide (DMF)-$CuCl_2$ or Poly(methyl methacrylate)(PMMA)—DMF-$CuCl_2$ membranes were significantly improved as compared to pure PC or PMMA membranes. There are many studies about the use of cobalt compounds for oxygen enrichment from air.[4-10]

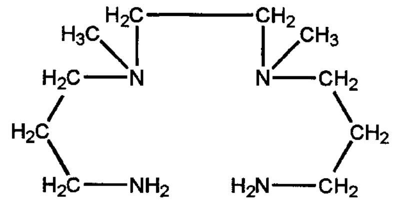
Polyurethanes (PU) are multiblock copolymers usually consisting of hard segments and polyether or polyester soft segments. These materials have been used to separate oxygen from air.[11-15] The complexation of PU polymers was generally obtained by incorporating a chain extender containing tertiary amines and then reacting with alkyl halides[16] or glycolic acid.[17] Others are formed by the use of sulfonate containing chain extender[18] or by the addition of $LiClO_4$ to the PU.[19,20]

Previously we have reported N-methyldiethanolamine (MDEA) as chain extender based PUs to study the gas permeability of polyurethane complexes.[21] The purpose of this study is to synthesize 4,7-dimethyl-4,7-diazadecanediamide (4,7-N,N′-Me_2-L-2,2,2) and 1,10-diamino-4,7-dimethyl-4,7-diazadecane (4,7-N,N′-Me_2-3,2,3-tet) and investigate the formation of their copper(II) complexes in aqueous solution. These two types of diaminodiamide and diaminodiamine can be used as chain extenders for the preparation of polyurethane-urea polymer and then complexed with cupric chloride or nickel chloride. This metal-containing polyurethane-urea can be used in many fields, such as the separation of oxygen from air. All the above programs are under further investigation in our laboratory. These ligands are depicted in Chart I. Their complexes with copper(II) have been studied by potentiometry and visible absorption spectrophotometry.

Chart I



4,7-N,N'-Me_2-L-2,2,2



4,7-N,N'-Me_2-3,2,3-tet

EXPERIMENTAL

Reagents

The ligand 4,7-N,N′-Me_2-L-2,2,2 was prepared from N,N′-dimethylethylenediamine (13.2 mL, 0.2 mol) and acrylamide (28.4 g, 0.4 mol) in 50 mL of acetonitrile by heating under reflux for 1.5 h. The solution was cooled and the product filtered off, washed with chloroform, recrystallized from chloroform, and dried in air; Anal. Calcd for $C_{10}H_{22}N_4O_2$: C, 52.1; H, 9.63; N, 24.3. Found: C, 51.3; H, 9.54; N, 23.6. ^{13}C NMR spectra (D_2O, DSS), δ (ppm): 33.17, 42.14, 53.58, 54.02, 178.07.

The ligand 4,7-N,N′-Me_2-3,2,3-tet was prepared from 4,7-N,N′-Me_2-L-2,2,2 (20 g) and lithium aluminum hydride (10 g) in 100 mL of THF by heating under reflux for 24 h. The solution was cooled and added 30 mL 5N NaOH solution to precipitate $Al(OH)_3$, filtered off, washed with THF. The solution of filtration was concentrated to dry. The residue was separated by reduced pressure distillation. The product 4,7-N,N′-Me_2-3,2,3-tet was a colorless liquid. Anal. Calcd for $C_{10}H_{26}N_4$: C, 59.4; H, 12.9; N, 27.7. Found: C, 58.7; H, 12.6; N, 27.1; ^{13}C NMR spectra (D_2O, DSS), δ (ppm): 24.16, 38.77, 42.79, 52.12, 56.17. Before titration, 4,7-N,N′-Me_2-L-2,2,2 was prepared to be diprotonated and 4,7-N,N′-Me_2-3,2,3-tet to be tetraprotonated by adding HCl solution. These ligands were 99.8% pure as determined by titration with a standard base. All other chemicals used were of reagent grade from Merck. A saturated solution of sodium hydroxide (reagent grade) was prepared to precipitate sodium carbonate. A sample of this was diluted with freshly boiled, distilled, deionized water and stored in a Nalgene Teflon bottle. It was standardized against weighed amounts of potassium hydrogen phthalate. The copper(II) ion concentration was standardized by EDTA titration.

Measurements

For pH measurements a Radiometer VIP-90 instrument was used. The pH was standardized with NBS buffers. The hydrogen ion and hydroxide ion concentrations in 0.1 M KCl were calculated from $-\log[H^+] = pH-0.11$ and $K_w = 10^{-13.78}$.[22,23]

Appropriate aliquots of standard solutions of ligand or ligand and metal were titrated with a standard sodium hydroxide solution. In all titrations the ionic strength was maintained relatively constant by using 0.10 M KCl as supporting electrolyte. The solutions were protected from air by a stream of humidified prepurified nitrogen and were maintained at 25.0 ± 0.1 °C during measurements. The equilibrium constants were obtained by using software-PKAS, BEST and SPE program by Martell.[24] A Hitachi 3410 uv-visible spectrophotometer with a thermostated cell compartment was used to record absorption spectra.

RESULTS AND DISCUSSION

Protonation Constants

A potentiometric titration curve of the chloride salt of diprotonated ligand 4,7-N,N′-Me_2-L-2,2,2 with standard base yielded the experimental data shown as the smooth curve 1 in Fig. 1. In this Figure a represents the number of mols of hydroxide ion added per mol of ligand present in the solution. Equation (1) and (2) are obtained from the usual mass- and charge-balance relationships, where C_{HnL} is the total concentration of ligand.[25] The values of the protonation constants of this ligand obtained from these experimental data are listed in Table 1. The non-methylated ligand, 4,7-diazadecanediamine (L-2,2,2), is also given for comparison.[26]

$$\log K_1^H = \log \frac{(2-a)C_{HnL} + [OH^-] - [H^+]}{(a-1)C_{HnL} - [OH^-] + [H^+]} - \log[H^+] \quad (1)$$

$$\log K_2^H = \log \frac{(1-a)C_{HnL} + [OH^-] - [H^+]}{aC_{HnL} - [OH^-] + [H^+]} - \log[H^+] \quad (2)$$

Another potentiometric titration curve of the chloride salt of tetraprotonated ligand 4,7-N,N′-Me_2-3,2,3-tet with standard base yielded the experimental data shown as the smooth curve 1 in Fig. 2. The protonation constants of polyacidic bases can be determined by Schwarzenbach's method[27,28] if the difference between the logarithms of the sucessive constants is smaller than 2.8. The K_1^H and K_2^H of 4,7-N,N′-Me_2-3,2,3-tet are obtained from the following equa-

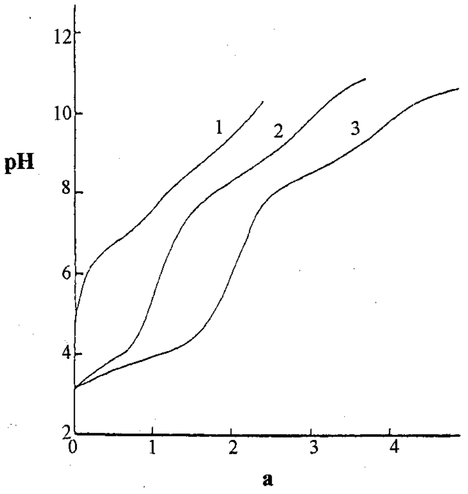


Fig. 1. Titration curves for 4,7-N,N′-Me_2-L-2,2,2 in the presence and absence of Cu^{2+} at 25 °C and 0.1 M KCl. Test solution: (1) 20.0 mL, 0.00553 M [H_2 4,7-N,N′-Me_2-L-2,2,2][Cl]$_2$; (2) 30.0 mL 0.00352 M $CuCl_2$ and 0.00705 M [H_2 4,7-N,N′-Me_2-L-2,2,2][Cl]$_2$; (3) 20.0 mL 0.00549 M $CuCl_2$ and 0.00551 M [H_2 4,7-N,N′-Me_2-L-2,2,2][Cl]$_2$. Titrant: 0.1058 M NaOH; a = number of moles of NaOH added per mol of ligand. 4,7-N,N′-Me_2-L-2,2,2 was prepared to be diprotonated by adding HCl solution before titration.

Table 1. Protonation Constants of 4,7-N,N′-Me$_2$-L-2,2,2 and 4,7-N,N′-Me$_2$-3,2,3-tet at 25.0 ± 0.1 °C and μ = 0.10 M (KCl)

Ligand	log K_1^H	log K_2^H	log K_3^H	log K_4^H
L-2,2,2[a]	8.78 ± 0.04	5.82 ± 0.03	—	—
4,7-N,N′-Me$_2$-L-2,2,2	8.21 ± 0.04	4.59 ± 0.03	—	—
4,7-N,N′-Me$_2$-3,2,3-tet	9.98 ± 0.05	9.48 ± 0.03	7.21 ± 0.04	4.14 ± 0.03

[a] From ref. 26

tion by using Schwarzenbach's method.

$$\frac{1}{K_1^H} = AK_2^H + B \tag{3}$$

$$A = \frac{[H^+]^2(aC_{HnL} + [H^+] - [OH^-])}{[OH^-] - [H^+] + (2 - a)C_{HnL}}$$

$$B = \frac{[H^+]\{(a - 1)C_{HnL} - [OH^-] + [H^+]\}}{[OH^-] - [H^+] + (2 - a)C_{HnL}}$$

A and B were calculated from several sets of values of a and [H$^+$] taken from titration curves. The calculation of K_3^H and K_4^H of 4,7-N,N′-Me$_2$-3,2,3-tet is the same as equation (1) and (2), respectively, because the difference in the logarithms of K_3^H and K_4^H is greater than 2.8.

The values of the protonation constants of the ligand obtained from these experimental data are also listed in Table 1.

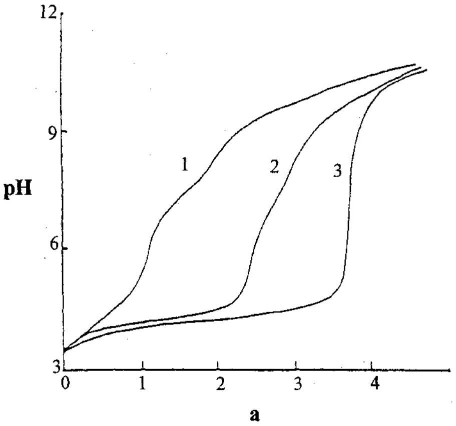


Fig. 2. Titration curves for 4,7-N,N′-Me$_2$-3,2,3-tet in the presence and absence of Cu^{2+} at 25 °C and 0.1 M KCl. Test solution: (1) 20.0 mL, 0.00212 M [H$_4$ 4,7-N,N′-Me$_2$-3,2,3-tet][Cl]$_4$; (2) 20.0 mL 0.00103 M CuCl$_2$ and 0.00207 M [H$_4$ 4,7-N,N′-Me$_2$-3,2,3-tet][Cl]$_4$; (3) 20.0 mL 0.00208 M CuCl$_2$ and 0.00221 M [H$_4$ 4,7-N,N′-Me$_2$-3,2,3-tet][Cl]$_4$. Titrant: 0.1062 M NaOH; a = number of moles of NaOH added per mol of ligand. 4,7-N,N′-Me$_2$-3,2,3-tet was prepared to be tetraprotonated by adding HCl solution before titration.

The ligand, 4,7-N,N′-Me$_2$-L-2,2,2, has two protonation constants,

$$K_1^H = \frac{[HL^+]}{[L][H^+]} \text{ and } K_2^H = \frac{[H_2L^{2+}]}{[H^+][HL^+]}$$

but the ligand, 4,7-N,N′-Me$_2$-3,2,3-tet, has four protonation constants,

$$K_1^H = \frac{[HL^+]}{[L][H^+]},\ K_2^H = \frac{[H_2L^{2+}]}{[HL^+][H^+]},\ K_3^H = \frac{[H_3L^{3+}]}{[H_2L^{2+}][H^+]}$$

$$\text{and } K_4^H = \frac{[H_4L^{4+}]}{[H_3L^{3+}][H^+]}$$

The values of log K_1^H and log K_2^H of 4,7-N,N′-Me$_2$-3,2,3-tet are very much greater than the corresponding constants of 4,7-N,N′-Me$_2$-L-2,2,2. It shows that the terminal primary nitrogen is protonated during the first two stages of protonation in 4,7-N,N′-Me$_2$-3,2,3-tet, while the tertiary nitrogen is protonated in 4,7-N,N′-Me$_2$-L-2,2,2. For 4,7-N,N′-Me$_2$-L-2,2,2, the value of K_2^H is less than that of K_1^H as might have been expected on the basis of both statistical factors[29] and electrostatic repulsion between the hydrogen ion and the protonated ligand. In general, values for secondary amines are larger than those of similar tertiary amines. The values of K_1^H and K_2^H of 4,7-N,N′-Me$_2$-L-2,2,2, which contains tertiary amines, are all significantly lower than the corresponding constants of L-2,2,2, which contains secondary amines. For 4,7-N,N′-Me$_2$-3,2,3-tet, the value of K_2^H is close to that of K_1^H. This is obviously due to smaller electrostatic repulsion exerted by the positive terminal, which is further from the terminal primary nitrogen atom. The values of log K_3^H and log K_4^H of 4,7-N,N′-Me$_2$-3,2,3-tet are much less than those of log K_1^H and log K_2^H. It shows that the first two stages of protonation involve the two equivalent primary nitrogen atoms and the last two stages of protonation involve the two equivalent tertiary nitrogen atoms.

Composition of the Copper(II) Complexes

Job's method of continuous variations[30] was used to determine the composition of the copper(II) complexes. Fig. 3

shows Job's plot in which the absorbance is plotted against the ratio $[Cu^{2+}]/([Cu^{2+}] + [4,7\text{-}N,N'\text{-}Me_2\text{-}L\text{-}2,2,2])$. The pH of the solution was kept at 5.34, and the total molarity of Cu^{2+} and 4,7-N,N′-Me_2-L-2,2,2 was 4.50×10^{-3} M. From the experimental results shown in Fig. 3, it is evident that copper(II) forms 1:1 complex with 4,7-N,N′-Me_2-L-2,2,2. Copper (II) also forms a 1:1 complex with 4,7-N,N′-Me_2-L-3,2,3-tet by using the same method.

Equilibrium Constants of Copper(II) Complexes

The titration curves for copper(II)-4,7-N,N′-Me_2-L-2,2,2 systems are shown in Fig. 1 (curves 2 and 3). The reactions are fast. At the start of the titration the reactants exist as Cu^{2+} and H_2L^{2+}, during titration the color of the solution changed from blue, through deep blue, to violet. For the 1:1 copper(II)-4,7-N,N′-Me_2-L-2,2,2 solution (curve 3) a definite break at a = 2 is seen. In the first sloping buffer region, the two protons attached to the amine groups of the ligand are dissociated by the copper(II) ion. In the second sloping buffer region, the two amide protons are dissociated in overlapping steps.

The following complex equilibria were found to describe the reactions of copper(II) with 4,7-N,N′-Me_2-L-2,2,2

$$Cu^{2+} + L \rightarrow CuL^{2+},\ K_{CuL^{2+}} = \frac{[CuL^{2+}]}{[Cu^{2+}][L]} \qquad (4)$$

$$CuL^{2+} \rightarrow CuH_{-1}L^{+} + H^{+}$$

$$K_A = \frac{[CuH_{-1}L^{+}][H^{+}]}{[CuL^{2+}]} \qquad (5)$$

$$CuH_{-1}L^{+} \rightarrow CuH_{-2}L + H^{+}$$

$$K_B = \frac{[CuH_{-2}L][H^{+}]}{[CuH_{-1}L^{+}]} \qquad (6)$$

in which L presents the 4,7-N,N′-Me_2-L-2,2,2 and the negative subscript on H represents the number of amide protons removed from the complex. The possible solution structures of the three complexes CuL^{+2}, $CuH_{-1}L^{+}$, and $CuH_{-2}L$ are shown in Chart II. Below a = 2 for the 1:1 titration (or below a = 1 in the 1:2 titration), only reaction 1 ($Cu^{2+} + L \rightarrow CuL^{2+}$) takes

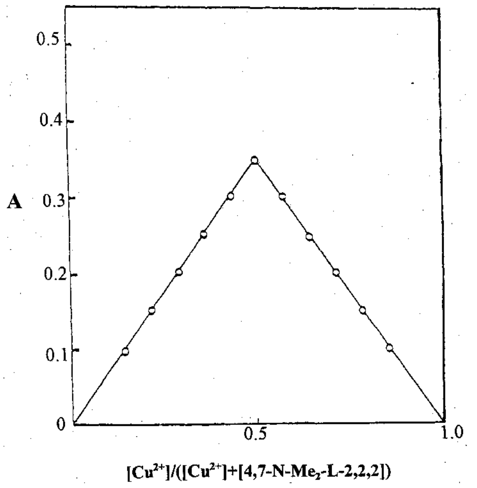
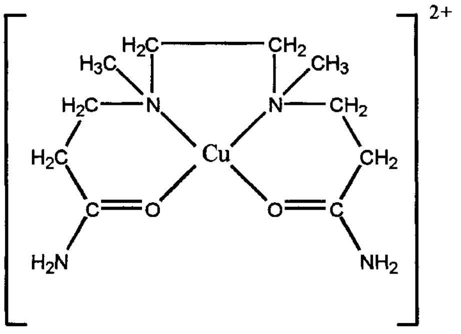
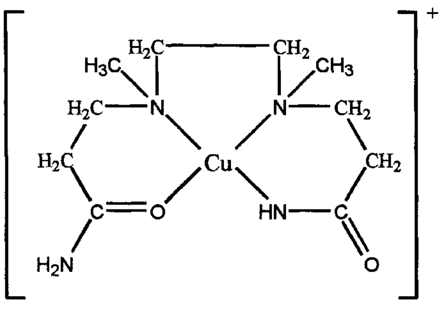


Fig. 3. Determination of compositions of copper(II)-4,7-N,N′-Me_2-L-2,2,2 by continuous variations, [Cu(II) 4,7-N,N′-Me_2-L-2,2,2] = 4.50×10^{-3} M, PH = 5.34, 664 nm.

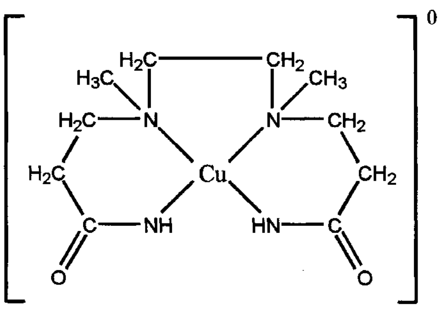
Chart II



$Cu(4,7\text{-}N\text{-}N'\text{-}Me_2\text{-}L\text{-}2,2,2)^{2+}$



$Cu(H_{-1}\text{-}4,7\text{-}N,N'\text{-}Me_2\text{-}L\text{-}2,2,2)^{+}$



$Cu(H_{-2}\text{-}4,7\text{-}N\text{-}N'\text{-}Me_2\text{-}L\text{-}2,2,2)^{0}$

place. For this reaction, the following equations are obtained from the usual mass-balance and charge-balance relationships.

$$\log K_f = \log \frac{\bar{n}}{1-\bar{n}} - \log[L] \qquad (7)$$

$$[L] = \frac{(2C_{HnL} - aC_M + [OH^-] - [H^+])}{\alpha'}$$

$$\bar{n} = \frac{(C_{HnL} - \alpha[L])}{C_M}$$

$$\alpha' = 2K_1^H K_2^H [H^+]^2 + K_1^H [H^+]$$

$$\alpha = K_1^H K_2^H [H^+]^2 + K_1^H [H^+] + 1$$

where C_{HnL} and C_M are the total concentration of ligand and metal species. The stability constant obtained is listed in Table 2.

Deprotonation reactions of Cu(4,7-N,N′-Me$_2$-L-2,2,2)$^{2+}$ take place in the region from a = 2 to 4 of the 1:1 titration curve (or in the region from a = 1 to 3 of the 1:2 titration curve). For these reactions, the relationship between K_A and K_B is as follows.

$$\frac{1}{K_A} = A \times K_B + B \qquad (8)$$

$$A = \frac{(2-a)C_{HnL} + 2C_M - [H^+] + [OH^-] - \alpha'[L]}{[H^+]^2((a-2)C_{HnL} + [H^+] - [OH^-] + \alpha'[L])}$$

$$B = \frac{(a-2)C_{HnL} - C_M + [H^+] - [OH^-] + \alpha'[L]}{[H^+]((2-a)C_{HnL} - [H^+] + [OH^-] - \alpha'[L])}$$

$$[L] = \frac{(C_{HnL} - C_M)}{\alpha}$$

A and B were calculated from several sets of values of a, $[H^+]$, C_M and C_{HnL} taken from each of the titration curves. The values of K_A and K_B obtained are listed in Table 2. The Cu-O to Cu-N bond rearrangements at the two amide sites occur in this region.

Above a = 4 for the 1:1 solution and above a = 3 for the 1:2 solution the titration curves are the same as those calculated assuming no further reaction between [CuH$_{-2}$L] and hydroxide ions. For the purpose of comparison, the corresponding values for the stability constants of Cu(L-2,2,2)$^{2+}$ are also given in the Table 2.[26]

The titration curves for copper(II)-4,7-N,N′-Me$_2$-3,2,3-tet systems are shown in Fig. 2 (curves 2 and 3). At the start of the titration the reactants exist as Cu^{2+} and H$_4$L^{4+}. During titration the color of the solution changed from light blue to violet.

The equilibria 9-10 show the reactions of copper(II) with -4,7-N,N′-Me$_2$-3,2,3-tet.

$$Cu^{2+} + LH^+ \rightarrow CuHL^{3+}$$

$$K_{CuHL^{3+}} = \frac{[CuHL^{3+}]}{[Cu^{2+}][LH^+]} \qquad (9)$$

$$Cu^{2+} + L \rightarrow CuL^{2+}$$

$$K_{CuL^{2+}} = \frac{[CuL^{2+}]}{[Cu^{2+}][L]} \qquad (10)$$

The structural formula of the two complexes CuHL^{3+} and CuL^{2+} are shown in Chart III. The calculation of stability constants is also obtained from the usual mass- and charge-balance relationships similar to the K_A and K_B of Cu[4,7-N,N′-Me$_2$-L-2,2,2]$^{+2}$. The stability constants obtained are listed in Table 2.

The result indicates that Cu(II) and 4,7-N,N′-Me$_2$-3,2,3-tet form a normal complex CuL^{2+} and a protonated complex CuHL^{3+} because CuL^{2+} has 6-5-6-membered ring structure. The steric strain makes CuL^{2+} complex easily form a protonated CuHL^{3+} to release the ring strain.[31]

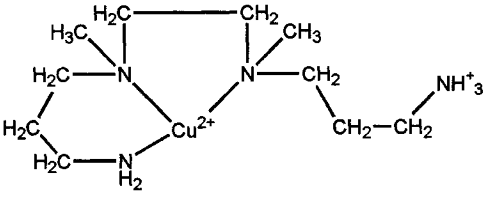
Comparing the stability constant of copper(II) of 4,7-N,N′-Me$_2$-L-2,2,2 with the corresponding constant of 4,7-N,N′-Me$_2$-3,2,3-tet, the value of log $K_{CuL}{}^{2+}$ for [Cu(4,7-N,N′-Me$_2$-3,2,3-tet)$^{2+}$ given in Table 2 is about 7 log units higher than the corresponding constant for [Cu(4,7-N,N′-Me$_2$-L-2,2,2)]$^{2+}$. The significant higher stability in the former indicates that the amino groups are much more strongly bonded to the metal ion in [Cu(4,7-N,N′-Me$_2$-3,2,3-tet)]$^{2+}$ than the am-

Table 2. Equilibrium Constants for the Interactions of 4,7-N,N′-Me$_2$-L-2,2,2 and 4,7-N,N′-Me$_2$-3,2,3-tet with Copper(II) at 25.0 ± 0.1 °C and μ = 0.10 M (KCl)

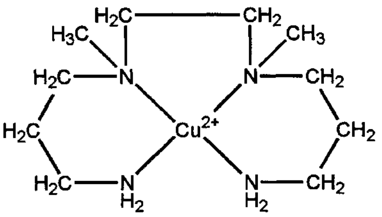
Ligand	log $K_{CuHL^{3+}}$	log $K_{CuL^{2+}}$	log K_A	log K_B
L-2,2,2[a]	—	12.58 ± 0.07	-8.08 ± 0.06	-9.33 ± 0.05
4,7-N,N′-Me$_2$-L-2,2,2	—	9.25 ± 0.05	-7.32 ± 0.05	-8.97 ± 0.06
4,7-N,N′-Me$_2$-3,2,3-tet	19.28 ± 0.06	16.54 ± 0.07	—	—

[a] From ref. 26

Chart III



$CuH(4,7\text{-}N,N'\text{-}Me_2\text{-}3,2,3\text{-}tet)^{3+}$



$Cu(4,7\text{-}N,N'\text{-}Me_2\text{-}3,2,3\text{-}tet)^{2+}$

ide groups in $[Cu(4,7\text{-}N,N'\text{-}Me_2\text{-}L\text{-}2,2,2]^{2+}$. This result is in complete accord with the base-weakening effect of the $CONH_2$ group.[32] Comparing the stability constant of copper(II) of 4,7-N,N′-Me_2-L-2,2,2 with the corresponding constant of L-2,2,2, the value of K_f is $Cu(L\text{-}2,2,2)^{2+} > Cu(4,7\text{-}N,N'\text{-}Me_2\text{-}L\text{-}2,2,2)]^{2+}$. This result indicates that the bulky alkyl group attached to the donor nitrogen atom prevents the coordinated diamino diamide from assuming a planar configuration, resulting in a weakening of the metal-ligand bonds.

The values of K_A and K_B are $Cu(L\text{-}2,2,2)^{2+} < Cu(4,7\text{-}N,N'\text{-}Me_2\text{-}L\text{-}2,2,2)^{2+}$. This sequence indicates that the values of both K_A and K_B increase as the number of N-alkyl groups increases. This trend is mainly attributed to the solvation energy of the copper(II) complex. In general, the solvation energy of a copper(II) complex decreases with the number of the N-alkyl groups. For each of these diamino diamides, the solvation energy increases in the order $CuH_{-2}L < CuH_{-1}L^+ < CuL^{2+}$. Thus, the desolvation effect attributed to the number of N-alkyl groups decreases in the order $CuL^{2+} > CuH_{-1}L^+ > CuH_{-2}L$. Consequently, the values of K_A and K_B increase as the number of N-alkyl groups increases.

Electronic Spectra

The electronic absorption spectra of copper(II)-(4,7-N,N′-Me_2-L-2,2,2) solutions are shown in Fig. 4. At pH 1.32, the spectrum is the same as that of $CuCl_2$. As the pH increases, the band maximum increases intensity (curves 2-4). Curve 4, at a = 2, is almost entirely due to the species $Cu(4,7\text{-}N,N'\text{-}Me_2\text{-}L\text{-}2,2,2)^{2+}$. Further increase in pH beyond a = 2 (curves 5-8) causes the absorption band to shift to a shorter wavelength due to the Cu-O to Cu-N bond rearrangements and the deprotonation reactions at the two amide sides. Curves 9 and 10 are probably due to the deprotonated species $Cu(H_{-2}\text{-}4,7\text{-}N,N'\text{-}Me_2\text{-}L\text{-}2,2,2)$. No further changes were observed when the hydroxide ion was added. This result confirms the potentiometric observation that above a = 4 for the 1:1 solution the titration curve is the same as that calculated on the assumption that there is no further reaction between $Cu(H_{-2}\text{-}4,7\text{-}N,N'\text{-}Me_2\text{-}L\text{-}2,2,2)$ and hydroxide ion.

Using the various equilibrium constants in Table 2, the degree of formation of copper(II)-4,7-N,N′-Me_2-L-2,2,2 species in a 1:1 solution can be calculated and is shown in Fig. 5. By means of the calculated concentrations of all species present in the solution, the spectra can be resolved into their components by using eq. 11. The absorption characteristics of all species so obtained are given in Table 3.

$$A = b(\varepsilon_{Cu^{2+}}[Cu^{2+}] + \varepsilon_{CuL^{2+}}[CuL^{2+}] + \varepsilon_{CuH_{-1}L^{+}}[CuH_{-1}L^{+}] + \varepsilon_{CuH_{-2}L}[CuH_{-2}L]) \qquad (11)$$

These results show that the crystal field stabilization en-

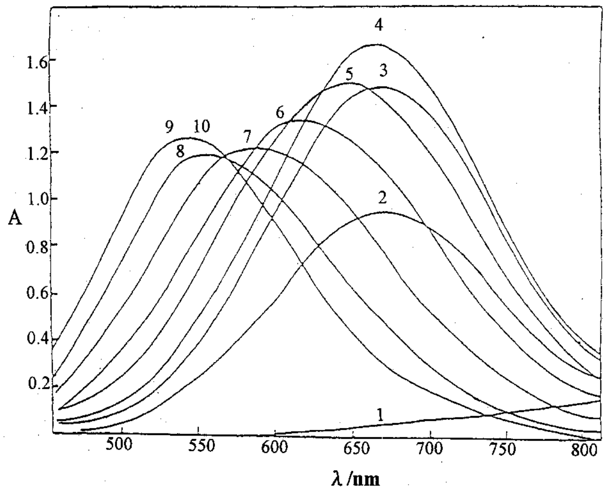


Fig. 4. Visible absorption spectra of copper(II)-4,7-N,N′-Me_2-L-2,2,2 solutions. All solutions contain 0.00105 M $CuCl_2$ and 0.00106 M $[H_2\ 4,7\text{-}N,N'\text{-}Me_2\text{-}L\text{-}2,2,2][Cl]_2$ at 25 °C and 0.1 M KCl. The pH values of the solutions are as follows: (1) 1.32; (2) 3.32; (3) 4.87; (4) 6.13; (5) 7.38; (6) 8.85; (7) 9.48; (8) 10.24; (9) 11.93; (10) 12.04.

Table 3. Electronic Absorption Spectra of Copper(II) Complexes of 4,7-N,N′-Me_2-L-2,2,2 and 4,7-N,N′-Me_2-3,2,3-tet in Aqueous Solution

Compd.	λmax, nm
$Cu(L\text{-}2,2,2)^{2+}$ [a]	645
$Cu(H_{-1}\text{-}L\text{-}2,2,2)^{+}$ [a]	580
$Cu(H_{-2}L\text{-}2,2,2)$ [a]	535
$Cu(4,7\text{-}N,N'\text{-}Me_2\text{-}L\text{-}2,2,2)^{2+}$	664
$Cu(H_{-1}\text{-}4,7\text{-}N,N'\text{-}Me_2\text{-}L\text{-}2,2,2)^{+}$	600
$Cu(H_{-2}\text{-}4,7\text{-}N,N'\text{-}Me_2\text{-}L\text{-}2,2,2)^{0}$	545
$CuH(4,7\text{-}N,N'\text{-}Me_2\text{-}3,2,3\text{-}tet)^{3+}$	576
$Cu(4,7\text{-}N,N'\text{-}Me_2\text{-}3,2,3\text{-}tet)^{2+}$	554

[a] From ref. 26

ergy of the copper(II) complex increases in the order $CuL^{2+} < CuH_{-1}L^{+} < CuH_{-2}L$. Thus, the effect attributed to the distortion from a square-planar structure on the CFSE of the copper(II) complex increases in the order $CuL^{2+} < CuH_{-1}L^{+} < CuH_{-2}L$.

The electronic absorption spectra of copper(II)-(4,7-N,N′-Me_2-3,2,3-tet) solutions are shown in Fig. 6. As the pH increases, the absorption bands shift gradually to shorter wavelengths.

At pH 4.04, the wavelength of the band maximum is 577 nm (curve 3). At pH 10.30, the wavelength of the band maximum is 554 nm (curve 10). This result confirms that there are two CuL^{2+} and $CuHL^{3+}$ species in the solution.

Using the various equilibrium constants in Table 2, the degree of formation of copper(II)-4,7-N,N′-Me_2-3,2,3-tet species in a 1:1 solution can be calculated and is shown in Fig. 7.

By means of the calculated concentrations of all species present in the solution, the spectra can be resolved into their components by using eq. 12. The absorption characteristics of all species so obtained are given in Table 3.

$$A = b(\varepsilon_{Cu^{2+}}[Cu^{2+}] + \varepsilon_{CuHL^{3+}}[CuHL^{3+}] + \varepsilon_{CuL^{2+}}[CuL^{2+}]) \quad (12)$$

From Table 3, $Cu(4,7\text{-}N,N'\text{-}Me_2\text{-}3,2,3\text{-}tet)^{2+}$ and $Cu(H_{-2}\text{-}4,7\text{-}N,N'\text{-}Me_2\text{-}L\text{-}2,2,2)$ have similar values of λ_{max} because their coordinated atoms, 4N, are the same. The small difference appears to arise from different amino and amide groups.

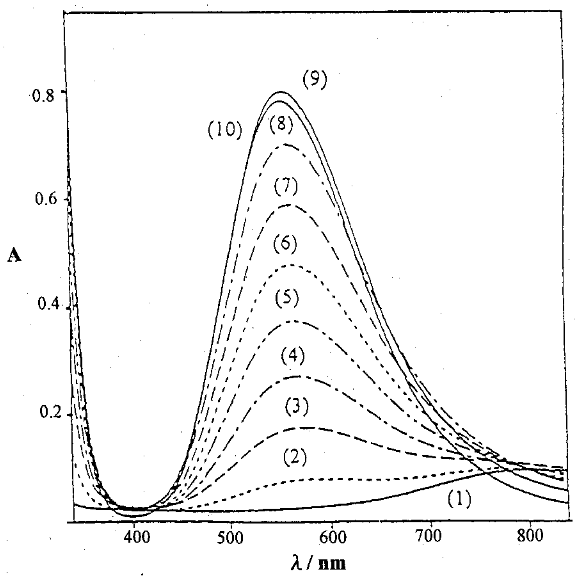


Fig. 6. Visible absorption spectra of copper(II)-4,7-N,N′-Me_2-3,2,3-tet solutions. All solutions contain 0.00205 M $CuCl_2$ and 0.00210 M [H_4 4,7-N,N′-Me_2-3,2,3-tet]$[Cl]_4$ at 25 °C and 0.1 M KCl. The pH values of the solutions are as follows: (1) 3.40; (2) 3.85; (3) 4.04; (4) 4.17; (5) 4.26; (6) 4.37; (7) 4.52; (8) 4.75; (9) 8.07; (10) 10.30.

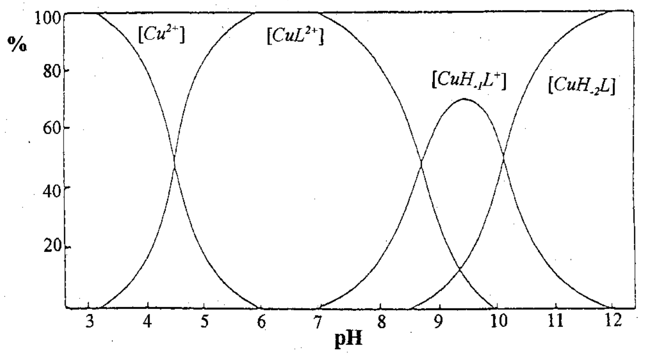


Fig. 5. Degree of formation of copper(II)-4,7-N,N′-Me_2-L-2,2,2 complexes in 1:1 metal-to-ligand solution.

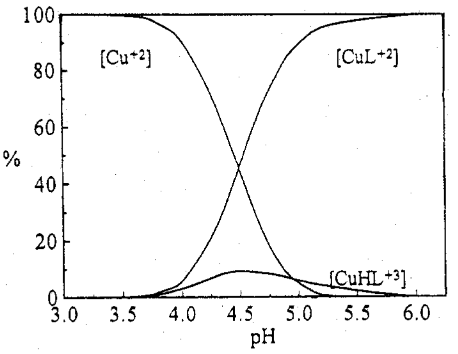


Fig. 7. Degree of formation of copper(II)-4,7-N,N′-Me_2-3,2,3-tet complexes in 1:1 metal-to-ligand solution.

$Cu(H_{-1}$-4,7-N,N′-Me_2-L-2,2,2$)^+$ and CuH(4,7-N,N′-Me_2-3,2,3-tet$)^{3+}$ have the same coordinated atoms, 3N and 1O. We may expect that they would have absorption maxima of similar wavelengths. The wavelength of $Cu(H_{-1}$-4,7-N,N′-Me_2-L-2,2,2$)^+$ is slightly larger than that of the corresponding CuH(4,7-N,N′-Me_2-3,2,3-tet$)^{3+}$. These differences are that $Cu(H_{-1}$-4,7-N,N′-Me_2-L-2,2,2$)^{2+}$ contains three linked 6-5-6-membered ring and CuH(4,7-N,N′-Me_2-3,2,3-tet$)^{3+}$ contains two linked 6-5-membered ring. The steric strain increases as the number of chelate rings increases.

The wavelength for each of the copper(II)-4,7-N,N′-Me_2-L-2,2,2 complexes is slightly larger than that of the corresponding copper(II)-L-2,2,2 species. These differences reflect the distorted planar structures of the copper(II)-4,7-N,N′-Me_2-L-2,2,2. In general, the lower the degree of distortion from a square-planar structure, the smaller is λ_{max}. The distortions are mainly attributed to the large steric constraints of the N-alkyl groups.

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Key Words

Complex; Diamino diamide; Diamino diamine.

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