

Geometric Factors in the Structural and Thermodynamic Properties of Copper(II) Complexes with Tripodal Tetraamines

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Received May 22, 1996[⊗]

The tripodal tetramine ligands $N(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3$ (trpn) and $N[(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2(\text{CH}_2\text{CH}_2\text{NH}_2)]$ (332) react with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in water to give light blue copper(II) complexes. These were characterized by X-ray crystallography to be the square-pyramidal binuclear Cu(II) species $[\text{Cu}(\text{trpn})(\text{NO}_3)]_2(\text{NO}_3)_2$ and $[\text{Cu}(332)(\text{NO}_3)]_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. Selected crystallographic details are as follows, respectively: formula $\text{C}_{18}\text{H}_{48}\text{Cu}_2\text{N}_{12}\text{O}_{12}$, $\text{C}_{16}\text{H}_{48}\text{Cu}_2\text{N}_{12}\text{O}_{14}$; $M = 751.74, 759.72$ Da; both triclinic; both $P\bar{1}$; $a = 8.4346(8), 8.446(4)$ Å; $b = 9.0785(9), 8.744(3)$ Å; $c = 11.9310(12), 12.007(3)$ Å; $\alpha = 94.50(1), 102.68(2)^\circ$; $\beta = 103.56(1), 94.79(3)^\circ$; $\gamma = 117.42(1), 117.69(4)^\circ$; $V = 769.7(5), 748.2(13)$ Å³; both $Z = 1$; $R = 4.16, 4.00$; $R_w = 11.34, 6.74$ for 2887 ($I \geq 2\sigma(I)$), 2457 ($F_o^2 \geq 3\sigma(F_o^2)$) structure factors and 199, 209 refined parameters. The binuclear complex dications exhibit a square-pyramidal coordination geometry around the copper atoms. Three amine functions (one tertiary and two primary) are coordinated to one copper atom and the remaining primary amine arm bridges to the second copper center. Potentiometric and visible spectrophotometric studies show that a protonated square-pyramidal $[\text{Cu}(\text{HL})(\text{H}_2\text{O})_2]^{3+}$ cation ($L = \text{trpn}, 332, 322$ ($322 = N[(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{CH}_2\text{CH}_2\text{NH}_2)_2]$)) predominates in the intermediate pH region, in contrast to the established trigonal-bipyramidal structure of the tren (tren = tris(2-aminoethyl)amine) complex of Cu(II). Each $[\text{Cu}(\text{HL})(\text{H}_2\text{O})_2]^{3+}$ has one protonated uncoordinated ligand arm which explains the formation of the binuclear species at neutral pH.

Introduction

Extensive and elegant studies of different aspects of copper(II) and copper(I) chemistry have shown that this transition metal possesses a wide repertoire of coordination geometries and properties.¹ Investigations are stimulated, in part, by widespread interest in the bioinorganic chemistry of copper because of the presence of the metal in many metalloproteins and metalloenzymes.¹

Copper(II) aqua ions have a distorted (Jahn–Teller) octahedral structure of coordinated water, which has the consequence of conferring extreme lability of water exchange, a fact which

thwarted the efforts at a detailed kinetic characterization until recently.^{2,3} In turn, hexaaquacopper(II) reacts to form complexes with extreme rapidity. Upon coordination of the ligand tren [tren = tris(2-aminoethyl)amine] the geometry at the copper center is changed to trigonal-bipyramidal from octahedral. From a combination of temperature-jump relaxation kinetics measurements and NMR spectroscopy measurements of water exchange at ambient and elevated pressures, it has been concluded⁴ that ligand substitution occurs by an I_a mechanism, whereas an I_d mechanism is operative for octahedral copper aqua complexes.

These findings have encouraged us to determine which factors influence the geometry and reactivity of copper complexes with tripodal tetraamine ligands. To address this problem, we have studied the coordination chemistry of copper(II) with the symmetric and unsymmetric tripodal N_4 ligands (Figure 1) and

[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1996.

(1) For example: (a) Zubieta, J.; Karlin, K. D. *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Adenine Press: New York, 1983. (b) Wei, N.; Murthy, N. N.; Karlin, K. D. *Inorg. Chem.* **1994**, *33*, 6093. (c) Knowles, P. F.; Brown, R. D., III; Koenig, S. H.; Wang, S.; Scott, R. A.; McGuirol, M. A.; Brown, D. H.; Dooley, D. M. *Inorg. Chem.* **1995**, *34*, 3895. (d) Karlin, K. D.; Tyeklar, Z. *Bioinorganic Chemistry of Copper*; Chapman and Hall: New York, 1993.

(2) Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *37*, 307.

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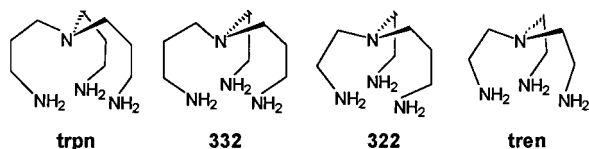


Figure 1. Topology of the tripodal tetraamine ligands used.

we have also examined the lability of the coordinated water in these complexes.

Previous studies have shown that the tripodal tetraamines depicted in Figure 1 react with $\text{Cu}(\text{OH})_2$ and NH_4PF_6 under basic conditions to yield trigonal-bipyramidal complexes $[\text{Cu}(\text{N}_4)(\text{NH}_3)](\text{PF}_6)_2$.^{5,6} In this contribution we report on the reaction of these ligands with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ at neutral pH, yielding binuclear square-pyramidal complexes. A mechanism for the formation of the binuclear species is proposed on the basis of solution thermodynamics and spectroscopic measurements.

Experimental Section

Preparation of Complexes. Tren was obtained from Aldrich. The preparation of the other tripodal ligands has been described earlier.⁶ The copper complexes of trpn and 332 were prepared in an analogous manner. The preparation of the trpn complex is described as an example. To a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (6.1 g, 25 mmol) in 25 mL of water was added 5.0 g of trpn. Upon this addition, a precipitate of copper hydroxide was formed; however, during the course of the reaction most of the precipitate redissolved. The reaction mixture was stirred at 50 °C for 1 h, filtered, and concentrated to 5 mL. Blue crystals formed overnight; yield, 7.4 g (78% based on Cu) of $[\text{Cu}(\text{trpn})(\text{NO}_3)]_2(\text{NO}_3)_2$. Anal. Calcd (found) for $\text{C}_{18}\text{H}_{48}\text{Cu}_2\text{N}_{12}\text{O}_{12}$ ($M = 751.74$): C, 28.76 (28.64); H, 6.43 (6.33); N, 22.36 (22.17). MS (+FAB, 3-nitrobenzyl alcohol/dimethyl sulfoxide (DMSO), m/z): 688 (2, $\text{M}^+ - \text{NO}_3$), 626 (1, $\text{M}^+ - 2\text{NO}_3$), 564 (1, $\text{M}^+ - 3\text{NO}_3$), 517 (6), 501 (1), 446 (2), 417 (3), 384 (45), 313 (29), 251 (100, $[\text{Cu}(\text{trpn})]^+$). The complex with the ligand 332 crystallized with two molecules of water as $[\text{Cu}(332)(\text{NO}_3)]_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$; yield, 45.3% based on Cu. Anal. Calcd (found) for $\text{C}_{16}\text{H}_{48}\text{Cu}_2\text{N}_{12}\text{O}_{14}$ ($M = 759.72$): C, 25.30 (26.46); H, 6.37 (6.24); N, 22.12 (22.97). MS (+FAB, 3-nitrobenzyl alcohol/DMSO, m/z): 660 (1, $\text{M}^+ - \text{NO}_3$), 598 (1, $\text{M}^+ - 2\text{NO}_3$), 536 (1, $\text{M}^+ - 3\text{NO}_3$), 492 (2), 403 (2), 370 (14), 299 (32), 237 (100, $[\text{Cu}(332)]^+$).

Crystal Structure Analyses. Deep blue crystals of both complexes were grown at room temperature from water and are air-stable. Suitable specimens were mounted on an Enraf-Nonius CAD-4 diffractometer. Important crystal and data collection details are listed in Table 1. Diffraction data were collected at 20(2) and -100(2) °C for the trpn and the 332 complexes, respectively, using ω - 2θ scans. Raw data were reduced to structure factors⁷ (and their estimated standard deviations) by correcting for scan speed and Lorentz and polarization effects. No decay or absorption corrections were necessary. The space group was found to be $P\bar{1}$ for both complexes. This choice was confirmed by the successful solution and refinement of the structure. Both structures were solved by standard Patterson methods. The positional parameters for all non-hydrogen atoms were refined by using first isotropic and later anisotropic thermal parameters. Difference Fourier maps calculated at this stage showed for both complexes the positional parameters of the hydrogen atoms; however, hydrogen atoms were added to the structure models on calculated positions [$d(\text{C}-\text{H}) = 0.95 \text{ \AA}$, $d(\text{N}-\text{H}) = 0.87 \text{ \AA}$]⁸ and are unrefined. No hydrogen positions were calculated for the water molecules in $[\text{Cu}(332)(\text{NO}_3)]_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. The isotropic temperature factors for hydrogens were fixed to be 1.3 times the U_{eq}

Table 1. Summary of Crystallographic Data for $[\text{Cu}(\text{trpn})(\text{NO}_3)]_2(\text{NO}_3)_2$ and $[\text{Cu}(332)(\text{NO}_3)]_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$

parameter	$[\text{Cu}(\text{trpn})(\text{NO}_3)]_2(\text{NO}_3)_2$	$[\text{Cu}(332)(\text{NO}_3)]_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$
formula	$\text{C}_{18}\text{H}_{48}\text{Cu}_2\text{N}_{12}\text{O}_{12}$	$\text{C}_{16}\text{H}_{48}\text{Cu}_2\text{N}_{12}\text{O}_{14}$
mol wt	751.74	759.72
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a , Å	8.4346(8)	8.446(4)
b , Å	9.0785(9)	8.744(3)
c , Å	11.9310(12)	12.007(3)
α , deg	94.50(1)	102.68(2)
β , deg	103.56(1)	94.79(3)
γ , deg	117.42(1)	117.69(4)
V , Å ³	769.7(5)	748.2(13)
Z	1 (binuclear complex)	1 (binuclear complex)
cryst size, mm	$0.32 \times 0.25 \times 0.20$	$0.30 \times 0.30 \times 0.25$
ρ_{expt} , g/cm ³	1.60	1.69
ρ_{calc} , g/cm ³	1.622	1.686
μ , cm ⁻¹	14.58	15.05
radiation, Å	Mo K α , 0.710 73	
data collec temp, K	293(2)	173(2)
2θ -range, deg	$5 \leq 2\theta \leq 54$	$2 \leq 2\theta \leq 80$
unique data	3200	2633
obsd data	2887 ($I \geq 2\sigma(I)$)	2457 ($F_o^2 \geq 3\sigma(F_o^2)$)
R , %	4.16	4.00
R_w , %	11.34	6.74
GOF	1.01	1.64
no. of var	199	209

$$^a R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, R_w = \frac{[\sum |F_o| - |F_c|]^2 / \sum w |F_o|^2]^{1/2}}{}$$

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[\text{Cu}(\text{trpn})(\text{NO}_3)]_2(\text{NO}_3)_2$ and $[\text{Cu}(332)(\text{NO}_3)]_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}^a$

parameter	$[\text{Cu}(\text{trpn})(\text{NO}_3)]_2(\text{NO}_3)_2$	$[\text{Cu}(332)(\text{NO}_3)]_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$
Cu—O1(O1A)	2.391(2)	2.421(2)
Cu—N1	2.100(2)	2.078(3)
Cu—N2	2.008(2)	1.975(3)
Cu—N3	1.998(2)	1.976(3)
Cu—N4*	2.075(2)	2.041(3)
N1—Cu—O1(O1a)	101.58(8)	102.6(1)
N1—Cu—N2	93.60(8)	85.1(1)
N1—Cu—N3	91.50(8)	92.3(1)
N1—Cu—N4*	156.82(8)	164.3(1)
N2—Cu—O1(O1A)	84.84(8)	82.7(1)
N2—Cu—N3	172.15(8)	171.5(1)
N2—Cu—N4*	88.68(8)	92.6(1)
N3—Cu—O1(O1A)	88.30(9)	90.0(1)
N3—Cu—N4*	88.97(9)	92.1(1)
N4*—Cu—O1(O1A)	101.61(8)	92.44(9)

^a Atoms marked with an asterisk represent transformed coordinates related by an inversion center.

or B_{eq} , respectively, of the parent atom. Calculations were carried out with the MolEN package⁹ (refinement on F values) for $[\text{Cu}(332)(\text{NO}_3)]_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and with SHELX-93¹⁰ (refinement on F^2 values) for $[\text{Cu}(\text{trpn})(\text{NO}_3)]_2(\text{NO}_3)_2$. ORTEP¹¹ was used for all molecular drawings. Table 2 lists selected bond distances and angles, and ORTEP drawings are shown in Figures 2 and 3.

Equilibrium Measurements. Visible spectra were recorded on a Shimadzu UV-2100 spectrophotometer. The potentiometric measurements were performed with a Metrohm automatic buret (Dosimat 665), either a Fisher Acumet 950 pH meter or an Orion EA-920 pH meter, and an Orion Ross glass electrode and calomel reference electrode or an Orion Ross combination pH electrode. The electrodes were calibrated before each titration by titrating a known amount of aqueous HCl with a known concentration of NaOH. A Gran plot¹² of millivolt

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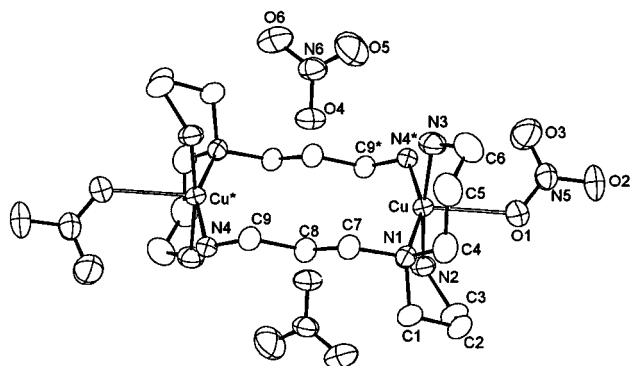


Figure 2. ORTEP plot of $[\text{Cu}(\text{trpn})(\text{NO}_3)_2](\text{NO}_3)_2$ with the employed crystallographic numbering scheme. Atoms marked by an asterisk are related by an inversion center.

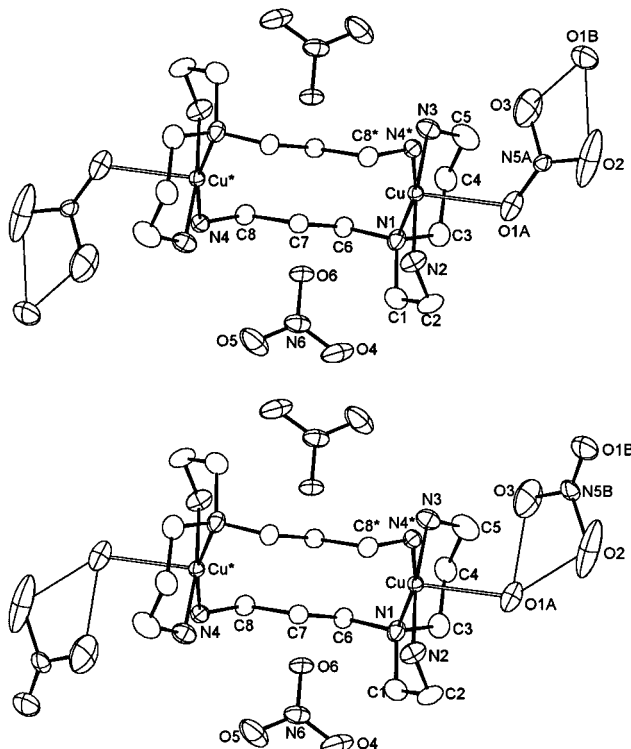


Figure 3. ORTEP plots of $[\text{Cu}(332)(\text{NO}_3)_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ with the employed crystallographic numbering scheme. Atoms marked with an asterisk are related by an inversion center. The atoms O1A, O1B, N5A, and N5B are part of a disorder. O1A can be part of a nitrate anion which is bonded to Cu and hydrogen bonded to a water molecule (O1B, upper picture). Alternatively O1A represents the oxygen atom of a water molecule bonded to Cu and hydrogen bonded to the oxygen atoms of the nitrate anion O2, O3, O1B, and N5B (lower picture).

(measured) versus pH (calculated) gave a working slope and intercept in order to convert the measured millivolt data to $-\log[\text{H}^+]$. Both the pH meter and the automatic buret were interfaced to a PC in order to perform automatic titrations and data acquisition. The temperature was kept constant at 25.0 ± 0.1 °C by a Julabo bath circulating into water-jacketed, covered beakers. Argon, scrubbed and humidified by bubbling through 10% NaOH, was used to exclude ambient CO_2 . Water was purified by ion-exchange followed by distillation. NaOH solutions (~ 0.15 M) were prepared by dilution of 50% NaOH with degassed water and standardized against potassium hydrogen phthalate using the Gran method.¹² The ionic strength of the solutions was kept constant at $\mu = 0.15$ M NaCl. The ratio of ligand to metal was in the range $10:1 \geq \text{L}:\text{M} \geq 0.5:1$ with concentrations in the range $0.66\text{--}3.9$ mM. A minimum of five titrations for each ligand, and for each ligand in the presence of Cu(II) ions, was performed in the pH range $2 \leq \text{pH} \leq 11.5$.

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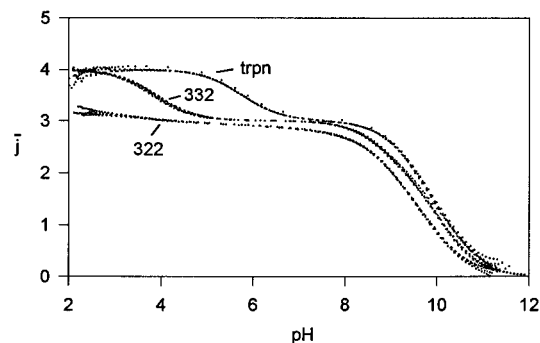


Figure 4. Plot of average number of protons per ligand (\bar{j}) versus pH.

Table 3. Potentiometrically Determined $\text{p}K_a$ Values (25 °C, $\mu = 0.15$ M NaCl) for the Four Tripodal Tetraamines and Literature Values (25 °C, $\mu = 0.1$ M KCl) for Tren¹⁴ and Trpn¹⁵

	tren ¹⁴	322	332	trpn	trpn ¹⁵
$\text{p}K_{a1}$	10.14	10.14(9)	10.4(1)	10.58(2)	10.51
$\text{p}K_{a2}$	9.43	9.72(6)	9.87(7)	9.92(4)	9.82
$\text{p}K_{a3}$	8.41	8.40(4)	8.85(3)	9.28(4)	9.13
$\text{p}K_{a4}$	< 2	2.1(3)	3.86(5)	5.80(8)	5.62

Computations with Potentiometric Data. The protonation constants for the ligands, and the stability constants for the Copper(II)–ligand complexes, were determined using the program BEST.¹³ This program performs a least-squares fit of calculated pH to measured pH, using a mass balance equation and a varied set of stability constants. An indication (goodness) of the fit σ is calculated according to eq 1 (N is the total number of data points). In all of the titrations with trpn, $\sigma < 0.01$ (eq 1), while with either 332 or 322 $\sigma < 0.05$; the larger σ

$$\sigma = \sum (\text{pH}_{\text{calc}} - \text{pH}_{\text{obs}})^2 / (N - 1) \quad (1)$$

in the latter two cases can be attributed to CO_2 contamination of the stored amines. Plots of the average number of protons per ligand (\bar{j}) calculated from the titrations (Figure 4) showed that the protonated ligands trpn, 332, and 322 each acted as tetraprotic acids. The four $\text{p}K_a$'s for each ligand were determined by potentiometry (Table 3).

For determination of the stability constants of the Cu(II) complexes, titrations were carried out in the presence of Cu(II) ions. Plots of the average number of bound ligands per Cu(II) ion (\bar{n}) calculated from the titrations (Figure 5) showed that the ligands trpn, 332, and 322 each formed 1:1 L:M complexes and that the presence of hydrolysis and/or protonated species was significant. The stability constants shown in Table 4 were determined using the protonation constants of the ligands and $K = 10^{-10.61}$ for the formation of the hydrolysis species $[\text{Cu}_2(\text{OH})_2]^{2+}$.¹⁷ All three metal–ligand systems also included a protonated species $[\text{Cu}(\text{HL})(\text{H}_2\text{O})_2]^{3+}$ and a hydroxo complex $[\text{CuL}(\text{OH})]^+$, as well as the $[\text{CuL}(\text{H}_2\text{O})]^{2+}$ complex. When species corresponding to $[\text{CuL}_2]^{2+}$, $[\text{CuL}(\text{HL})]^{3+}$, $[\text{Cu}(\text{HL})_2]^{4+}$, or $[\text{CuL}(\text{OH})_2]$ were included, the fit of the calculated curve against the measured curve did not change significantly. Speciation diagrams for each of the four ligands with Cu(II) are shown in Figure 6 (for tren, literature data¹⁶ were used).

Computations with Visible Spectrophotometric Data. An independent confirmation of the solution equilibria was also obtained by least-squares fit of electronic (visible) spectra at different wavelengths and pH's in order to ascertain the geometries about the Cu(II) centers. The model describes the concentrations of each metal-containing species as a function of pH according to eqs 2–5.

C_M and C_{MLH} are the concentrations of the free metal and of the protonated complex, respectively; C_{ML} is the concentration of the

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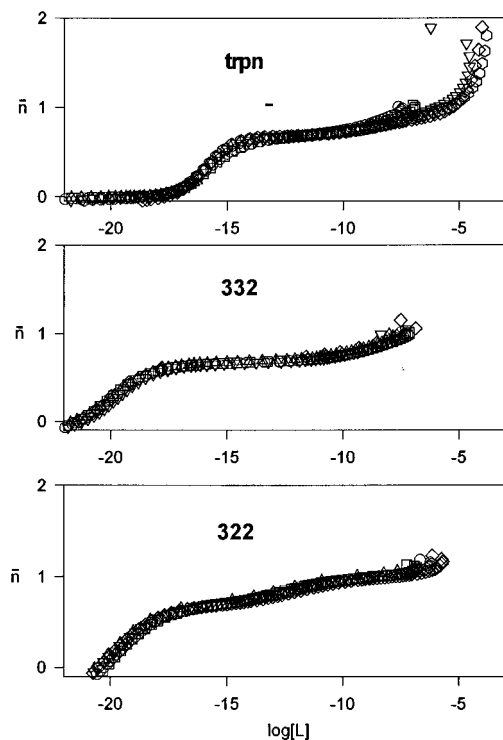
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Table 4. Stability Constants Determined for the 322, 332, and trpn Complexes with Cu(II) (25 °C, $\mu = 0.15$ M NaCl) and Literature Values for Tren¹⁶ (37 °C, $\mu = 0.15$ M KNO₃) and Trpn¹⁵ (25 °C, $\mu = 0.1$ M KCl) (Values Determined from Visible Spectra for Trpn and 322 in Square Brackets^a)

	tren ¹⁶	322	332	trpn	trpn ¹⁵
Cu + L → CuL	18.5	17.1(1) [16.6(1)]	16.0(1)	13.21(7) [12.8(1)]	13.12
CuL + H → CuHL	3.6	6.4(2) [6.3(1)]	7.9(1)	8.29(7) [8.5(1)]	8.15
Cu + L + H → CuHL	11.9	13.3(2)	13.5(1)	10.92(7)	10.76
CuL → CuLOH + H	-9.09	-9.4(3) [-9.6(1)]	-9.8(1)	-9.9(1) [-9.9(1)]	-9.77

^a Changes in ionic species are omitted.**Figure 5.** Plot of average number of ligands per metal (\bar{n}) versus $\log[L]$.

$$C_M = C_{\text{Minit}} - C_{\text{Minit}} a_1^{(\text{pH}-b_1)/\{a_1^{(\text{pH}-b_1)} + 1\}} \quad (2)$$

$$C_{\text{MLH}} = C_{\text{Minit}} a_1^{(\text{pH}-b_1)/\{a_1^{(\text{pH}-b_1)} + 1\}} - C_{\text{Minit}} a_2^{(\text{pH}-b_2)/\{a_2^{(\text{pH}-b_2)} + 1\}} \quad (3)$$

$$C_{\text{ML}} = C_{\text{Minit}} a_2^{(\text{pH}-b_2)/\{a_2^{(\text{pH}-b_2)} + 1\}} - C_{\text{Minit}} a_3^{(\text{pH}-b_3)/\{a_3^{(\text{pH}-b_3)} + 1\}} \quad (4)$$

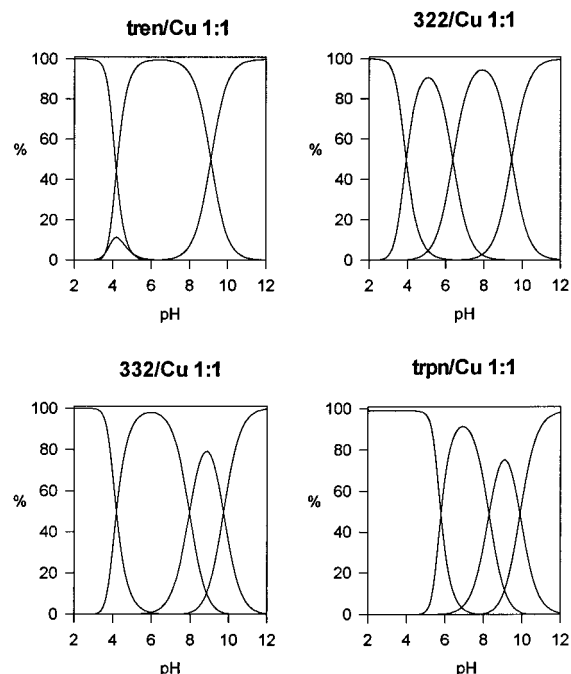
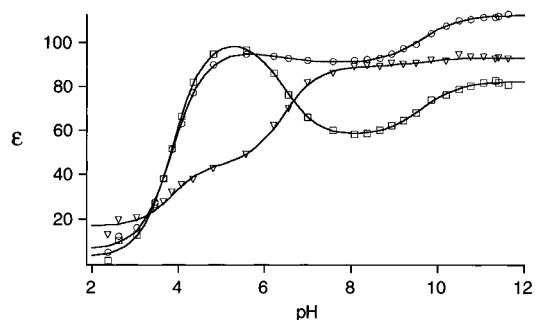
$$C_{\text{MLOH}} = C_{\text{Minit}} a_3^{(\text{pH}-b_3)/\{a_3^{(\text{pH}-b_3)} + 1\}} \quad (5)$$

complex; C_{MLOH} is the concentration of the hydroxo complex; C_{Minit} is the initial concentration of free metal; the factors a_n (which control the slope) and b_n (which control the inflection point for each curve) are free variables during the refinement; therefore the extinction is given as eq 6 (where ϵ is the extinction coefficient, for each species, and d is the cell pathlength).

$$E = \epsilon_1 C_M d + \epsilon_2 C_{\text{MLH}} d + \epsilon_3 C_{\text{ML}} d + \epsilon_4 C_{\text{MLOH}} d \quad (6)$$

A nonlinear least-squares fit of this model yielded extinction coefficients and a pH-dependent speciation for each of the Cu(II) complexes; the speciation model was in complete agreement with the potentiometric results (see Table 4). An example of the fit for 322 is shown in Figure 7.

Kinetics. The kinetics of substitution of the coordinated water of $[\text{Cu}(322)(\text{H}_2\text{O})]^{2+}$ and of $[\text{Cu}(\text{trpn})(\text{H}_2\text{O})]^{2+}$ by pyridine were investigated at 25 °C using a standard temperature-jump instrument, as described earlier for the measurements on $[\text{Cu}(\text{tren})(\text{H}_2\text{O})]^{2+}$.⁴

**Figure 6.** Speciation diagrams of tren, 322, 332, and trpn in a 1:1 ratio with Cu(II) (2 mM). Only metal-containing species are shown. In order of increasing pH, they are Cu^{2+} , $[\text{Cu}(\text{HL})(\text{H}_2\text{O})_2]^{3+}$, $[\text{CuL}(\text{H}_2\text{O})_2]^{2+}$, and $[\text{CuL}(\text{OH})]^+$.**Figure 7.** Observed and fitted visible absorption of 322 complexation with Cu(II): at 600 (○), 680 (□), and 760 (▽) nm.

Results and Discussion

Preparation of Complexes and Molecular Structures. We recently reported that the reaction of the tripodal ligands trpn, 332, and 322 with $\text{Cu}(\text{OH})_2$ and NH_4PF_6 in water under basic condition yields trigonal-bipyramidal complexes of the type $[\text{Cu}(\text{N}_4)(\text{NH}_3)](\text{PF}_6)_2$ (N_4 = tripodal tetraamine).⁶ A similar complex has been previously reported with tren.⁵ The reaction of the ligands trpn and 332 with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in water at neutral pH yields lighter blue copper complexes. Mass spectrometry indicated that binuclear complexes of the composition $[\text{Cu}(\text{N}_4)(\text{NO}_3)_2]_2$ had formed. To establish the coordination geometry in these complexes, X-ray structure analyses were carried out. These analyses showed that binuclear, square-pyramidal complexes were indeed obtained. The asymmetric

unit contains a half-molecule related to the other half by an inversion center. The copper atoms are coordinated by four amine nitrogen atoms in the basal plane, and an oxygen atom in the apical position. The tripodal amine ligands coordinate with the central amine nitrogen atom and two primary amine functions to one copper atom, while the third amine arm of the ligand bridges to the second copper atom. The apical position for each Cu in $[\text{Cu}(\text{trpn})(\text{NO}_3)_2](\text{NO}_3)_2$ is occupied by a nitrate oxygen atom, while the remaining two nitrate anions are hydrogen-bonded to amine nitrogen atoms (Figure 2, hydrogen bonds are not shown). A slight change of this binding situation was observed in $[\text{Cu}(332)(\text{NO}_3)_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. In this complex the apical position of the square-pyramid is also taken by an oxygen atom; however, owing to a disorder of atoms O1A/O1B and N5A/N5B, oxygen atom O1A can be considered as part of a nitrate anion (Figure 3, upper plot) or as the oxygen atom of a water molecule (Figure 3, lower plot). Positions N5A and N5B have $\text{SOF} = 1/2$.

A comparison of the bond parameters (Table 2) in the trpn and 332 complexes reveals little sensitivity toward the topology of the amine ligands used. Among the Cu–N bonds, those involving the tertiary amine nitrogen atoms are the longest in both complexes. The second longest Cu–N bond formed in both complexes involves the bridging amine group. In general, the Cu–N separations in the square-pyramidal complexes fall in the range observed for the trigonal-bipyramidal Cu(II) complexes with tripodal tetraamines.^{5,6}

A simple alteration (basic to neutral pH) in the conditions of preparation changes both the nuclearity and the coordination geometry in the isolated copper complexes. The reasons for this behavior can be deduced from the following investigation of the solution thermodynamics.

Protonation Constants. The protonation constants for the ligands trpn, 332, and 322 are summarized in Table 3; literature values for tren¹⁴ and trpn¹⁵ are also given. There is a general trend in this series; the first three $\text{p}K_a$'s, assigned to the primary amine functions, show only a small shift, whereas the fourth $\text{p}K_a$ is increased dramatically, about 2 orders of magnitude for every change of a $-\text{CH}_2\text{CH}_2-$ arm into a $-\text{CH}_2\text{CH}_2\text{CH}_2-$ arm, tren to 322 to 332 to trpn. The unusual acidity of the central fourth nitrogen in tren results from the electrostatic interaction between the protonated primary amines. The increase in distance between these charges by a longer chain results in the observed increase in basicity of the tertiary nitrogen atom.

Complex Stability Constants. In the complexation of Cu(II) ions with the tripodal tetraamines 322, 332, and trpn, 1:1 five coordinate complexes are expected.⁶ The stoichiometry was verified by the \bar{n} plots calculated from the experimental titration curves in the presence of Cu(II) (Figure 6). These plots also indicate a protonated complex $[\text{Cu}(\text{HL})(\text{H}_2\text{O})_2]^{3+}$ as a relevant species in all three systems, as well as a hydroxo complex $[\text{CuL}(\text{OH})]^+$ in the high-pH region. There was no evidence for a $[\text{CuL}_2]^{2+}$ complex.

The most obvious difference between the complex formation of Cu(II) with tren and that with the other amines trpn, 332, and 322 is in the formation of protonated complexes (Figure 6). Between pH 3 and 5 tren forms with Cu(II) less than 20% of a protonated $[\text{Cu}(\text{HL})(\text{H}_2\text{O})_2]^{3+}$ complex.^{16,18}

For the ligands with at least one propyl chain (all but tren), the protonated complex becomes predominant. The $[\text{Cu}(\text{H}322)(\text{H}_2\text{O})_2]^{3+}$ cation is the major species between pH 4 and 6, while $[\text{Cu}(\text{H}332)(\text{H}_2\text{O})_2]^{3+}$ dominates between pH 4 and 7. Unique among the systems, trpn does not form any complex at pH < 5. The $[\text{Cu}(\text{Htrpn})(\text{H}_2\text{O})_2]^{3+}$ complex dominates between pH

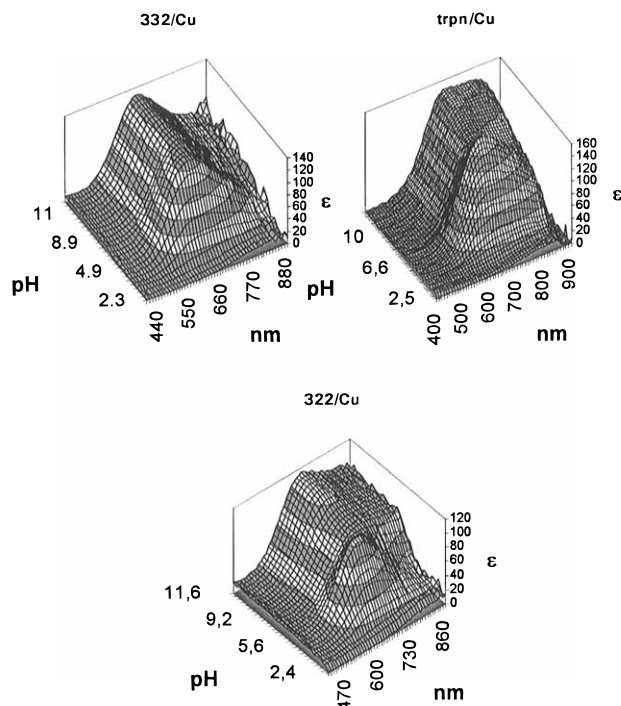


Figure 8. Three-dimensional plots of the L/Cu(II) visible spectrophotometric titrations, molar extinction vs pH vs λ .

6 and 8. This difference can be explained by the absence of any five-membered chelate rings in the case of trpn. The formation constants for the reaction $\text{Cu}(\text{II}) + \text{L} + \text{H}^+ \rightarrow [\text{Cu}(\text{HL})(\text{H}_2\text{O})_2]^{3+}$ show the same trend (Table 4); the stability constant of $[\text{Cu}(\text{Htrpn})(\text{H}_2\text{O})_2]^{3+}$ ($\log K = 10.92(7)$) is 2 orders of magnitude smaller than the analogous values for 332 (13.5(1)) and 322 (13.3(2)) and 1 order of magnitude smaller than that for tren (11.9).¹⁶

The $[\text{CuL}(\text{H}_2\text{O})]^{2+}$ complexes exhibit the expected sequence of decreasing stability: tren ($\log K = 18.5$ ¹⁶) > 322 (17.1(1)) > 332 (16.0(1)) > trpn (13.21(7)). This decrease clearly parallels the loss of five-membered chelate rings in the respective complexes. $[\text{Cu}(\text{tren})(\text{H}_2\text{O})]^{2+}$ predominates between pH 4.5 and 8, $[\text{Cu}(322)(\text{H}_2\text{O})]^{2+}$ between pH 7 and 9.5, and $[\text{Cu}(332)(\text{H}_2\text{O})]^{2+}$ and $[\text{Cu}(\text{trpn})(\text{H}_2\text{O})]^{2+}$ between pH 8 and 10 (Figure 6). The $\text{p}K_a$ values for the deprotonation of the coordinated water molecule to form the $[\text{CuL}(\text{OH})]^+$ hydroxo complexes remain constant within an order of magnitude between $\log K_a = -9$ and $\log K_a = -10$.

Electronic Spectra. The visible spectra in the region 500–900 nm show the d–d transitions of the Cu(II) ion (Figure 8); these spectra are dependent on the coordination geometry around the Cu(II) ion.^{5,19,20} Square-pyramidal coordination with five nitrogen atoms as in the $[\text{Cu}(\text{NH}_3)_5]^{2+}$ cation results in an absorption maximum λ_{max} at 654 nm, with a shoulder at 909 nm.⁵ The other principal coordination geometry, the trigonal-bipyramid realized in $[\text{Cu}(\text{tren})(\text{NH}_3)]^{2+}$ has $\lambda_{\text{max}} = 877$ nm, with a shoulder at 658 nm.⁵ The data allow us to draw some qualitative conclusions from the visible spectrophotometric titrations (Figure 8).

At pH 6–7 trpn forms a protonated complex $[\text{Cu}(\text{Htrpn})(\text{H}_2\text{O})_2]^{3+}$ with $\lambda_{\text{max}} = 661$ nm ($\epsilon = 149 \pm 5 \text{ M}^{-1} \text{ cm}^{-1}$), indicative of square-pyramidal coordination. The $[\text{Cu}(\text{trpn})(\text{H}_2\text{O})]^{2+}$ cation, formed upon deprotonation of $[\text{Cu}(\text{Htrpn})(\text{H}_2\text{O})_2]^{3+}$, changes its coordination geometry toward a more

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trigonal-bipyramidal (or less square-pyramidal) structure (the absorption maximum shifts somewhat to 689 nm ($\epsilon = 108 \pm 5 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder at 820 nm appears). Upon subsequent deprotonation, $[\text{Cu}(\text{trpn})(\text{OH})]^+$ becomes even more trigonal-bipyramidal (or less square-pyramidal), with $\lambda_{\text{max}} = 708 \text{ nm}$ ($\epsilon = 139 \pm 5 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder at 810 nm is formed. Changes in the visible absorption spectra as a function of pH were used to calculate the concentrations of the Cu(II)-containing species. This information allowed the calculation of stability constants based on the metal concentration, and these values agree well with those determined by potentiometry (Table 4).

In the case of the tripodal tetraamine 332, only a small shift of λ_{max} is observed, indicating that the structural changes in the coordination geometries during the deprotonations from $[\text{Cu}(\text{H332})(\text{H}_2\text{O})_2]^{3+}$ to $[\text{Cu}(\text{332})(\text{H}_2\text{O})]^{2+}$ and $[\text{Cu}(\text{332})(\text{OH})]^+$ are less than in the analogous trpn complexes. The respective λ_{max} values of 630, 654, and 645 nm (each with a shoulder at $\sim 820 \text{ nm}$) are indicative of square-pyramidal coordination.^{5,19} Due to the small differences in these spectra, a least-squares fit for the determination of the various 332/Cu complex constants was not possible. Ligand 322 coordinates similarly to trpn, with a square-pyramid for the $[\text{Cu}(\text{H322})(\text{H}_2\text{O})_2]^{3+}$ cation ($\lambda_{\text{max}} = 631 \text{ nm}$ ($\epsilon = 114 \pm 5 \text{ M}^{-1} \text{ cm}^{-1}$)) and complete deprotonation of the ligand, instigating a transition to a more trigonal-bipyramidal coordination for $[\text{Cu}(\text{322})(\text{H}_2\text{O})]^{2+}$ with $\lambda_{\text{max}} = 700 \text{ nm}$ ($\epsilon = 97 \pm 5 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder at 815 nm ($\epsilon = 91 \pm 5 \text{ M}^{-1} \text{ cm}^{-1}$). The $[\text{Cu}(\text{322})(\text{OH})]^+$ cation is like the hydroxo complex in the trpn system with more of a trigonal-bipyramidal geometry ($\lambda_{\text{max}} = 670 \text{ nm}$ ($\epsilon = 93 \pm 5 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder at 806 nm ($\epsilon = 99 \pm 5 \text{ M}^{-1} \text{ cm}^{-1}$)). Stability constants for the Cu(II)–322 system were also deduced from the visible spectral data, and these are shown in Table 4.

Kinetics. In the temperature-jump experiments, the observations were consistent with substitution of the coordinated water by pyridine occurring within the heating time (ca. 20 μs) of the temperature pulse. This indicates that the substitution reactions considered here are orders of magnitude faster than is the case in $[\text{Cu}(\text{tren})(\text{H}_2\text{O})]^{2+}$.⁴ This is in agreement with the structural conclusions drawn from the visible spectra.

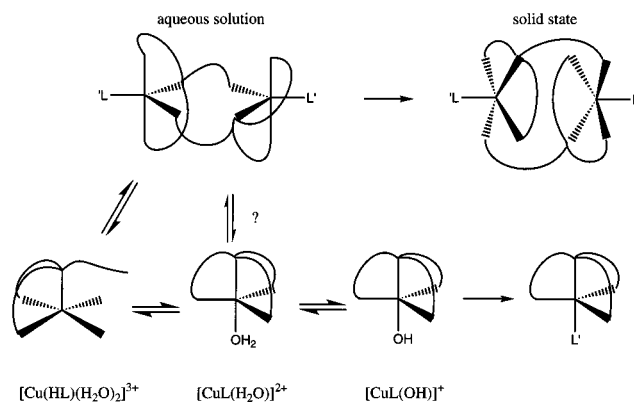


Figure 9. Correlation of coordination geometries in the solution and the solid state from a combination of potentiometry, electronic spectroscopy, and X-ray crystallography.

Concluding Remarks. The pH-dependent coordination of the ligands trpn, 332, and 322 (including the coligands H_2O or OH^-) shows varying degrees of geometry intermediate between trigonal-bipyramidal and square-pyramidal. At high pH all four nitrogen donors are coordinated. This leads, in the reaction of $\text{Cu}(\text{OH})_2$ with a tripodal tetraamine and NH_4PF_6 , to mononuclear $[\text{CuN}_4(\text{NH}_3)](\text{PF}_6)_2$ ^{5,6} (see Figure 9). In the low-pH range, one arm of the ligand is protonated and not coordinated and can, on deprotonation, coordinate to a second Cu(II) center, leading to the binuclear species depicted in Figures 2 and 3. These binuclear species isolated from neutral $\text{Cu}(\text{NO}_3)_2$ salts cannot be detected in solution but are clearly formed in the solid state.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Natural Sciences and Engineering Research Council for financial support. F.T. acknowledges support of the Studienstiftung des Deutschen Volkes; F.E.H. and C.O. acknowledge NATO for a Collaborative Research grant (CRG 930121).

Supporting Information Available: Tables of atomic coordinates, bond distances and angles, and thermal parameters and figures of ORTEP diagrams (10 pages). Ordering information is given on any current masthead page.

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