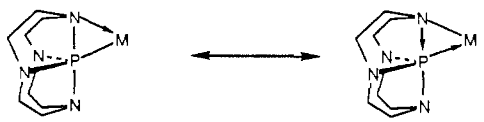
is significantly disrupted by coordination to the metal. In addition, consider the geometry about the coordinated nitrogen in **1**: the sum of the two Pt-N-C angles and one C-N-C angle (i.e., neglecting the P-N interaction) is 353°, very close to planar.[14] The geometry about this nitrogen suggests the Pt-N interaction may be more amide-like, while the Pt-P interaction may be more phosphine-like, leaving the lone pair on nitrogen to donate to phosphorus to complete its 10-P-5 geometry. Both of the above electronic descriptions represent extremes that are illustrated below; the actual electronic situation is probably a hybrid of these.



Acknowledgment. We wish to thank the Robert A. Welch Foundation for generous financial support; M.L. and D.K. thank Thomas K. Clark for assistance in the synthesis of cyclenPH.

Registry No. **1**, 108148-24-9; **2**, 108148-25-0; **3**, 118474-27-4; **4**, 118494-04-5.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances, bond angles, and torsion angles for **2** and **3** and a table of hydrogen atom coordinates and isotropic thermal parameters for **3** (7 pages); tables of observed and calculated structure factors for **2** and **3** (35 pages). Ordering information is given on any current masthead page.

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(14) This value can be compared to the corresponding value of 342° in **3** (neglecting the N-H interaction). Note that this represents a difference of 25°, since the N in **1** is on the same side of the C-Pt-C plane as the P, while it lies on the opposite side in **3**.

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Steric, Inductive, and Ring-Strain Effects in Chelation Thermodynamics and Kinetics. Reactions of Copper(II) Ion with *N*-Alkyl-Substituted Diamino Diamides

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Received October 14, 1987

In order to study the steric, inductive, and ring-strain effects of diamino diamides on the thermodynamic, spectral, and kinetic properties of copper(II)-diamino diamide complexes, four new tetradentate ligands, 4-methyl-4,7-diazadecanediamide (4-Me-L-2,2,2), 4,7-dimethyl-4,7-diazadecanediamide (4,7-Me$_2$-L-2,2,2), 4-ethyl-4,7-diazadecanediamide (4-Et-L-2,2,2), and 4-methyl-4,8-diazaundecanediamide (4-Me-L-2,3,2), have been synthesized. Synthetic procedures for these new ligands are described. Their protonation constants have been determined potentiometrically in 0.10 M NaClO$_4$ at 25.0 °C. The formation of their copper(II) complexes and the Cu-O to Cu-N bond rearrangements at the two amide sites of these complexes have been investigated quantitatively by the potentiometric technique and by the measurement of their electronic spectra. The kinetics of complexation obtained by using the stopped-flow technique indicates that the first metal-nitrogen bond formation between copper(II) and the unprotonated ligands is the rate-determining step and that the proton loss is the rate-limiting step in the reactions of copper(II) with the monoprotonated ligands. The reactivity order for the dissociation reaction is Cu(4-Me-L-2,3,2)$^{2+}$ > Cu(4,7-Me$_2$-L-2,2,2)$^{2+}$ > Cu(4-Me-L-2,2,2)$^{2+}$ > Cu(4-Et-L-2,2,2)$^{2+}$. The thermodynamic, spectroscopic, and kinetic data are discussed in relation to a combination of steric, inductive, statistical, solvation, and ring-strain effects.

Introduction

Previously, we have reported the thermodynamics and kinetics of the complexation reactions of divalent nickel ion[1] and copper ion[2] with four closely related diamino diamides, two of which are depicted in Chart I. The ligand $NH_2CO(CH_2)_nNH(CH_2)_mNH(CH_2)_pCONH_2$ is denoted by the symbol L-*n*,*m*,*p*. The current investigation is designed to gain more detailed understanding of the steric, inductive, and ring-strain effects that arise from the substitution at the amino nitrogen donor atom on the thermodynamic, spectral, and kinetic properties of copper(II)-diamino diamide complexes. Thus we have synthesized four new *N*-alkyl-substituted diamino diamides, 4-methyl-4,7-diazadecanediamide (4-Me-L-2,2,2), 4,7-dimethyl-4,7-diazadecanediamide (4,7-Me$_2$-L-2,2,2), 4-ethyl-4,7-diazadecanediamide (4-Et-L-2,2,2), and 4-methyl-4,8-diazaundecanediamide (4-Me-L-2,3,2). These ligands are depicted in Chart I. Their complexes with copper(II) have been studied by potentiometry and visible absorption spectrophotometry, and the reaction kinetics have been studied by stopped-flow methods.

Experimental Section

Reagents. The ligand 4-Me-L-2,2,2 was prepared from *N*-methylethylenediamine (12.4 mL, 0.2 mol) and acrylamide (28.4 g, 0.4 mol) in 80 mL of acetonitrile by refluxing for 2 h. The solution was cooled in a refrigerator for 3 weeks, and the product was filtered off, recrystallized from acetonitrile, and dried in vacuo; mp 88-89 °C. Anal. Calcd for $C_9H_{20}N_4O_2$: C, 50.0; H, 9.30; N, 25.9. Found: C, 50.8; H, 9.3; N, 26.5. The ligand 4,7-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; mp 101-102 °C. Anal. Calcd for $C_{10}H_{22}N_4O_2$: C, 52.1; H, 9.63; N, 24.3. Found: C, 51.8; H, 9.58; N, 24.6. The ligand 4-Et-L-2,2,2 was prepared from *N*-ethylethylenediamine (21.1 mL, 0.2 mol) and acrylamide (28.4 g, 0.4 mol) in 80 mL of acetonitrile by refluxing the mixture for 2 h. The solution was cooled in a refrigerator and the product filtered off, recrystallized from acetonitrile, and dried in vacuo; mp 81-82 °C. Anal. Calcd for $C_{10}H_{22}N_4O_2$: C, 52.1; H, 9.63; N, 24.3. Found: C, 51.4; H, 9.48; N, 24.8. The ligand 4-Me-L-2,3,2 was prepared from *N*-methyltrimethylenediamine (13.6 mL, 0.2 mol) and acrylamide (28.4 g, 0.4 mol) in 60 mL of acetonitrile by refluxing it for 2 h. The solution was cooled; the product was recrystallized from chloroform and dried in vacuo; mp 55-56 °C. Anal. Calcd for $C_{10}H_{22}N_4O_2$: C, 52.1; H, 9.63; N, 24.3. Found: C, 51.6; H, 9.51; N, 23.8. 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. Standard solutions of ligands, borate-mannitol buffers, and sodium perchlorate were prepared by weight. The copper(II) ion concentration was standardized by EDTA titration.

Measurements. For pH measurements a Radiometer PHM 64 instrument equipped with a GK 2401B combined electrode was used. The

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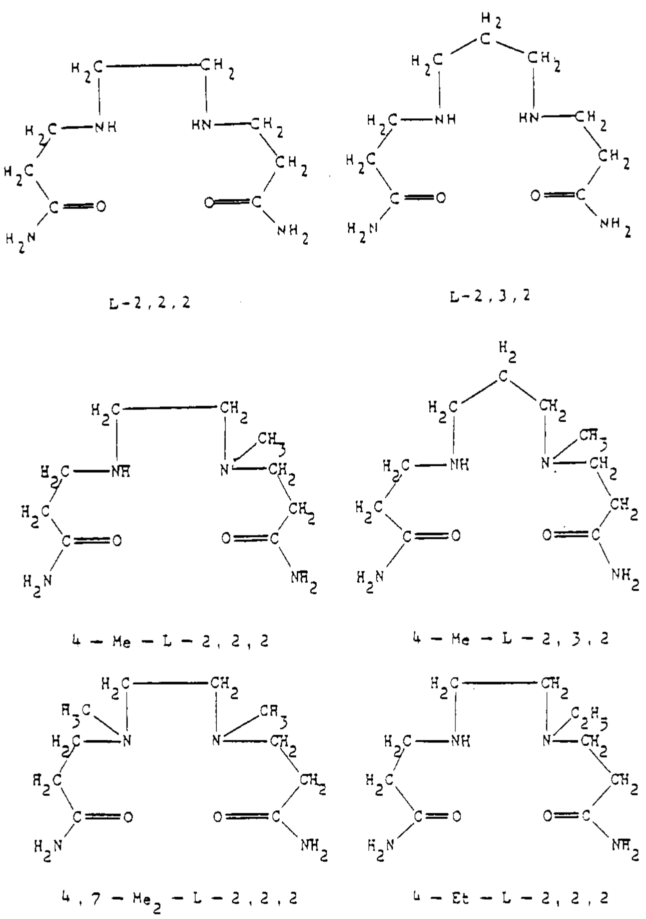
Chart I



L-2,2,2

L-2,3,2

4-Me-L-2,2,2

4-Me-L-2,3,2

4,7-Me$_2$-L-2,2,2

4-Et-L-2,2,2

pH was standardized with NBS buffers. The hydrogen ion and hydroxide ion concentrations in 0.10 M NaClO$_4$ were calculated from −log [H$^+$] = pH − 0.11 and K_w = 10$^{-13.78}$.[3,4] Appropriate aliquots of solutions of ligand or ligand and metal ion were titrated with a standard CO$_2$-free sodium hydroxide solution. In all titrations the ionic strength was maintained relative constant by using 0.10 M NaClO$_4$ as the supporting electrolyte. The solutions were protected from air by a stream of humidified prepurified nitrogen gas and were maintained at a temperature of 25.0 ± 0.1 °C during the measurements. The concentrations of ligand and metal ion for the equilibrium constant measurements were in the range of (4–9) × 10^{-3} M, obtained by using previously reported methods[5,6] of calculation.

The kinetics of the complexation reactions between copper(II) and 4-Me-L-2,2,2, 4,7-Me$_2$-L-2,2,2, 4-Et-L-2,2,2, and 4-Me-L-2,3,2 were studied at 654, 664, 655, and 668 nm, respectively, with a Union Giken RA-401 stopped-flow spectrophotometer equipped with a Union RA-415 rapid-scan attachment. The pH of the solutions was controlled with a borate–mannitol buffer,[7] which was also incorporated into the reference solution; the ionic strength was maintained constant at μ = 0.10 M (NaClO$_4$) for all solutions. Kinetic studies were carried out under pseudo-first-order conditions by using at least a 12-fold excess of copper(II) concentrations to those (in the range 2 × 10^{-4} to 7 × 10^{-3} M) of the ligands.

Results and Discussion

Table I. Protonation Constants[a] of Diamino Diamides at 25.0 ± 0.1 °C and μ = 0.10 M (NaClO$_4$)

ligand	log K_1^H	log K_2^H
L-2,2,2[b]	8.78 ± 0.04	5.82 ± 0.03
L-2,3,2[b]	9.22 ± 0.06	6.98 ± 0.04
4-Me-L-2,2,2	8.69 ± 0.04	5.05 ± 0.05
4,7-Me$_2$-L-2,2,2	8.21 ± 0.03	4.59 ± 0.05
4-Et-L-2,2,2	8.72 ± 0.03	5.49 ± 0.04
4-Me-L-2,3,2	9.02 ± 0.04	6.78 ± 0.05

[a] K_1^H = [HL$^+$]/[H$^+$][L]; K_2^H = [H$_2$L^{2+}]/[H$^+$][HL$^+$]. [b] From ref 9.

Protonation Constants. Protonation constant K^H_1 and K^H_2 calculated according to Schwarzenbach's method[8] from the potentiometric titration curves of the perchlorate salts of diprotonated 4-Me-L-2,2,2, 4,7-Me$_2$-L-2,2,2, 4-Et-L-2,2,2, and 4-Me-L-2,3,2 are given in Table I. The titration curves have been deposited as supplementary material (Figures 1S–4S). Those of the unsubstituted ligands, L-2,2,2 and L-2,3,2, are also given for comparison.[9,10]

The first protonation constants, K^H_1, vary in the order L-2,3,2 > 4-Me-L-2,3,2 > L-2,2,2 > 4-Et-L-2,2,2, 4-Me-L-2,2,2 > 4,7-Me$_2$-L-2,2,2. This order can be explained by considering the chain length between the amino groups, the solvation and inductive effects of the *N*-alkyl groups, and the statistical factor. The base-weakening effects pointed out by Perrin and co-workers[11,12] indicates an attenuation factor of 0.4 across each –CH$_2$– group with increasing chain length. Thus the acidity of –CH$_2$CH$_2$CH$_2$NRR′ is only about two-fifths that of –CH$_2$CH$_2$NRR′. Therefore, the K^H_1 values of L-2,3,2 and 4-Me-L-2,3,2 are larger than those of L-2,2,2, 4-Et-L-2,2,2, 4-Me-L-2,2,2 and 4,7-Me$_2$-L-2,2,2. In general, values for secondary amines are larger than those of similar tertiary amines. It has been suggested that having only one N–H bond for the latter cation decreases the stability of the solvated ion due to lack of hydrogen bonding. Thus the first protonation constant of 4,7-Me$_2$L-2,2,2, which contains only tertiary amines, is smaller than for those compounds containing secondary amine or amines. When 4-Me-L-2,3,2, 4-Et-L-2,2,2, and 4-Me-L-2,2,2 react with H$^+$, the secondary amines of these molecules are likely to be protonated first. The sequences for the first protonation constant, L-2,3,2 > 4-Me-L-2,3,2 and L-2,2,2 > 4-Et-L-2,2,2 and 4-Me-L-2,2,2, are mainly due to the statistical effect.[13]

The second protonation constant, K^H_2, varies in the order H(L-2,3,2)$^+$ > H(4-Me-L-2,3,2)$^+$ > H(L-2,2,2)$^+$ > H(4-Et-L-2,2,2)$^+$ > H(4-Me-L-2,2,2)$^+$ > H(4,7-Me$_2$-L-2,2,2)$^+$. The base-weakening effect of –CH$_2$CH$_2$NHRR′$^+$ is much largeer than that of –CH$_2$CH$_2$CH$_2$NHRR′$^+$. Thus the K^H_2 values of H(L-2,3,2)$^+$ and H(4-Me-L-2,3,2)$^+$ are larger than those of H(L-2,2,2)$^+$, H(4-Et-L-2,2,2)$^+$, H(4-Me-L-2,2,2)$^+$, and H(4,7-Me$_2$-L-2,2,2)$^+$. H(L-2,3,2)$^+$ and H(L-2,2,2)$^+$ react with H$^+$ at the secondary amine site; the other ligands react with H$^+$ at the tertiary amine site. Thus, the K^H_2 value of H(L-2,3,2)$^+$ is larger than that of H(4-Me-L-2,3,2)$^+$, and the K^H_2 value of H(L-2,2,2)$^+$ is larger than those of H(4-Et-L-2,2,2)$^+$, H(4-Me-L-2,2,2)$^+$, and H(4,7-Me$_2$-L-2,2,2)$^+$. The symmetry numbers of H(4-Me-L-2,2,2)$^+$, H$_2$(4-Me-L-2,2,2)$^{2+}$, and H(4,7-Me$_2$-L-2,2,2)$^+$ are 1, whereas that of H$_2$(4,7-Me$_2$-L-2,2,2)$^{2+}$ is 2. Thus, the difference of protonation constants between H(4-Me-L-2,2,2)$^+$ and H(4,7-Me$_2$-L-2,2,2)$^+$ is mainly due to the symmetry or statistical effect.[13] Because the base-strengthening effect of the ethyl group is slightly larger than that of the methyl group, the K_2^H value of H(4-Et-L-2,2,2)$^+$ is slightly larger than that of H(4-Me-L-2,2,2)$^+$.

Composition of the Copper(II) Complexes. Job's method of continuous variations[14] was used to determine the composition of the copper(II) complexes (supplementary material Figures 5S–8S). Copper(II) forms a 1:1 complex with each of the *N*-

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Table II. Equilibrium Constants for the Interactions of Diamino Diamides with Copper(II) at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$)

ligand	log K_f[a]	log K_A[b]	log K_B[c]
L-2,2,2[d]	12.58 ± 0.07	-8.08	-9.33
L-2,3,2[d]	10.27 ± 0.08	-8.62	-10.10
4-Me-L-2,2,2	10.56 ± 0.06	-7.63	-9.30
4,7-Me_2-L-2,2,2	9.25 ± 0.06	-7.32	-8.97
4-Et-L-2,2,2	11.07 ± 0.08	-7.51	-9.25
4-Me-L-2,3,2	8.17 ± 0.08	-8.34	-10.01

[a] $K_f = [CuL^{2+}]/[Cu^{2+}][L]$. [b] $K_A = [CuH_{-1}L^+][H^+]/[CuL^{2+}]$. [c] $K_B = [CuH_{-2}L][H^+]/[CuH_{-1}L^+]$. [d] From ref 9.

alkyl-substituted diamino diamides.

Equilibrium Constants for the Interactions of Copper(II) with *N*-Alkyl-Substituted Diamino Diamides. The complexation reactions of copper(II) with *N*-alkyl-substituted diamino diamides were very rapid. 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. The titration curves for solutions with various copper(II) to ligand molar ratio have been deposited as supplementary material (Figures 1S–4S). Equilibria 1–3 show the reactions of copper(II) with these ligands,

$$Cu^{2+} + L \rightarrow CuL^{2+} \qquad K_f = [CuL^{2+}]/[Cu^{2+}][L] \tag{1}$$

$$\begin{gathered} CuL^{2+} \rightarrow CuH_{-1}L^+ + H^+ \\ K_A = [CuH_{-1}L^+][H^+]/[CuL^{2+}] \end{gathered} \tag{2}$$

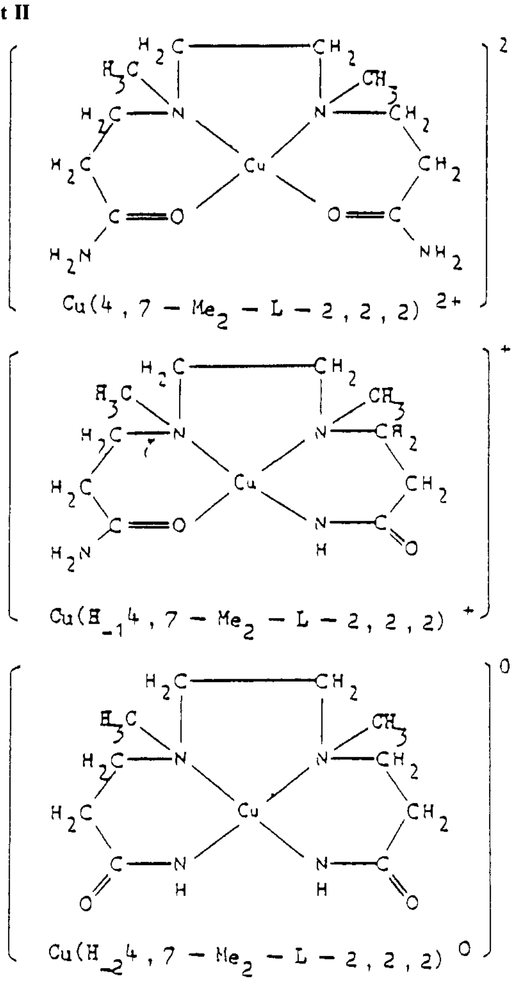
$$\begin{gathered} CuH_{-1}L^+ \rightarrow CuH_{-2}L + H^+ \\ K_B = [CuH_{-2}L][H^+]/[CuH_{-1}L^+] \end{gathered} \tag{3}$$

in which L represents the *N*-alkyl-substituted diamino diamide and the negative subscript on H represents the number of amide protons removed from the complex. The structures of the three complexes CuL^{2+}, $CuH_{-1}L^+$, and $CuH_{-2}L$ are shown in Chart II. The stability constants obtained by methods reported previously[6] are listed in Table II. For the purpose of comparison the corresponding values for the stability constants of $Cu(L\text{-}2,2,2)^{2+}$ and $Cu(L\text{-}2,3,2)^{2+}$ are also given in the Table II.[9]

The crystal structures indicate that the amide oxygen atoms are coordinated to the Cu(II).[15-18] The electronic spectral characteristics of these complexes in aqueous solution are similar to those of the solid state. Furthermore, the stability constant for each of these diamino diamide complexes is much larger than that of the corresponding copper(II) diamine complex. All this evidence indicates that the amide oxygen atom is coordinated to Cu(II) in aqueous solution.

The value of the stability constant varies in the order $Cu(L\text{-}2,2,2)^{2+}$ > $Cu(4\text{-}Et\text{-}L\text{-}2,2,2)^{2+}$ > $Cu(4\text{-}Me\text{-}L\text{-}2,2,2)^{2+}$ > $Cu(L\text{-}2,3,2)^{2+}$ > $Cu(4,7\text{-}Me_2\text{-}L\text{-}2,2,2)^{2+}$ > $Cu(4\text{-}Me\text{-}L\text{-}2,3,2)^{2+}$. The two important factors that influence this sequence are the number of *N*-alkyl groups and the girdle strains among the three linked chelate rings. The crystal structures of a few metal complexes of these *N*-alkyl-substituted diamino diamides have been determined by X-ray crystallography.[15-18] These structures indicate 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. Thus the stability constant of the complex decreases as the number of *N*-alkyl groups increases. For $Cu(4\text{-}Me\text{-}L\text{-}2,3,2)^{2+}$ and $Cu(L\text{-}2,3,2)^{2+}$, the cumulative ring strain among the three linked six-membered chelate rings is too great to allow copper(II) to lie in the center of the N_2O_2 plane. In contrast, the copper(II) complexes containing alternate five- and six-membered chelate rings suffer less strain and are more stable than those containing three adjacent six-membered rings.[19,20]

Chart II



Deprotonation reactions of these complexes (eq 2 and 3) 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). The values of K_A and K_B for these copper(II) complexes according to Schwarzenbach's method as previously described[6] are given in Table II together with the corresponding values for the copper(II) complexes of L-2,2,2 and L-2,3,2.[9] As shown in this table, the value of K_A increases in the order $Cu(L\text{-}2,3,2)^{2+}$ < $Cu(4\text{-}Me\text{-}L\text{-}2,3,2)^{2+}$ < $Cu(L\text{-}2,2,2)^{2+}$ < $Cu(4\text{-}Me\text{-}L\text{-}2,2,2)^{2+}$ < $Cu(4\text{-}Et\text{-}L\text{-}2,2,2)^{2+}$ < $Cu(4,7\text{-}Me_2\text{-}L\text{-}2,2,2)^{2+}$. Similarly the value of k_B increases in the order $Cu(H_{-1}\text{-}L\text{-}2,3,2)^+$ < $Cu(H_{-1}\text{-}4\text{-}Me\text{-}L\text{-}2,3,2)^+$ < $Cu(H_{-1}\text{-}L\text{-}2,2,2)^+$ < $Cu(H_{-1}\text{-}4\text{-}Me\text{-}L\text{-}2,2,2)^+$ < $Cu(H_{-1}\text{-}4\text{-}Et\text{-}L\text{-}2,2,2)^+$ < $Cu(H_{-1}\text{-}4,7\text{-}Me_2\text{-}L\text{-}2,2,2)^+$.

These sequences indicate that the values of both K_A and K_B increase as the steric strains among the linked six-membered chelate rings decrease and as the number and the size of the N-alkyl groups increase. In order to account for these results, it is necessary to consider the crystal field stabilization energies and the solvation energies of the copper(II) complexes. The large steric constraints in the three linked six-membered chelate rings distort the planar structures of these copper(II) complexes. For each of these diamino diamides, the crystal field stabilization energy of the copper(II) complex increases in the order CuL^{2+} < $CuH_{-1}L^+$ < $CuH_{-2}L$. Thus the effect attributed to the distortion form 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 values of K_A and K_B for the copper(II) complexes containing three linked six-membered rings are therefore smaller than those for the complexes containing 6,5,6-membered rings.

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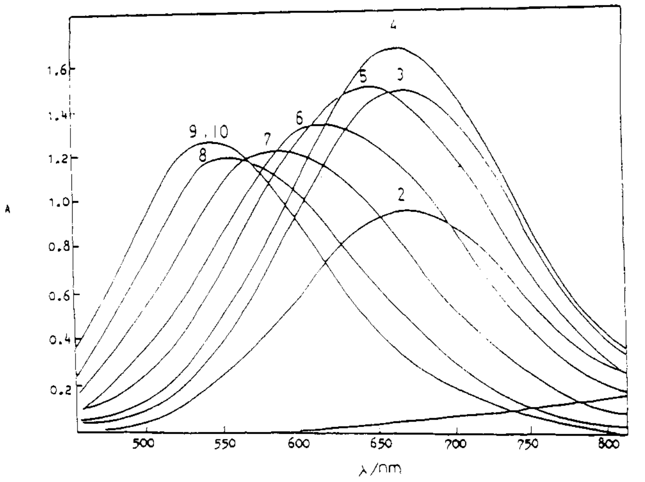

Figure 1. Visible absorption spectra of copper(II)–4,7-Me_2-L-2,2,2 solutions. All solutions contain 0.00103 M $Cu[ClO_4]_2$ and 0.00105 M $[H_2\text{-}4,7\text{-}Me_2\text{-}L\text{-}2,2,2][ClO_4]$ at 25.0 ± 0.1 °C and 0.10 $M[NaClO_4]$. The pH values of the solutions are as follows: (1) 1.30; (2) 3.31; (3) 4.85; (4) 6.12; (5) 7.36; (6) 8.86; (7) 9.46; (8) 10.25; (9) 11.97; (10) 12.12.

For the complexes containing the same chelate ring system, the values of K_A and K_B increase as the number and the size of the *N*-alkyl groups increase. This trend is mainly attributable to the solvation energy of the copper(II) complex. In general, the solvation energy of a copper(II) complex decreases with the number and the size 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 and the size 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 and the size of *N*-alkyl groups increase.

Electronic Spectra. The electronic absorption spectra of copper(II)–(4-Me-L-2,2,2), copper(II)–(4-Et-L-2,2,2), and copper(II)–(4-Me-L-2,3,2) solutions are deposited as supplementary material (Figures 9S–11S). The electronic spectra of copper(II)–(4,7-Me_2-L-2,2,2) solutions are shown in Figure 1. At pH 1.30, the spectrum is the same as that of $Cu(ClO_4)_2$ (curve 1). As the pH increases, the intensity of the band at 670 nm increases (curves 2–4), reaching a maximum at $a = 2$; curve 4 is due to $Cu(4,7\text{-}Me_2\text{-}L\text{-}2,2,2)^{2+}$. Further increase in pH beyond $a = 2$ (curves 5–8) causes the absorption band to shift to a shorter wave length due to the Cu–O to Cu–N bond rearrangements and the deprotonation reactions at the two amide sides (eq 2 and 3). Curves 9 and 10 are probably due to the deprotonated species $Cu(H_{-2}\text{-}4,7\text{-}Me_2\text{-}L\text{-}2,2,2)$, as 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 $Cu(H_{-2}\text{-}4,7\text{-}Me_2\text{-}L\text{-}2,2,2)$ and hydroxide ion.

By means of the various equilibrium constants listed in Table II, the degree of formation of each copper(II)–(4,7-Me_2-L-2,2,2) species in a 1:1 metal–ligand solution as a function of pH can be calculated (supplementary material, Figure 12S). The corresponding results for copper(II)–(4-Me-L-2,2,2), copper(II)–(4-Et-L-2,2,2), and copper(II)–(4-Me-L-2,3,2) complexes are deposited as supplementary material (Figures 13S–15S). By means of the calculated concentrations of all species present in each of these solutions, the spectra can be resolved into their components by using eq 4. The absorption characteristics of all species so obtained are given in Table III.

$$A = b(\epsilon_{Cu^{2+}}[Cu^{2+}] + \epsilon_{CuL^{2+}}[CuL^{2+}] + \epsilon_{CuH_{-1}L^{+}}[Cu(H_{-1}L)^{+}] + \epsilon_{CuH_{-2}L}[Cu(H_{-2}L)]) \quad (4)$$

For CuL^{2+}, the frequency of the maximum absorption, ν_{max}, follows the order $Cu(L\text{-}2,2,2)^{2+} > Cu(4\text{-}Me\text{-}L\text{-}2,2,2)^{2+} > Cu(4\text{-}Et\text{-}L\text{-}2,2,2)^{2+} > Cu(L\text{-}2,3,2)^{2+} > Cu(4,7\text{-}Me_2\text{-}L\text{-}2,2,2)^{2+} > Cu(4\text{-}Me\text{-}L\text{-}2,3,2)^{2+}$; so do the $CuH_{-1}L$ and $CuH_{-2}L$ species with their hydrogen ions removed. These sequences indicate the frequency at the maximum absorption decreases as the steric strains among the three linked chelate rings increase and as the number and the size of the *N*-alkyl groups increase.

Table III. Electronic Absorption Spectra of Copper(II) Complexes of Diamino Diamides in Aqueous Solution

compd	λ_{max}, nm	$10^{-4}\nu_{max}$, cm^{-1}	ϵ_{max}, $M^{-1}\,cm^{-1}$
$Cu(L\text{-}2,2,2)^{2+}$ [a]	645	1.550	126
$Cu(H_{-1}\text{-}L\text{-}2,2,2)^{+}$ [a]	580	1.724	102
$Cu(H_{-2}\text{-}L\text{-}2,2,2)$ [a]	535	1.869	95
$Cu(4\text{-}Me\text{-}L\text{-}2,2,2)^{2+}$	654	1.529	137
$Cu(H_{-1}\text{-}4\text{-}Me\text{-}L\text{-}2,2,2)^{+}$	592	1.689	127
$Cu(H_{-2}\text{-}4\text{-}Me\text{-}L\text{-}2,2,2)$	540	1.852	115
$Cu(4\text{-}Et\text{-}L\text{-}2,2,2)^{2+}$	655	1.527	139
$Cu(H_{-1}\text{-}4\text{-}Et\text{-}L\text{-}2,2,2)^{+}$	594	1.684	130
$Cu(H_{-2}\text{-}4\text{-}Et\text{-}L\text{-}2,2,2)$	542	1.845	116
$Cu(4,7\text{-}Me_2\text{-}L\text{-}2,2,2)^{2+}$	664	1.506	156
$Cu(H_{-1}\text{-}4,7\text{-}Me_2\text{-}L\text{-}2,2,2)^{+}$	600	1.667	144
$Cu(H_{-2}\text{-}4,7\text{-}Me_2\text{-}L\text{-}2,2,2)$	545	1.835	118
$Cu(L\text{-}2,3,2)^{2+}$ [a]	658	1.520	85
$Cu(H_{-1}\text{-}L\text{-}2,3,2)^{+}$ [a]	595	1.681	100
$Cu(H_{-2}\text{-}L\text{-}2,3,2)$ [a]	555	1.802	120
$Cu(4\text{-}Me\text{-}L\text{-}2,3,2)^{2+}$	668	1.497	95
$Cu(H_{-1}\text{-}4\text{-}Me\text{-}L\text{-}2,3,2)^{+}$	614	1.629	124
$Cu(H_{-2}\text{-}4\text{-}Me\text{-}L\text{-}2,3,2)$	563	1.776	148

[a] From ref 9.

The crystal structures of some of these complexes have been determined by X-ray crystallography.[15-18] They indicate that the steric strains in complexes having three consecutive six-membered chelate rings and those with the bulky alkyl group attached to the donor nitrogen atom distort the planarity of Cu(II) and its coordinated atoms, 2N and 2O. The frequencies of the absorption maxima of these complexes consequently decrease.

Kinetic Results. The kinetics of the complexation reactions of copper(II) with these *N*-alkyl-substituted diamino diamides have been studied at 25.0 °C, $\mu = 0.10$ M ($NaClO_4$), and pH 4.63–5.78. Under these conditions, the complexation of copper(II) with 4-Me-L-2,2,2, 4-Et-L-2,2,2, and 4,7-Me_2-L-2,2,2 was found to proceed to completion, whereas the complexation reaction of copper(II) with 4-Me-L-2,3,2 did not proceed to completion. Kinetic studies were carried out under pseudo-first-order conditions by using at least a 12-fold excess of copper(II). The observed pseudo-first-order rate constants are deposited as supplementary material (Tables 1S–4S).

For the complexation reactions of copper(II) with 4-Me-L-2,2,2, 4-Et-L-2,2,2, and 4,7-Me_2-L-2,2,2, plots of k_{obsd} vs. $[Cu^{2+}]$ gave straight lines indicating a rate of

$$d[CuL^{2+}]/dt = k_{obsd}[\Sigma L] = k_f[Cu^{2+}][\Sigma L] \quad (5)$$

where $[\Sigma L]$ represents the total concentration of all species of the uncomplexed ligand (supplementary material, Figures 16S–18S). The slopes of these plots lead to the values of the formation rate constants, which are functions of pH (supplementary material, Table 5S).

In the pH range of this study, the predominant form of the ligand is H_2L^{2+}, and the reactive species are L and HL^+, L being the unprotonated diamino diamide. Their reactions with Cu^{2+} are then considered to proceed according to

$$H_2L^{2+} \rightleftarrows HL^+ + H^+$$

$$1/K_2^H = [HL^+][H^+]/[H_2L^{2+}]$$

$$HL^+ \rightleftarrows L + H^+$$

$$1/K_1^H = [L][H^+]/[HL^+]$$

$$Cu^{2+} + HL^+ \rightarrow CuL^{2+} + H^+ \quad k_{Cu}^{HL}$$

$$Cu^{2+} + L \rightarrow CuL^{2+} \quad k_{Cu}^{L} \quad (6)$$

Table IV. Values of Resolved Rate Constants for the Formation and Dissociation of Copper(II) Complexes of Diamino Diamides in Aqueous Solution at 25.0 ± 0.1 °C and μ = 0.10 M (NaClO$_4$)

ligand	k_{Cu}^{L}, M^{-1} s^{-1}	k_{Cu}^{HL}, M^{-1} s^{-1}	k^{CuL}, s^{-1}	k_{H}^{CuL}, M^{-1} s^{-1}	k_{H}^{CuL}/K^{CuL}, M^{-1}
4-Me-L-2,2,2	9.46×10^{7}	1.72×10^{4}	2.01×10^{-3}[b]	2.51×10^{2}[b]	1.25×10^{5}
4,7-Me$_2$-L-2,2,2	8.45×10^{6}	3.51×10^{3}	4.75×10^{-3}[b]	3.21×10^{2}[b]	6.76×10^{4}
4-Me-L-2,3,2	4.86×10^{7}	3.24×10^{4}	3.28×10^{-1}	2.30×10^{5}	7.01×10^{5}
4-Et-L-2,2,2	9.82×10^{7}	1.96×10^{4}	8.34×10^{-4}[b]	8.76×10^{1}[b]	1.05×10^{5}
L-2,2,2[a]	3.35×10^{8}	4.75×10^{4}	8.81×10^{-5}	7.56	8.58×10^{4}
L-2,3,2[a]	1.48×10^{8}	9.21×10^{4}	7.94×10^{-3}	8.21×10^{3}	1.03×10^{6}

[a] From ref 2. [b] Calculated from the formation rate constants and the equilibrium constants.

Table V. Rate Constants for Formation (k_f) and Dissociation (k_d) of [Cu(4-Me-L-2,3,2)]$^{2+}$ and Equilibrium Constants for the Complexation Reaction of the Copper(II) Ion with 4-Me-L-2,3,2 at 25.0 ± 0.1 °C and μ = 0.10 M (NaClO$_4$)

			equil const, M^{-1}	
pH	k_f, M^{-1} s^{-1}	k_d, s^{-1}	kinetic[a]	potentiometric
5.78	5.03×10^{3}	0.83	6.06×10^{3}	6.01×10^{3}
5.67	3.07×10^{3}	0.98	3.14×10^{3}	3.25×10^{3}
5.57	2.74×10^{3}	1.11	2.47×10^{3}	2.37×10^{3}
5.46	1.99×10^{3}	1.32	1.5×10^{3}	1.44×10^{3}
5.35	1.47×10^{3}	1.69	8.72×10^{2}	8.79×10^{2}
5.25	1.07×10^{3}	1.96	5.46×10^{2}	5.60×10^{2}
5.13	8.23×10^{2}	2.45	2.36×10^{2}	3.24×10^{2}
5.02	6.31×10^{2}	3.32	1.90×10^{2}	1.96×10^{2}
4.91	4.93×10^{2}	3.98	1.24×10^{2}	1.19×10^{2}
4.82	3.91×10^{2}	4.88	8.01×10^{1}	7.86×10^{1}
4.74	3.27×10^{2}	5.61	5.82×10^{1}	5.44×10^{1}

[a] Kinetically determined value = k_f/k_d.

A rate law of a form that involves the predominant species is described by eq 7.[21,22]

$$d[CuL^{2+}]/dt = k[Cu^{2+}][H_2L^{2+}]/[H^+] + k'[Cu^{2+}][H_2L^{2+}]/[H^+]^2 \tag{7}$$

Combining this and eq 5 yields

$$k_f[\sum L] = k[H_2L^{2+}]/[H^+] + k'[H_2L^{2+}]/[H^+]^2$$

or

$$k_f[\sum L]/[L] = kK_1^HK_2^H[H^+] + k'K_1^HK_2^H \tag{8}$$

Here $[\sum L]$ represents the total concentration of all species of uncomplexed ligands. Plots of $k_f[\sum L]/[L]$ against [H$^+$] (supplementary material, Figures 19S–21S) gave the intercept of $k'K_1^HK_2^H$ and the slope of $kK_1^HK_2^H$, and the values of k_{Cu}^{L} and k_{Cu}^{HL} obtained respectively as $k'K_1^HK_2^H$ and kK_2^H are listed in Table IV. The dissociation rate constants obtained from the formation rate constants and the corresponding stability constants are given in Table IV.

For the reaction of copper(II) with 4-Me-L-2,3,2, the complex formation did not proceed to completion. Plots of k_{obsd} vs [Cu^{2+}] gave straight lines following eq 9 (supplementary material, Figure 22S).

$$k_{obsd} = k_f[Cu^{2+}] + k_d \tag{9}$$

The slopes are rate constants of formation, and the intercepts equal the rate constants of dissociation. These values are listed in Table V. The equilibrium constants calculated from these rate constants by means of eq 10 are in excellent agreement

$$K = k_f/k_d \tag{10}$$

with those obtained by potentiometric measurements under equilibrium conditions as shown in Table V.

The kinetic data are found to conform to a reaction scheme in which it is assumed that only the unprotonated and monoprotonated ligand species react at a significant rate. As the rate of proton transfer is much greater than that of any other reaction step, this scheme yields the expanded rate expression

$$d[CuL^{2+}]/dt = k_{Cu}^{L}[Cu^{2+}][L] + k_{Cu}^{HL}[Cu^{2+}][HL^+] - k^{CuL}[CuL^{2+}] - k_H^{CuL}[H^+][CuL^{2+}] \tag{11}$$

Combining eq 9 and 11, one can resolve the individual rate constants by plotting the expressions

$$k_f[\sum L]/[L] = k_{Cu}^{L} + k_{Cu}^{HL}K_1^H[H^+] \tag{12}$$

$$k_d = k^{CuL} + k_H^{CuL}[H^+] \tag{13}$$

For the reaction of copper(II) with 4-Me-L-2,3,2, plots according to eq 12 and 13 are deposited as supplementary material (Figures 23S and 24S). The resolved rate constants obtained from these plots are listed in Table IV.

Kinetics and Mechanism of the Complexation Reactions. The two possible pathways for the formation reactions of copper(II) with these diamino diamides are shown in Figure 2. In the first reaction pathway (initial bonding to an amino nitrogen donor atom a → b → c → d → e → f), the first step (a → b) is the diffusion-controlled association of copper(II) and the ligand. In the next step (b → c), one strongly basic amino nitrogen donor atom of the ligand is presumed to hydrogen bond to a coordinated water molecule to give a stronger outer-sphere complex (c). The third step (c → d) is the replacement of a water molecule in the inner coordination sphere of copper(II) by the amino nitrogen donor atom. This step, the formation of the first copper(II)–nitrogen bond, is the rate-determining step, and the subsequent steps (d → e → f) are rapid.

In the second reaction pathway (initial bonding to an amide oxygen donor atom a → b → c → g → h → e → f), the first (a → b) and the second (b → c) steps are the same as in the first reaction pathway. The third step (c → g) is the replacement of a water molecule in the inner coordination sphere of copper(II) by the amide oxygen donor atom. The fourth step (g → h), the formation of the first copper(II)–nitrogen bond, is the rate-determining step of this pathway. The subsequent steps, h → e → f, are rapid.

In general, the rate constant k_{Cu}^{L} increases as the size of the chelate ring decreases, the number of *N*-alkyl groups decreases, and the basicity of the ligand increases. The terminal chelate rings of these complexes have are the same size. If the second reaction pathway (initial bonding to an amide oxygen donor atom a → b → c → g → h → e → f) were the main reaction pathway, we would expect the rate of complexation increases as the basicity of the amine group increases; i.e., $k_{Cu}^{L-2,2,2} < k_{Cu}^{L-2,3,2}$ and $k_{Cu}^{4-Me-L-2,2,2} < k_{Cu}^{4-Me-2,3,2}$. The results listed in Table IV indicate the reverse order and, thus, the main reaction pathway for the reactions of L-2,2,2, 4-Me-L-2,2,2, 4-Et-L-2,2,2, and 4,7-Me$_2$-L-2,2,2 is the first reaction pathway (initial bonding to an amino nitrogen donor atom a → b → c → d → e → f). The rate constants decrease by a factor of 18 in going from L-2,2,2 to 4,7-Me$_2$-L-2,2,2. This large difference in rate constants may be due to a steric effect with some associative contribution, or due to the steric effect of alkyl groups, which can reduce the magnitude of the equilibrium constant for step b → c.

For the reactions of copper(II) with the protonated ligand, the main reaction pathway is the second reaction pathway (initial bonding to an amide oxygen donor atom) as shown in Figure 3. Proton loss (V → VI in Figure 3) is the rate-limiting step. The reactivity sequences H(L-2,3,2)$^+$ > H(L-2,2,2)$^+$ and H(4-Me-

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[21] Rorabacher, D. B.; Turan, T. S.; Defever, J. A.; Nickels, W. G. *Inorg. Chem.* **1969**, *8*, 1498–1506.

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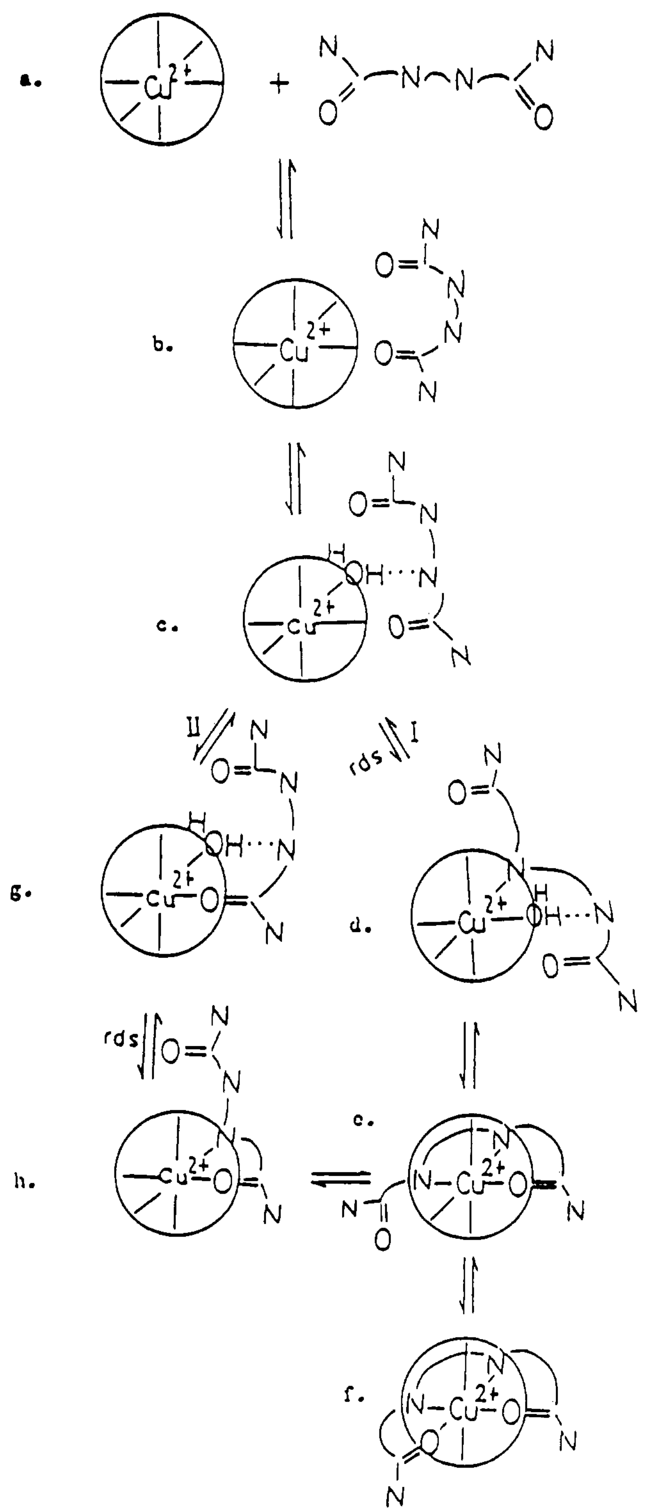

Figure 2. Possible pathways for the reaction of copper(II) with the unprotonated diamino diamide. The circle represents the division between inner-sphere coordination and outer-sphere association.

L-2,3,2)$^+$ > H(4-Me-L-2,2,2)$^+$ are mainly due to the basicity of the protonated ligand. The rate constants decrease by a factor of 14 in going from H(L-2,2,2)$^+$ to H(4,7-Me$_2$-L-2,2,2)$^+$. This difference may be due to the steric effects of the methyl groups.

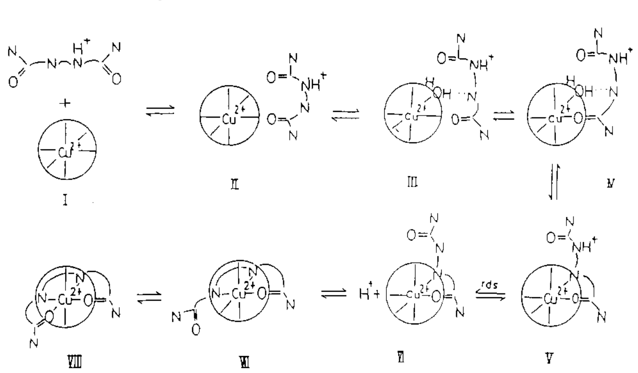

Figure 3. Possible pathways for the reaction of copper(II) with the monoprotonated ligand diamino diamide. The circle represents the division between the inner-sphere coordination and outer-sphere association.

Margerum and co-workers[23,24] have studied the steric effects in the complexation kinetics of polyamines with copper(II) and have found that alkyl substitution at the nitrogen donor atoms caused significant decreases in the formation rate constant, although the steric factors were not calculated. The results listed in Table IV indicate that for the formation reactions of 4-Me-L-2,2,2, 4-Et-L-2,2,2, and 4-Me-L-2,3,2 with copper(II) the secondary amino group coordinates before the tertiary amino group. The 3-fold decreases of $k_{\mathrm{Cu}}{}^{\mathrm{L}}$ and $k_{\mathrm{Cu}}{}^{\mathrm{HL}}$ in going from L-2,2,2 to either 4-Me-L-2,2,2 or 4-Et-L-2,2,2 and in going from L-2,3,2 to 4-Me-L-2,3,2 are due to a statistical effect and an outer-sphere effect.

The results in Table IV indicate that protonation causes a large decrease in the formation rate, causing the $k_{\mathrm{Cu}}{}^{\mathrm{L}}/k_{\mathrm{Cu}}{}^{\mathrm{HL}}$ ratio to be (1–7) × 10^3. The large ratio for $k_{\mathrm{Cu}}{}^{\mathrm{L}}/k_{\mathrm{Cu}}{}^{\mathrm{HL}}$ suggests that the reaction of copper(II) with HL$^+$ is probably proton-transfer limiting.

Kinetics and Mechanism of the Dissociation Reactions. The increase of k_{d} values with decreasing pH indicates the active role of the proton in assisting the dissociation of the complex. Under the conditions used in this work, both k^{CuL} and $k_{\mathrm{H}}{}^{\mathrm{CuL}}[\mathrm{H}^+]$ contribute significantly to the observed k_{d} value. Individual steps in the unwrapping of diamino diamide from copper(II) are expected to be fast, but unless the reaction is assisted by protonation of the partially coordinated intermediate, thus stabilizing it, the successive equilibria leading to the cleavage of the second copper–nitrogen bond are very unfavorable and a slow rate results. The pathways for k^{CuL} and $k_{\mathrm{H}}{}^{\mathrm{CuL}}$ have been defined as the water dissociation pathway and the proton-assisted pathway, respectively.[2] The dissociation steps of these two pathways can be described as the reverse processes in Figures 2 and 3, respectively. The successive equilibrium constants for VIII → VII and VII → VI in Figure 3 depend heavily on the nature of the diamino diamide; therefore, the rate constants k^{CuL} and $k_{\mathrm{H}}{}^{\mathrm{CuL}}$ are always very sensitive to the nature of the diamino diamide, whether the mechanism of these reactions is dissociative or associative.

The rate constant for the protonation of the released amino group (VI → V in Figure 3) is expected to increase with increasing chain length because of the ligand basicity and electrostatic repulsion between Cu^{2+} and H$^+$. The fact that the value of the ratio $k_{\mathrm{H}}{}^{\mathrm{CuL}}/k^{\mathrm{CuL}}$ (Table IV) for the complex with a 6,6,6-membered ring system is larger than that for the complex with a 6,5,6-membered ring system lends support to this point of view.

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Registry No. 4-Me-L-2,2,2, 118334-46-6; 4,7-Me$_2$-L-2,2,2, 57356-17-9; 4-Et-L-2,2,2, 118334-47-7; 4-Me-L-2,3,2, 115684-03-2; Cu^{2+}, 15158-11-9.

Supplementary Material Available: Tables 1S–4S, showing the experimental observed rate constants for the reactions of copper(II) ion with 4-Me-L-2,2,2, 4,7-Me$_2$-L-2,2,2, 4-Et-L-2,2,2, and 4-Me-L-2,3,2, respectively, at 25.0 ± 0.1 °C and μ = 0.10 M (NaClO$_4$), Table 5S, showing the rate constants for formation of [Cu(4-Me-L-2,2,2)]$^{2+}$, [Cu(4,7-Me$_2$-L-2,2,2)]$^{2+}$, and [Cu(4-Et-L-2,2,2)]$^{2+}$ at 25.0 ± 0.1 °C and μ = 0.10 M (NaClO$_4$), Figures 1S–4S, showing the titration curves for

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(23) Lin, C.-T.; Rorabacher, D. B.; Cayley, G. R.; Margerum, D. W. *Inorg. Chem.* **1975**, *14*, 919–925.

(24) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. In *Coordination Chemistry*; Martell, A. E., Ed.; ACS Monograph 174; American Chemical Society: Washington, D.C. 1978; Vol. 2, pp 1–220.

4-Me-L-2,2,2, 4,7-Me_2-L-2,2,2, 4-Et-L-2,2,2, and 4-Me-L-2,3,2, respectively, in the presence and absence of Cu^{2+} at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$), Figures 5S-8S, showing the results of Job's method of isomolar solutions of copper(II) and (4-Me-L-2,2,2), copper(II) and (4,7-Me-L-2,2,2), copper(II) and (4-Et-L-2,2,2), and copper(II) and (4-Me-L-2,3,2), respectively, at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$), Figures 9S-11S, showing the electronic absorption spectra of copper(II) and (4-Me-L-2,2,2), copper(II) and (4-Et-L-2,2,2), and copper(II) and (4-Me-L-2,3,2) solutions, respectively, Figures 12S-15S, showing the degree of formation of copper (II)-(4,7-Me_2-L-2,2,2), copper(II)-(4-Me-L-2,3,2), copper(II)-(4-Et-L-2,2,2), and copper(II)-(4-Me-L-2,3,2) complexes, respectively, in 1:1 metal-ligand solution, Figures 16S-18S, showing the observed first-order rate constants (k_{obs}) as a function of [Cu^{2+}] for the formation of [Cu(4,7-Me_2-L-2,2,2)]$^{2+}$, [Cu(4-Me-L-2,2,2)]$^{2+}$, and [Cu(4-Et-L-2,2,2)]$^{2+}$, respectively, at 25.0 ± 0.1 °C and μ = 0.1 M ($NaClO_4$), Figures 19S-21S, showing the resolution of the formation rate constants for copper(II) reacting with unprotonated and monoprotonated 4-Me-L-2,2,2, 4-Et-L-2,2,2, and 4,7-Me_2-L-2,2,2, respectively, at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$), Figure 22S, showing the observed rate constants (k_{obs}) as a function of [Cu^{2+}] for the formation of [Cu(4-Me-L-2,3,2)]$^{2+}$ at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$), Figure 23S, showing the resolution of the formation rate constants for copper(II) reacting with unprotonated and monoprotonated 4-Me-L-2,3,2 at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$), and Figure 24S, showing the resolution of the dissociation rate constants involving proton-independent and proton-dependent terms for [Cu(4-Me-L-2,3,2)]$^{2+}$ at 25.0 ± 0.1 °C and μ = 0.10 M ($NaClO_4$) (34 pages). Ordering information is given on any current masthead page.

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Chelating Ditelluroether Complexes of Palladium and Platinum: Synthesis and Multinuclear NMR Studies. Structure of Dibromo(*meso*-1,3-bis(phenyltelluro)propane)palladium(II), [Pd{*meso*-PhTe(CH_2)$_3$TePh}Br_2]

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Palladium(II) and platinum(II) complexes of two chelating ditelluroether ligands [M(L-L)X_2] (M = Pd or Pt, X = Cl, Br, or I, and L-L = PhTe(CH_2)$_3$TePh or MeTe(CH_2)$_3$TeMe) are described. The complexes have been characterized by analysis and IR, UV-visible and multinuclear NMR (^{1}H, ^{125}Te{^{1}H}, ^{195}Pt{^{1}H}) spectroscopy. The NMR studies show that two diastereoisomers of the ligand are present in solution in each complex, *meso* and *dl* invertomers, with the former having the higher abundance. The structure of [Pd{*meso*-PhTe(CH_2)$_3$TePh}Br_2] has been determined by X-ray diffraction. Crystals belong to the triclinic crystal system, space group $P\bar{1}$, with a = 8.968 (1) Å, b = 10.978 (1) Å, c = 11.070 (2) Å, α = 108.16 (1)°, β = 113.15 (1)°, γ = 98.95 (1)°, and Z = 2. The structure was refined to an R value of 0.023 from 2545 reflections ($F > 3\sigma(F)$). The trends in the ^{125}Te and ^{195}Pt NMR chemical shifts and $^1J(^{195}\mathrm{Pt}-^{125}\mathrm{Te})$ coupling constants are reported and discussed and are compared with data on the corresponding diselenoether complexes. Close parallels exist between ^{125}Te and ^{77}Se chemical shifts in comparable complexes. Attempts to halogen oxidize the complexes to the M(IV) state have failed.

Introduction

The coordination chemistry of organotellurium ligands is mainly limited to complexes of RTe^-, R_2Te, and R_2Te_2.[1] All attempts to prepare 1,2-di-R-telluroethanes have failed,[2,3] but we have recently reported[3] that 1,3-di-R-telluropropanes, RTe(CH_2)$_3$TeR (R = Me or Ph), can be made in high yield from RTeLi and Cl(CH_2)$_3$Cl at low temperatures. Here we report the synthesis and properties of palladium and platinum complexes of these two ligands and their ^{1}H, ^{125}Te{^{1}H}, and ^{195}Pt{^{1}H} NMR spectra. The work is an extension of our previous studies of diselenoether complexes[4,5] with which detailed comparisons are drawn.

Results and Discussion

The reaction of MeTe(CH_2)$_3$TeMe or PhTe(CH_2)$_3$TePh with the appropriate [M(MeCN)$_2X_2$] (M = Pd or Pt, X = Cl, Br or I) in CH_2Cl_2 or MeCN gave [M{RTe(CH_2)$_3$TeR}X_2] complexes (Table I). There is no evidence for the formation of [M(RTe(CH_2)$_3$TeR)$_2$]$^{2+}$ ions even with a large excess of ligand. The solid complexes are air-stable in contrast to the air-sensitivity of the free ligands[3] and are poorly soluble in chlorocarbons and MeCN to give stable solutions. The complexes are more soluble in dimethyl sulfoxide (DMSO) and in *N,N*-dimethylformamide (DMF); however, decomposition is often apparent in DMSO over time. The physical data (Table I) are consistent with the formulation of all twelve complexes as cis planar materials, and this is confirmed by comparison with the data for the thio-[6] and selenoether[4] analogues, and by the X-ray study of [Pd{PhTe(CH_2)$_3$TePh}Br_2] (below). Chelating bidentate group 16 donor ligand complexes exist in two isomeric forms, containing *meso* and *dl* geometries (Figure 1), and these interconvert by pyramidal inversion at the heteroatoms.[7]

Structure of [Pd{PhTe(CH_2)$_3$TePh}Br_2]. The structure in the solid state consists of discrete molecules and is shown in Figure 2. The expected square-planar geometry around the Pd is found, and the principal feature of interest is the stereochemistry of the chelating ditellurium ligand. Inspection of the crystallographic literature[8] shows few examples of the monodentate Te ligands R_2Te and apparently no examples of chelating ditellurium ligands although one example of a PTe donor ligand is known.[9] The Pd-Te distances in the present compound (2.528, 2.525 Å) (Table II) may be compared with 2.606 (1) Å in *trans*-Pd(SCN)$_2$(TeR_2)$_2$ (R = $Me_3Si(CH_2)_2$)[10] and the Pd-Br distance (2.480 (1) Å) with 2.456 (1), 2.468 (1) Å in *cis*-PdBr_2($C_6H_{12}S_3$)[11] and 2.431 (1) Å

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