the succession of complexes formed by all of the metal ions listed in Table I. While it would seem logical to assign the protonated sites of the protonated complexes to uncoordinated phenolic donor groups and to consider the stepwise displacement of these protons to be due to stepwise involvement of the phenolate donors in coordination, as was the case for Cu(II)-HBED,[2] the situation here is probably entirely different. Since the first coordination step in the Cu(II)-PLED system involves displacement of four protons from the ligand to give a neutral species having the formulation CuH_2L (with the protons probably residing on the pyridinium nitrogens), it seems that, in contrast to the behavior of HBED, both aliphatic amino nitrogens and the phenolate groups are involved initially in Cu(II) ion coordination. Easier access to the phenolate groups may be due in this case to their lower proton affinity (compared to HBED) because of the inductive electron-withdrawal effects of the protonated pyridinium groups.

A more complicated system involving competition between TTHA and PLED for Ga(III) is illustrated by Figure 3. Above $-\log [H^+] = 4$, the distribution pattern for Ga(III)-PLED species is analogous to that of Cu(II) in Figure 2, with displacement of the curves to lower pH in accordance with the higher stabilities of the Ga(III) chelates. At the lowest pH indicated, above 70% of the Ga(III) is complexed by TTHA, while 30% is in the initial PLED form GaH_2L. The relative concentration of the latter rises rapidly to a maximum at pH 4 but never reaches 100% because of a residual low concentration of monoprotonated and completely deprotonated TTHA chelates that finally disappear above pH 7.

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Registry No. 3, 88969-06-6; *N,N'*-dipyridoxylideneethylenediamine, 88969-07-7; *N,N'*-dipyridoxylethylenediamine, 88969-08-8.

Contribution from the Department of Chemistry, University of Malaya, Pantai Valley, Kuala Lumpur, Malaysia

Copper(II) Complexes of 3,8-Dimethyl-4,7-diazadeca-3,7-dienediamide in Solution

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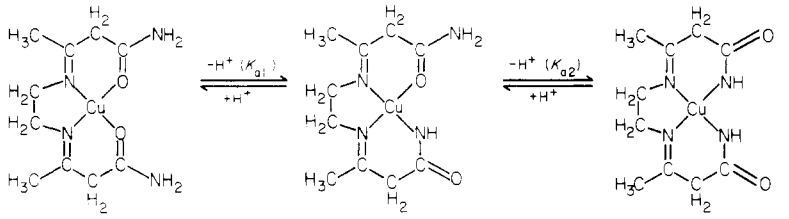
The complexes formed between copper(II) and 3,8-dimethyl-4,7-diazadeca-3,7-dienediamide (DDA) in solution at different pHs have been investigated by means of potentiometric titration, spectrophotometry, and electron spin resonance spectroscopy. The combined evidence from the three techniques established unequivocally that the equilibria



A B C

exist in solution at room temperature with equilibrium constants $pK_{a_1} = 7.35 \pm 0.01$ and $pK_{a_2} = 8.76 \pm 0.01$, respectively. Species A absorbs at λ_{max} 624 nm with ϵ_{max} 105.4 cm^{-1} M^{-1} and shows five superhyperfine lines in its ESR spectrum whereas species C absorbs at 522 nm with ϵ_{max} 72.9 cm^{-1} M^{-1} and shows nine superhyperfine lines in its ESR spectrum.

It is well-known that certain amide groups, including naturally occurring peptides, can coordinate to copper(II) ions in two fashions, with or without deprotonation of the amide nitrogen.[1] While it is relatively easy to establish the site of coordination in the former case because such coordination invariably results in complexes with characteristic purple color (biuret test) that persist in solution as well as in the solid state so much so that X-ray crystallographic results of single crystals may be extrapolated to species in solution with confidence, it is much more difficult to establish unequivocally the structure of the species in solution prior to deprotonation. This is reflected by the fact that although there is a general consensus that the site of coordination in the complexes prior to deprotonation is the carbonyl oxygen,[1-5] there are nevertheless persistent claims in the literature that the intact amide nitrogen can serve as the coordinating site.[6-9] The situation arises because hitherto there has been no experimental method that can distinguish definitively between the two alternative modes of binding of such species in solution. Despite the fact that all complexes whose solid-state structures have been determined crystallographically invariably show that the coordination is through the carbonyl oxygen,[10] there remains the possibility that such results may not be directly applicable to species in solution. Spectrophotometric studies provide strong supporting evidence of carbonyl oxygen coordination but are

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not definitive enough to completely rule out the alternative mode of coordination, because the amount of "red shift"[11] due to an intact amide nitrogen coordinating to copper is not known. Electron spin resonance spectroscopy appears to offer the best potential for resolving the problem since, in principle, it can determine the environment of copper(II) in the complex both in solid as well as in solution. It has been pointed out that the method has so far not contributed significantly to solving this type of problem because most work has been done in frozen systems where the species present may be different from those at room temperature.[11] This, however, merely reflects upon the experimental conditions chosen for study that are inappropriate but not the merit of the method itself. Wiersema and Windle[12] have shown in their study of electron spin resonance of some nitrogen-bonded copper(II) chelates that, in the room-temperature as well as liquid-nitrogen-temperature spectra, there is a direct correlation between the number of superhyperfine lines due to nitrogen with the number of nitrogen atoms directly bonded to the metal. The spectra show five, seven, or nine lines corresponding to two–four nitrogen atoms coordinated to copper respectively.[12] Since the method is applicable to solution at room temperature, it offers an easy means to distinguish between the two alternative modes of coordination of an intact amide group to copper in solution. Strangely, the method has not been fully exploited despite its simplicity.

In this paper we illustrate the application of the method to the copper(II) 3,8-dimethyl-4,7-diazadeca-3,7-dienediamide (DDA) system in solution at room temperature.

Experimental Section

Materials. The ligand was synthesized from ethane-1,2-diamine and acetoacetamide. A filtered solution of acetoacetamide (20.2 g, 0.2 mol) in methanol (75 mL) was added to ethane-1,2-diamine (6.0 g, 0.1 mol) in methanol (75 mL). The mixture was stirred thoroughly on a magnetic stirrer and left to stand overnight. The crystalline solid formed was filtered and washed thoroughly with methanol. A small sample was recrystallized from 95% ethanol for elemental analysis, and the rest of the product was used directly for the synthesis of the copper complex; mp 199 °C.

Anal. Calcd for $C_{10}H_{18}N_4O_2$: C, 53.1; H, 8.0; N, 24.8. Found: C, 52.6; H, 7.9; N, 24.6.

The ligand was found to be slightly soluble in hot methanol and 95% ethanol but is practically insoluble in hot or cold water.

A 2.3-g sample (0.01 mol) of the ligand prepared above was suspended in 75 mL of methanol. To this was added 2.4 g (0.01 mol) of $Cu(NO_3)\cdot 3H_2O$ in 75 mL of methanol. The mixture was heated with constant stirring until a clear blue solution was obtained. It was filtered while hot and left to stand overnight. Large blue crystals of the complex that separated out were collected by suction filtration and washed thoroughly with cold methanol. The complex may be recrystallized from a methanol–water mixture. It is very soluble in water; mp 213 °C.

Anal. Calcd for $C_{10}H_{18}N_4O_2\cdot Cu(NO_3)_2$: C, 29.0; H, 4.4; N, 20.3; Cu, 15.4. Found: C, 29.1; H, 4.4; N, 21.3; Cu, 15.6.

The percentage of copper in the complex was determined by the iodine–thiosulfate method,[13] while elemental analysis was done by the Australian Microanalytical Service, Chemical Research Laboratories, AMDEL.

Potentiometric Titration. A potentiometric titration was carried out on a solution containing $[Cu(DDA)](NO_3)_2$ (8.000×10^{-3} M) at 25 °C and 0.1 M KNO_3 constant ionic strength medium with standard NaOH solution. The apparatus and procedure have been described previously.[14]

Spectrophotometry. A stock solution of $[Cu(DDA)](NO_3)_2$ was prepared by dissolving a weighed amount of the complex in water. A series of test solutions were prepared from it by appropriate dilution and by adding appropriate amounts of NaOH solution so as to give 0.0, 0.5, 1.0, 1.5, and 2.0 equiv of base per ligand. Appropriate amounts of KNO_3 solution were also added to each test solution to give a constant ionic strength medium of 0.1 M KNO_3. The pH values of the solutions were 5.56, 7.31, 8.08, 8.81, and 9.89, respectively. The solutions were scanned in the visible region (800–400 nm) on a Varian Superscan spectrophotometer. The spectra are reproduced in Figure 1.

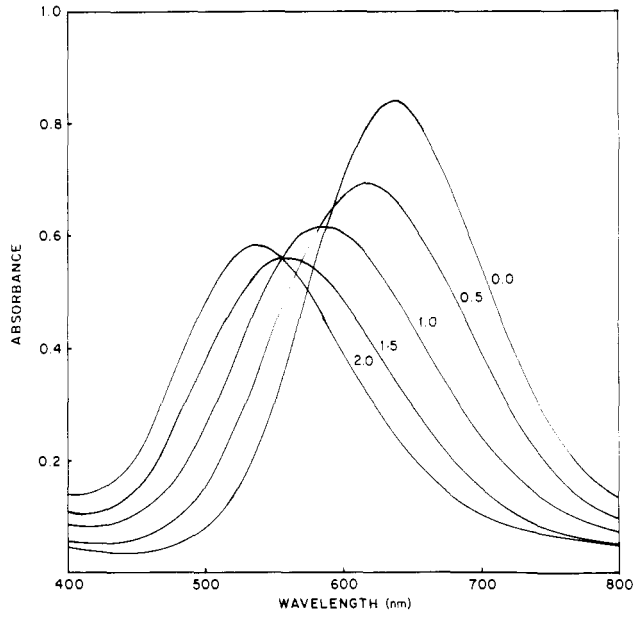

Figure 1. Plots of absorbance vs. wavelength for solutions of $[Cu(DDA)](NO_3)_2$ at different equivalents, a, of base per ligand.

Electron Spin Resonance Spectra. Samples were prepared by dissolving $[Cu(DDA)](NO_3)_2$ in water, degassing by passing nitrogen through the solutions, taking a portion of each solution up into a capillary ("melting point") tube, and sealing off both ends. For a number of solutions, excess base, in the form of solid potassium hydroxide, was added before degassing.

The room-temperature spectra were obtained with use of a Bruker B ER 420 X-band spectrometer employing 100-kHz modulation for detection of the signal. It was found that addition of methanol to give, approximately, 1:1 water–methanol solutions greatly improved the resolution of the superhyperfine structure but otherwise produced no change in the spectra.

Results and Discussion

Potentiometry. The pH titration curve of $[Cu(DDA)]^{2+}$ shows that it acts as a dibasic acid, and the equilibrium constants may be represented by

$$[Cu(DDA)]^{2+} \overset{K_{a_1}}{\rightleftharpoons} H^+ + [Cu(DDAH_{-1})]^+ \quad (1)$$

$$[Cu(DDAH_{-1})]^+ \overset{K_{a_2}}{\rightleftharpoons} H^+ + [Cu(DDAH_{-2})] \quad (2)$$

where

$$K_{a_1} = [H^+][[Cu(DDAH_{-1})]^+]/[[Cu(DDA)]^{2+}] \quad (3)$$

$$K_{a_2} = [H^+][[Cu(DDAH_{-2})]]/[[Cu(DDAH_{-1})]^+] \quad (4)$$

and $[Cu(DDAH_{-1})]^+$ and $[Cu(DDAH_{-2})]$ represent respectively species with one and two amide groups deprotonated.

Equilibrium constants K_{a_1} and K_{a_2} were evaluated by regarding $[Cu(DDA)]^{2+}$ as a simple dibasic acid with overlapping pK values. All actual numerical calculations were done on a UNIVAC 1100 computer.[15] The values of pK_{a_1} and pK_{a_2} are 7.35 ± 0.01 and 8.76 ± 0.01, respectively. The magnitudes of pK_{a_1} and pK_{a_2} are typical of the stepwise dissociation constants of complexes with two amide groups. The presence of

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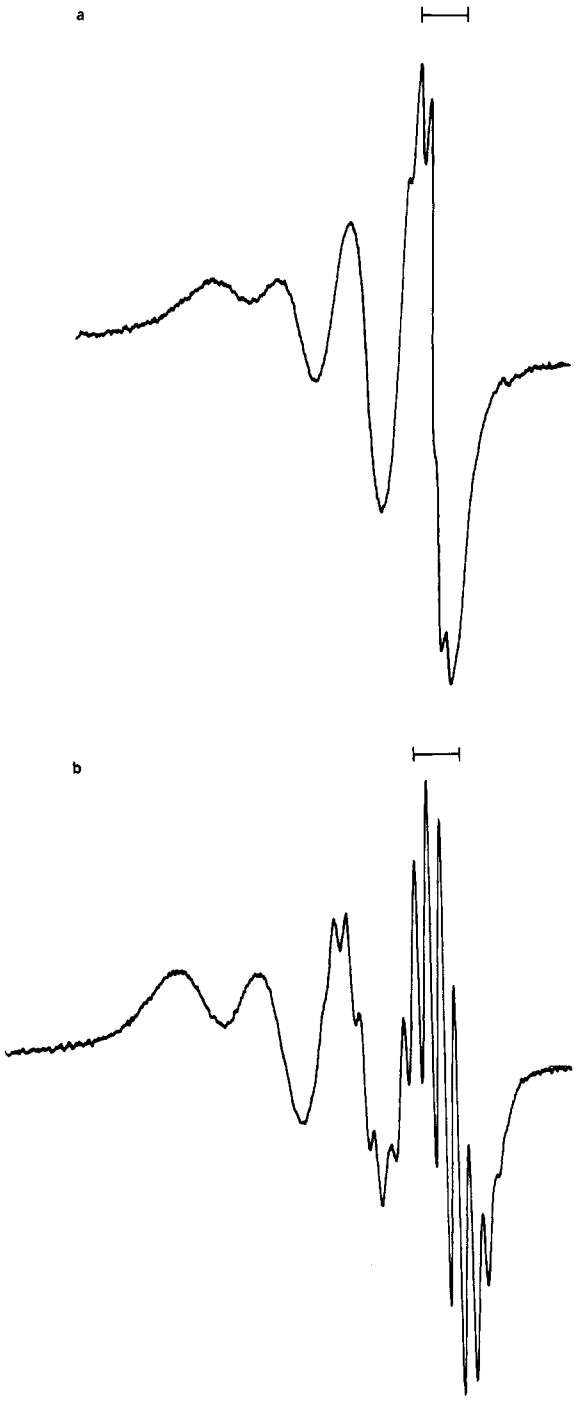
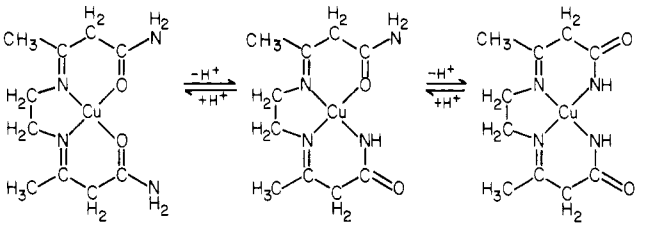


Figure 2. Electron paramagnetic resonance spectra: (a) in solution of blue species; (b) in solution of purple species. The marker indicates an interval of 50 G.

the Schiff base linkages in $[Cu(DDA)]^{2+}$ does not greatly influence the magnitude of its pK_{a_1} and pK_{a_2} values.

Spectrophotometry. The visible spectra of $[Cu(DDA)]^{2+}$ as a function of equivalents, a, of base per ligand are shown in Figure 1. At $a = 0$ there is an absorption maximum at λ_{max} 624 nm with ϵ_{max} 105.4 cm^{-1} M^{-1}. The position and intensity of the absorption are consistent with a complex where the copper is coordinated to two nitrogens and two oxygen centers. The two nitrogens here are from the Schiff base linkages while the oxygens are from the amide groups. As the value of a increases, there is a progressive shift of the absorption maximum toward shorter wavelengths until $a = 2$, thereafter the peak remains unchanged at λ_{max} 522 nm with ϵ_{max} 72.9 cm^{-1} M^{-1}. No isosbestic point was observed in the spectra. The shift toward shorter wavelengths in the absorption peak is an indication of additional nitrogen centers becoming coordinated to copper in the complex. The purple color of the solution at $a = 2$ is strongly indicative of a species containing deprotonated amide groups coordinating to copper. The absence of an isosbestic point in the spectra is consistent with a solution containing more than two species existing in simultaneous equilibria. Thus, the evidence from spectrophotometry and potentiometry supports the equilibria in Scheme I.

Scheme I



The extinction coefficient of the deprotonated complex is less than that of the complex with intact amide groups. This has been noted in other ligands with terminal amide groups.[15,16]

Electron Spin Resonance Spectroscopy. The spectra (Figure 2) show hyperfine structure of four lines due to the copper $I = {}^3/_2$ nuclei and superhyperfine structure due to interaction of the unpaired electron with the adjcent nitrogen (^{14}N) nuclei. In the solution of the blue species, five superhyperfine lines with a separation of 12.5 G and intensities in the ratio of approximately 1:2:3:2:1 are observed, showing the presence of two equivalent nitrogen nuclei. In the solution of the purple species, nine superhyperfine lines with separation of 14.2 G and intensity ratio of ca. 1:4:10:16:19:16:10:4:1 show the presence of four equivalent, or nearly equivalent, adjacent nitrogen nuclei.

Thus, prior to deprotonation two adjacent nitrogen nuclei are detected, while after deprotonation there are four. This provides further confirmation for Scheme I. In particular, the presence of two nitrogens adjacent to copper in the species with intact amide groups is demonstrated ambiguously.

The combined evidence from potentiometry, spectrophotometry, and electron spin resonance spectroscopy leaves little doubt that the equilibrium as depicted in Scheme I is correct and the intact amide groups in the ligand are coordinated to the copper(II) through the carbonyl oxygens.

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Registry No. A, 88969-10-2; C, 88969-11-3.

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