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Use of Hydrophobic Ligands for the Stabilization of Low-Valent Transition Metal Complexes. 1. The Effect of *N*-Methylation of Linear Tetraazaalkane Ligands on the Properties of Their Copper Complexes

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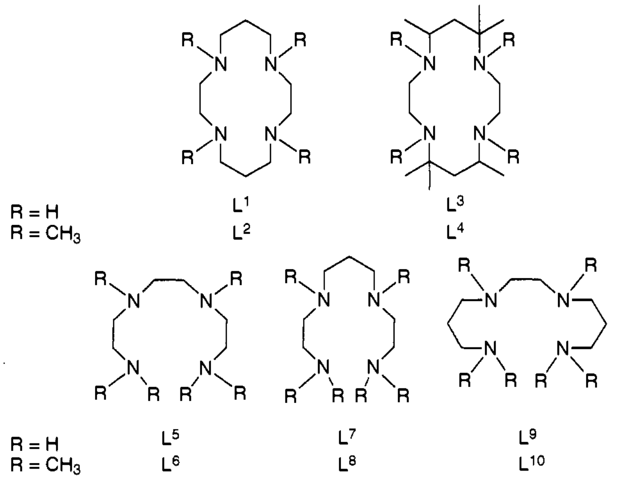
Abstract: The electrochemical reduction of the Cu(II) complexes with the ligands 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane, 2,5,9,12-tetramethyl-2,5,9,12-tetraazatridecane, and 2,6,9,13-tetramethyl-2,6,9,13-tetraazatetradecane in deaerated aqueous solutions yields the corresponding thermodynamically stable copper(I) complexes. The same complexes are obtained also via the comproportionation reaction of $\mathrm{CuL}^{i\,2+}$ and Cu^0 in the presence of excess ligand. ΔS^0 values of the reduction processes were determined. The basicity constants of L^i and the stability constants of their Cu(II) complexes were determined potentiometrically. The ESR spectra of $\mathrm{CuL}^{i\,2+}$ point out that these complexes are not significantly tetrahedrally distorted. The binding constants of axial singly charged anions to the $\mathrm{CuL}^{i\,2+}$ complexes were determined. Analysis of the data points out that the thermodynamic stabilization of the monovalent copper complexes via N-methylation is mainly due to the destabilization of the $\mathrm{CuL}^{i\,2+}$ complexes. It is concluded that a major factor contributing to the observed effects is the hydrophobic nature of the tertiary-amine ligands.

Introduction

There is a growing interest in developing ligands which thermodynamically or kinetically stabilize low-valent transition metal complexes, *e.g.* Cu(I) or Ni(I), in aqueous solutions. This interest stems from the wish to develop new single-electron reducing agents and redox catalysts for a large variety of processes. Furthermore such complexes might serve as models, though simple ones, to monovalent transition metal complexes occurring in biological systems.[2]

Recent results point out that the N-alkylation of the complexes of Ni, Cu, Pd, and Cr with the macrocyclic ligands L^1 and L^3 to yield the corresponding complexes with the ligands L^2 and L^4 thermodynamically stabilizes their low-valent complexes, *i.e.* Ni(I),[3] Cu(I),[4] Pd(I),[5] and Cr(II),[6] respectively. Furthermore it was shown that N-methylation of ethylenediamine lowers the electrode potential of the Ru(III)/Ru(II) couple,[7] N-methylation of diethylentriamine has a similar effect on the Cu(II)/Cu(I) redox couple,[8] and N-methylation of L^5 inhibits the oxidation of Co(II) by dioxygen.[9]



It seemed of interest to analyze why the N-alkylation of these ligands thermodynamically stabilizes their low-valent transition metal complexes. An understanding of this phenomenon might help in the systematic design of other ligands which will thermodynamically stabilize low-valent transition metal complexes.

In principle, the following properties of these ligands might affect the electrode potentials of the complexes.

(1) Electronic factors: These ligands are pure σ donors and are therefore expected to thermodynamically stabilize relatively

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high valent transition metal complexes.[10] It was however argued that tertiary-amine ligands are inherently poor ligands.[11] This claim is surprising as alkyls are electron-donating substituents. However, spectroscopic data clearly point out that indeed the N-alkylated ligands are poorer σ donors.[3a,d,e,6d] This observation might in principle be due to one of the following factors:

(a) The N-methylation of the macrocyclic ligand causes, due to steric hindrance, an increase of the cavity size, thus elongating the M−N bonds and therefore stabilizing the low-valent complexes.[3a] Analogous arguments could be applicable also to the open chain ligands. However, this explanation cannot explain the observation that the electrode potential of 1,4,8,12-tetraazacyclopentadecane−Ni(II) is similar to that of $NiL^{1\ 2+}$ [3d] and that the electrode potential of $NiL^{2\ 2+}$ is shifted cathodically when CH_3 is replaced by CH_2CH_2OH and $CH_2CO_2^-$.[12]

(b) The N-methylation affects the M−N−C bond angles in $M{-}N({-}C)_2$,[13] thus decreasing the M−N bond strength. Again the effect of replacing $R{=}CH_3$ by CH_2CH_2OH and $CH_2CO_2^-$ can be hardly explained via this argument.

(c) The N-alkylation weakens the M−N bond via eliminating the effect of M−N−H···O hydrogen bonds in aqueous[14] solutions on the electron density on the nitrogens. The effect of M−N−H···O hydrogen bonds on the electrode potential of transition metal complexes was analyzed recently in detail.[15] In less polar solvents the weakening of the interaction with the counterions is expected to have a similar effect.

(2) Steric factors: Chelating ligands might impose a coordination sphere of a given geometry, *e.g*. a tetrahedral one. If one of the oxidation states of the central cation prefers this geometry, it will be thermodynamically stabilized, *e.g* Cu(I) will be thermodynamically stabilized by a ligand imposing a tetrahedral coordination sphere. Alternatively ligands which due to steric hindrance elongate the metal−donor bond length thermodynamically stabilize transition metal complexes with lower oxidation states and vice versa.[5] Furthermore, the ligation might induce different strains in the ligand skeleton in complexes with different oxidation states.[13]

(3) Solvation factors: The outer sphere solvation energy has a major effect on the redox potential of all charged complexes.[15] Therefore ligands which endow a hydrophobic nature to the complex thermodynamically stabilize low-valent complexes whereas hydrophylic ligands thermodynamically stabilize complexes with high oxidation states.[16,17]

Tertiary-polyamine ligands are therefore expected to thermodynamically stabilize low-valent transition metal complexes due to the following reasons:

(1) σ-Donating properties weaken due to the exclusion of hydrogen bonds of the type M−N−H···O.

(2) Solvation energies decrease due to their hydrophobic nature and the increase of the radii of the complexes caused by N-methylation.

(3) They might also cause via steric hindrance M−N bond elongation and/or distortion of the inner coordination sphere. However, as the effect of N-methylation was observed for a variety of central cations, e.g. Ni(I),[3] Cu(I),[4] Pd(I),[5] Cr(II),[6] Co(II),[9] and Ru(II),[7] which prefer different coordination geometries, it is not likely that the effect of N-methylation on the electrode potentials is due to a geometry imposed by the ligands.

These ligands have an additional advantage, *i.e.* they cannot be reduced, in contrast with Π-acids which are commonly used to thermodynamically stabilize low-valent complexes.

Due to the role of copper complexes in catalytic redox and biological processes, it seemed of interest to study the redox properties of N-methylated, aliphatic, open chain, tetraaza ligands. Preliminary results indeed pointed out that the ligand 2,5,9,12-tetramethyl-2,5,9,12-tetraazatridecane (L^8) induces the comproportionation reaction of Cu(II) and Cu(0).[17] It was therefore decided to extend this study to include the ligands L^6 and L^{10}. As the results pointed out, these ligands indeed thermodynamically stabilize monovalent copper ions in aqueous solutions and this stabilization is due mainly to the lowering of the stability constants of the $CuL^{i\ 2+}$ complexes by N-methylation. The spectroscopic properties of the latter complexes were studied in detail in order of elucidating the major contributing factors to the thermodynamic stabilization of the Cu(I) complexes.

Experimental Section

Materials. All solutions were prepared from A. R. grade chemicals and from distilled water further purified by passing through a Milli Q Millipore setup (final resistivity > 10 MΩ/cm). The ligands (6, 8, and 10) were prepared by N-methylation of the unmethylated ligands (5, 7, and 9, Aldrich), using formaldehyde and formic acid according to a procedure described in the literature,[18] and crystallized as their HCl salts. The degree of N-methylation obtained was verified by C,H,N analysis and by H-NMR and C^{13}-NMR measurements. Both analyses indicated that more than 97% of the ligand molecules (6, 8, and 10) are fully methylated. All the ligands were used as their HCl salts.

Electrochemical measurements were carried out using an EG&G Potentiostat/Galvanostat model 263. The working electrode was EG&G parc model 303A SMDE. The software used was EG&G model 270/250 Research Electrochemistry 4.00.

Some of the experiments were performed with a Bioanalytical Systems Inc. CV-1B cyclic voltammograph, a three-electrode cell, and a Yokogawa Hokushin Electric X-Y recorder type 3080. A SCE served as a reference electrode, and HMDE was the working electrode.

The pH was measured with a Corning 220 pH meter.

Potentiometric measurements were carried out in 0.15 M $NaClO_4$ (C. Erba, ACS grade) and purified according to a procedure described earlier.[19] Standardized CO_2-free solutions of NaOH, used in the potentiometric titrations, were prepared by following the procedure described in ref 20. The potentiometric titrations were carried out by using equipment (potentiometer, buret, stirrer, cell microcomputer, etc.) that has been fully described.[21] The computer program SUPERQUAD[22] was used to process the data and calculate both basicity and stability constants.

UV−vis spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer, applying the syringe technique for anaerobic measurements.

ESR spectra were carried out with a Bruker ER 200 spectrometer operating at 9.5 GHz.

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Table 1. Basicity and Formation Constants for the System Copper(II)/L^i (i = 5−10) in Aqueous Solutions[a]

	log *K*					
reaction	L^5	L^6	L^7	L^8	L^9	L^{10}
$L + H^+ \rightleftharpoons LH^+$	9.74(6)	9.23(1)	10.25	9.21(2)	10.53	9.95(2)
$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	9.08(2)	8.47(1)	9.50	8.47(2)	9.77	9.20(2)
$LH_2^{2+} + H^+ \rightleftharpoons LH_3^{3+}$	6.56(2)	5.36(2)	7.28	5.68(3)	8.30	7.51(3)
$LH_3^{3+} + H^+ \rightleftharpoons LH_4^{4+}$	3.25(5)	1.68(3)	6.02	4.26(4)	5.59	4.35(4)
$L + Cu^{2+} \rightleftharpoons CuL^{2+}$	20.1	12.60(1)	23.9	10.08(6)	21.69	8.8(1)
$L + Cu^+ \rightleftharpoons CuL^+$ [b]	<12[c]	11.0(1)	<14[c]	10.0(1)	<13[c]	
$\log(K_2/K_1)$[d]	7.9<	1.6	10.1<	0.1	8.7<	
$CuL^{2+} + H^+ \rightleftharpoons CuLH^{3+}$	3.5	6.16(1)		5.19(6)	3.53	7.8(1)
$CuL^{2+} + OH^- \rightleftharpoons CuLOH^+$	3.2	6.43(3)		3.50(1)		

[a] Data of copper(II)/L^i (i = 5, 7, 9) were taken from the literature.[24] [b] Values for L^6 and L^8 were calculated from the electrochemical data; see results. The values for L^5, L^6, and L^9 were estimated as described in Appendix 1. [c] 12, 14, 13 > K_1. [d] K_1 is the stability constant for the Cu(I), and K_2 is the stability constant for the Cu(II).

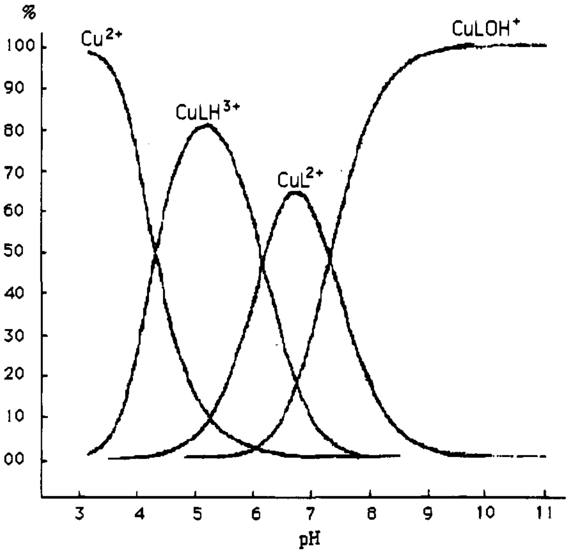

Figure 1. Distribution diagrams of the species formed as a function of pH in the system Cu^{II}/L^6 in a 0.15 M $NaClO_4$ solution at 25 °C. $[Cu^{II}] = [L^6] = 0.001$ M.

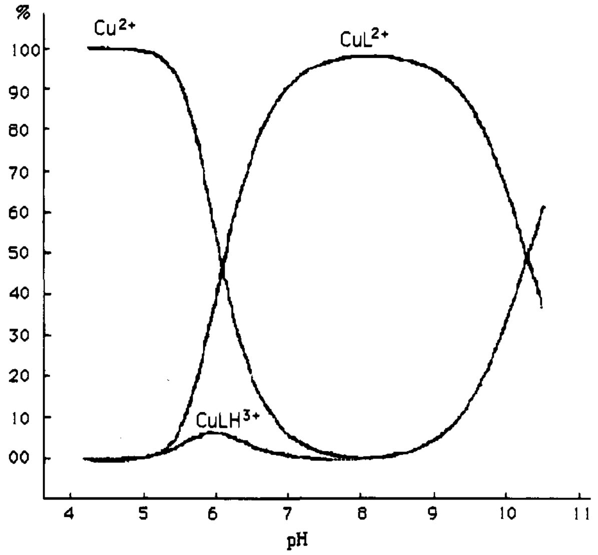

Figure 2. Distribution diagrams of the species formed as a function of pH in the system Cu^{II}/L^8 in a 0.15 M $NaClO_4$ solution at 25 °C. $[Cu^{II}] = [L^8] = 0.001$ M.

Molecular orbital calculations were carried out with a Tektronix CAChe system; the software used was Zindo 3.0, which computes semiempircal quantum mechanical values for optimal geometries.[23]

Results

In order to obtain a detailed characterization of the species in the solutions used in this study, potentiometric titrations of the solutions containing the ligands L^6, L^8, and L^{10} and of solutions containing equimolar mixtures of these ligands and $CuSO_4$ were performed. The results obtained are summed up in Table 1 and Figures 1 and 2. For comparison purposes, literature data concerning the ligands L^5, L^7, and L^9 and their copper complexes are included in the table. Due to the relatively low stability constant of CuL^{10}, the titration of solutions containing L^{10} and $CuSO_4$ resulted in the precipitation of $Na_2Cu(OH)_4$ at relatively low pHs. (Similar results are obtained when NaOH is replaced by LiOH or KOH.) Therefore, the error limit in the determination of the stability constants of this system is lower and the equilibrium constant for the formation of $CuL^{10}(OH)^+$ could not be determined.

The results presented in Table 1 clearly indicate that N-methylation decreases the basicity of the ligands studied. This finding is in accord with literature data concerning other tertiary-amine ligands. This observation is commonly attributed to the lower solvation of the tertiary-ammonium ions.[25]

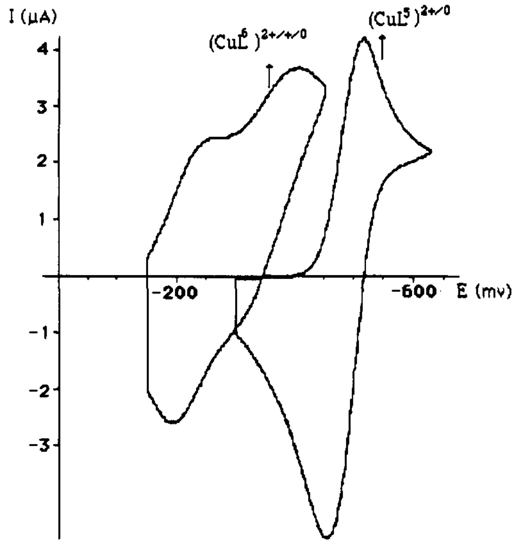

Figure 3. Cyclic voltammogram, HMDE vs SCE: rate = 5 mV/s; $[Cu^{II}] = 0.001$ M; [L] = 0.002 M; $[ClO_4^-] = 0.8$ M; pH 10.0.

The redox properties of the copper complexes with these ligands were studied using cyclic and square wave voltammetry. Typical results are shown in Figures 3 and 4. Figure 3 points out that reversible electrochemical waves are obtained in these

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Table 2. Reduction Potentials of the Copper Complexes[a]

	pH 5		pH 6		pH 7		pH 8		pH 9		pH 10		pH 11		pH 12	
ligands	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2
L^5											−260					
L^6	116	−101	80	−118	65	−118	60	−118	45	−137	12	−145	−48	−145	−105	−148
L^7											−300					
L^8			173	−63	143	−64	139	−64	135	−74	132	91	115	−96		
L^9											−310					
L^{10} [b]					100−60		90−55		80−50		20−10		0			

[a] Cyclic and square wave voltammetry; values in mV ± 5 mV; E_1, first process, E_2, second process vs NHE; working electrode HMDE, scan rate, 20 mV/s; $[Cu^{II}] = 0.001$ M; $[L] = 0.002$ M; $[ClO_4^-] = 0.5$ M. [b] In this case, we have two one-electron consecutive transitions overlapping one another.

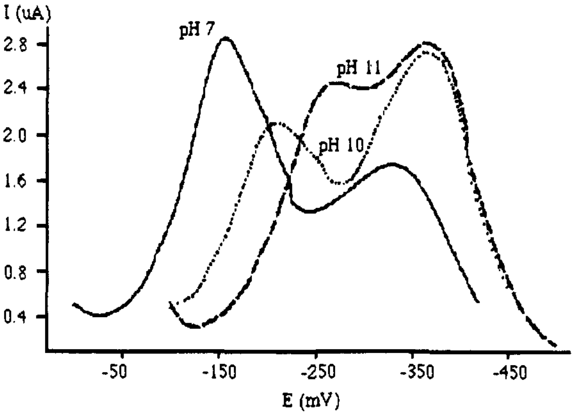

Figure 4. Square wave voltammogram, HMDE vs Ag/AgCl: frequency = 5 Hz; $[Cu^{II}] = 0.001$ M; $[L^6] = 0.002$ M; $[ClO_4^-] = 0.5$ M.

systems. In order to inhibit the precipitation of $Na_2Cu(OH)_4$ in solutions containing L^{10}, $(C_2H_5)_4NOH$ was used as the base and $((C_2H_5)_4N)_2SO_4$ as the supporting electrolyte. The results are summed up in Table 2. The results clearly demonstrate that $CuL^{i\,2+}$ ($i = 6, 8$) are reduced via two single-electron consecutive processes whereas $CuL^{i\,2+}$ ($i = 5, 7, 9$) are reduced via a single two-electron process. The cyclic voltammogram of $CuL^{10\,2+}$ has the form of a very broad single wave which does not fit a two-electron process. It is suggested that in this system two consecutive single-electron processes overlap with less than 40 mV between them.

From the data in Table 2 at pHs where $CuL^{i\,2+}$ is the major species in the solution, the ratios K_2/K_1 of the stability constants of the Cu(II)/Cu(I) complexes with the L^i ($i = 6, 8, 10$) ligands can be calculated using eqs 1−3:

$$Cu^{+}_{aq} + L^{i} \rightleftharpoons CuL^{i\,+} \qquad K_1 = [CuL^{i\,+}]/[Cu^{+}_{aq}][L^{i}] \quad (1)$$

$$Cu^{2+}_{aq} + L^{i} \rightleftharpoons CuL^{i\,2+} \qquad K_2 = [CuL^{i\,2+}]/[Cu^{2+}_{aq}][L^{i}] \quad (2)$$

$$\log(K_2/K_1) = (E_{[Cu^{2+}_{aq}]/[Cu^{+}_{aq}]} - E_{[CuL^{i\,2+}]/[CuL^{i\,+}]})/0.059 \quad (3)$$

where E is the electrode potential of the $CuL^{i\,2+/+}$ couple. The results are summed up in Table 1.

The pH dependence of the electrode potentials of the $CuL^{i\,2+/+}$ couples (Table 2) is in accord with the formation constants of the different species present in solution (Table 1 and Figures 1 and 2). The data for the $CuL^{6\,2+/+}$ couple at pH < 7 are attributed to the mixture of CuL^6H^{3+} and $CuL^{6\,2+}$, whereas the data at pH > 9 are attributed to the effect of the formation of $CuL^6(OH)^+$ on the electrode potential. The results seem to indicate that the pK_a for the formation of $CuL^6(OH)_2$ is not considerably below pH 10.5, in accord with the spectroscopic results, see below. The absence of a considerable pH effect on the potential of the second process suggests that the pK_a for the formation of $CuL^6(OH)$ is also above pH 10.5. The results for $CuL^{8\,2+/+}$ show no major pH effect in the pH range studied in accord with Figure 2. The limited results available, due to solubility problems, for the $CuL^{10\,2+/+}$ couple suggest that the pK_a for formation of $CuL^{10}(OH)^+$ is similar to that for the $CuL^6(OH)^+$, *i.e.* ca. 8.

The electrochemical data point out that, for L^i ($i = 6, 8, 10$), the comproportionation process reaction 4 should occur. Indeed,

$$CuL^{i\,2+} + Cu^0 + L^i \rightarrow 2CuL^{i\,+} \quad (4)$$

when solid copper is added to deaerated solutions containing $CuSO_4$ and these ligands in the range pH 7−12, the blue color of the solution disappears within several hours. When aliquots from the latter solutions are aerated, the solutions turn blue, *i.e.* reaction 5 occurs. A measurement of the spectra of these

$$2\,CuL^{i\,+} + 0.5O_2 \rightarrow 2CuL^{i\,2+} \quad (5)$$

solutions points out that the process caused a doubling in the concentration of $CuL^{i\,2+}$. These results prove that indeed reaction 4 occurs to completion for these ligands. No comproportionation is observed in analogous solutions containing the ligands L^i ($i = 5, 7$, and 9). From these results, the maximal binding constants of these ligands to Cu(I) can be estimated, see Appendix 1. The results of these calculations are included in Table 1.

The major factor contributing to the entropy gain when the $CuL^{i\,2+}$ complexes are reduced is the change in the outer sphere solvation caused by the charge of the complex. Therefore it was decided to measure $\Delta S°$ for this process. This, $\Delta S° = \Delta S_{red} - \Delta S_{ox}$, was done according to the procedure developed by Weaver et al.,[26] *i.e.* by the temperature dependence of the electrode potentials. Optimally these values should be compared with $\Delta S°$ for the reduction of $CuL^{i\,2+}$, $i = 5, 6, 7$. However, as the latter complexes are reduced electrochemically via two-electron processes (Table 2), it was decided to measure the $\Delta S°$ for the following processes:

$$Cu(NH_3)_4^{\,2+} + e^- \rightarrow Cu(NH_3)_2^{\,+} + 2NH_3 \quad (6)$$

$$Cu^{2+}_{aq} + nCH_3CN + e^- \rightarrow Cu(CH_3CN)_n^{\,+} \quad (7)$$

The results obtained are summed up in Table 3.

In order of obtaining further insight into the source of the effect of N-methylation on the properties of their copper complexes, the UV−vis spectra were measured. The results are summed up in Table 4, and the spectra of $CuL^{5,6\,2+}$ are shown in Figures 5 and 6. These spectra are pH-dependent;

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Table 3. $\Delta S°$ for Various $Cu^{2+/+}$ Couples

solution composition	redox couple	$\Delta S°$ [J/(deg mol)]
1 mM $CuSO_4$, 2 mM L^6	$CuL^{6\,2+} + e^- \rightarrow CuL^{6\,+}$	29 ± 10
1 mM $CuSO_4$, 2 mM L^8	$CuL^{8\,2+} + e^- \rightarrow CuL^{8\,+}$	23 ± 10
1 mM $CuSO_4$, 50 mM NH_3	$Cu(NH_3)_4^{2+} + e^- \rightarrow Cu(NH_3)_2^+ + 2NH_3$	230 ± 20
1 mM $CuSO_4$, 5% CH_3CN	$Cu^{2+} + nCH_3CN + e^- \rightarrow Cu(CH_3CN)_n^+$	145 ± 15
	$Cu^{2+}_{aq} + e^- \rightarrow Cu^+_{aq}$[a]	136 ± 3

[a] Value taken from ref 27.

Table 4. UV–Vis Spectra of the Copper(II) Complexes[a]

ligand	λ_1 (nm)	ϵ_1 ($M^{-1}\,cm^{-1}$)	λ_2 (nm)	ϵ_2 ($M^{-1}\,cm^{-1}$)
5	580	210	258	6450
6	666	260	300	5800
7	526	130	224	11000
8	636	360	312	13000
9	540	180	254	12000
10	666	200	280	6000

[a] Solution composition: $[Cu^{II}] = 0.0001$ M, $[L] = 0.0002$ M, for the charge transfer bands and $[Cu^{II}] = 0.001$ M, $[L] = 0.002$ M for the d–d bands, pH 10.0. Error limits are ±2 nm and ±10% for the molar absorption coefficient.

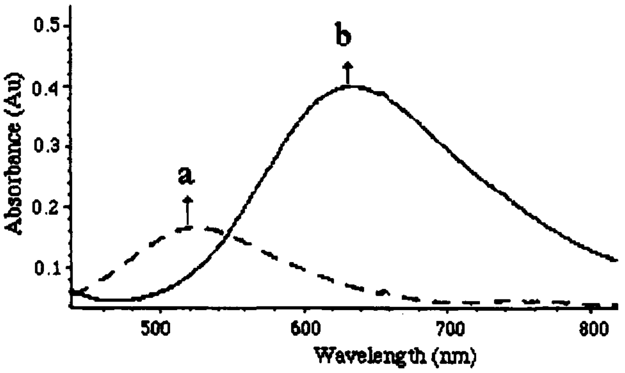

Figure 5. d–d absorption bands of the copper complexes: $[Cu^{II}] = 0.001$ M; $[L] = 0.002$ M; pH 10; (a) L^7; (b) L^8.

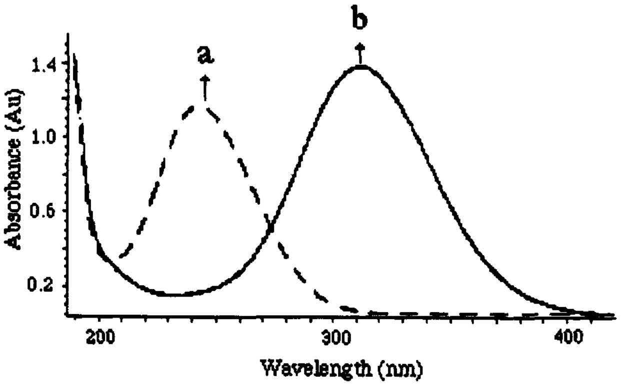

Figure 6. Charge transfer absorption band of the copper complexes: $[Cu^{II}] = 0.0001$ M; $[L] = 0.0002$ M; pH = 10; (a) L^7; (b) L^8.

thus, for example, for $CuL^{6\,2+}$, $\lambda_{max}(\epsilon_{max})$ are 636 (210), 302 (5250); 646 (190), 296 (4850); and 642 (120), 282 (4560) at pH 7, 10, and 12, respectively.

The spectrum of $CuL^{6\,+}$ was measured (Figure 7). The solution was prepared via the comproportionation process, reaction 4. The weak shoulder around 280 nm is attributed to a very low impurity of $CuL^{6\,2+}$ present in the solution. This was verified by letting some dioxygen to diffuse into the sample which increased the absorption in this region considerably while decreasing the bands at 210 and 228 nm which are attributed to $CuL^{6\,+}$.

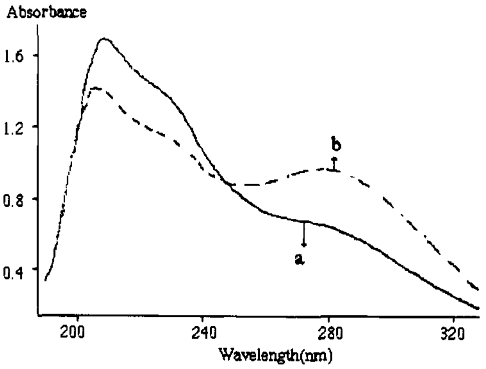

Figure 7. Spectrum of CuL^{6+}: (a) solution composition of 0.000 17 M Cu^I and 0.0004 M L^6, pH 10.0. (b) same as (a) but after the solution was exposed to a small amount of dioxygen.

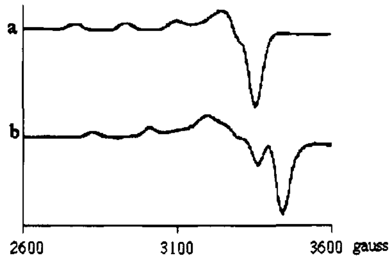

Figure 8. ESR spectra of the copper complexes: $[Cu^{II}] = 0.004$ M; 30% ethanol; pH = 10; temp = 116 K; (a) $[L^6] = 0.005$ M; (b) $[L^5] = 0.005$ M.

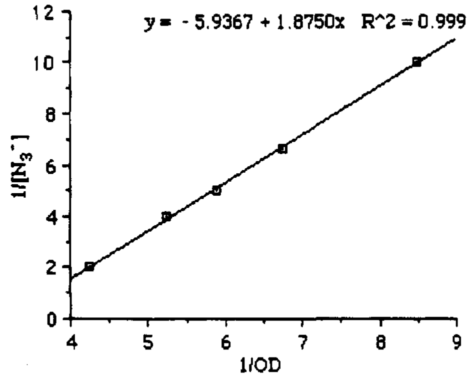

Figure 9. Dependence of the absorption due to $L^8CuN_3^+$ on $[N_3^-]$: $[Cu^{II}] = 0.0002$ M; $[L] = 0.0004$ M; pH = 8.0; I = 0.5 M. From the intercept, $K(Cu^{II}L{-}N_3^-) = 6\ M^{-1}$ is calculated.

The effect of N-methylation of the ligands on the electrode potentials and the d–d absorption bands of the copper complexes could in principle be attributed to a tetrahedral distortion of the ligation sphere due to steric hindrance. In order to check whether indeed such a distortion occurs in the solutions, the ESR spectra of the complexes were measured as it is known that a tetrahedral distortion causes a considerable decrease in the value of the A_{II} to $A_{II} < 0.01\ cm^{-1}$.[28] Typical ESR spectra are shown in Figure 8, and the results are summed up in Table 5.

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[28] Sigel, H. *Metal ions in biological systems*; New York and Basel, 1981; p 33.

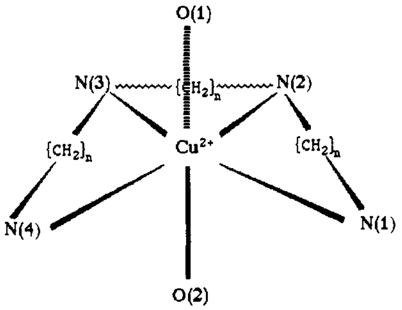

Figure 10. Schematic drawing of the $L^iCu(H_2O)_2^{2+}$ complexes. The numbering of the atoms is as used in Table 7.

Table 5. ESR Spectra of the Copper Complexes[a]

ligand	$A_{\parallel}$ (10^4 cm^{-1})	$g_{\parallel}$	$g_{\perp}$
5	192	2.21	2.07
6	173	2.25	2.06
7	204	2.21	2.07
8	168	2.26	2.06

[a] $[Cu^{II}] = 0.0001$ M, $[L] = 0.0002$ M, pH 10.0, 30% ethanol, 116 K.

Table 6. Axial Binding of Monodentate Anions to $CuL^{i\,2+}$ [a]

axial ligand	I^-	Br^-	F^-	N_3^-	OH^-
$K(Cu^{II}L^5-A^-)$	1.7	1.0	0.4	0.7	1580
$K(Cu^{II}L^6-A^-)$	<2	17	38	570	2.7×10^6

[a] Measured at pH 6.5, $I = 0.5$ M, accuracy ±15%.

The results in Table 1 indicate that the binding constants of OH^- to $CuL^{6\,2+}$ and $CuL^{8\,2+}$ are considerably higher than those to $CuL^{5\,2+}$ and $CuL^{7\,2+}$. It seemed of interest to check whether this is correct also for other axial ligands. The binding constants of F^-, Br^-, I^-, and N_3^- to $CuL^{5\,2+}$ and $CuL^{6\,2+}$ were measured spectrophotometrically using the relations derived in Appendixes 2 and 3. The measurements were carried out at pH 6.5, where $CuL^{6\,2+}$ is the major species present (Figure 1). As some L^6CuOH^+ is also present, the azide experiments (Appendix 2) were carried out at several pHs and the results were corrected for the formation of L^6CuOH^+. The results obtained are summed up in Table 6. It could be argued that the added ligand is bound equatorially as the tertiary-tetraamine ligand acts due to steric reasons only as a tridentate ligand or that the anion replaces one of the amine groups. However, the ESR results (Table 5) at pH 10.0, where the complex CuL^6OH^+ is the major species present (Table 1), clearly prove that L^6 is a symmetrical tetradentate ligand, *i.e.* the OH^- is axially bound. Furthermore, the complex of Cu(I) with 2,5,8-trimethyl-2,5,8-triazanonane is not stable in aqueous solutions and decomposes via disproportionation,[29] an observation that proves that the ligands studied are tetradentate also in the Cu(I) complexes.

An effort to measure the binding constants of axial ligands to $CuL^{7\,2+}$ and $CuL^{8\,2+}$ was made. The results point out that there is a dramatic decrease in the binding constants in comparison with those of $CuL^{5\,2+}$ and $CuL^{6\,2+}$. The binding constants of N_3^- and OH^- to $CuL^{8\,2+}$ are 6 and 1600, respectively; all the other binding constants for $CuL^{7\,2+}$ and $CuL^{8\,2+}$ are too low to be measured by this technique.

MO calculations of the optimal geometry of the $CuL^{i\,2+/+}$ complexes were carried out using the ZINDO program.[23] The results are summed up in Tables 7 and 8. It should be stressed that these calculations were carried out for hexacoordinated complexes (two axial water ligands) in the gas phase.

Table 7. Computer Simulation of the $CuL^{i\,2+}$ Geometry[a]

bond or angle	L^5	L^6	L^7	L^8	L^9	L^{10}
N(1)—Cu(II)	2.00	2.02	2.01	2.03	1.99	2.02
N(2)—Cu(II)	1.99	2.00	1.98	2.03	1.99	2.01
N(3)—Cu(II)	1.98	2.03	2.00	2.03	1.99	2.05
N(4)—Cu(II)	2.00	2.03	2.00	2.01	2.01	2.05
N—Cu(II) average	1.99	2.02	2.00	2.03	1.99	2.04
O(1)—Cu(II)	2.08	2.09	2.08	2.09	2.08	2.07
O(2)—Cu(II)	2.08	2.07	2.07	2.08	2.09	2.09
O—Cu(II) average	2.08	2.08	2.08	2.08	2.08	2.08
N(1)—Cu(II)—N(2)	88	85	87	85	89	89
N(2)—Cu(II)—N(3)	85	84	94	93	88	84
N(3)—Cu(II)—N(4)	87	86	86	85	94	91
N(1)—Cu(II)—N(4)	101	105	93	97	91	95
N(1)—N(2)—N(3)—N(4)[b]	16	11	10	7	13	1

[a] The numbering system is according to that shown in Figure 10. [b] The tetrahedral angle.

Table 8. Total Energies of the Copper Complexes as Calculated by ZINDO

ligand	E_{total} of Cu(I)L[a] (au)[b]	E_{total} of Cu(II)L (au)	ΔE_{total} (kJ/mol)
5	−183.006 327	−182.727 528	−732.6
6	−230.448 482	−230.171 374	−727.6
7	−190.920 371	−190.644 305	−724.8
8	−238.338 452	−238.084 036	−668.0
9	−198.824 944	−198.559 617	−696.6
10	−246.222 743	−245.958 095	−695.0

[a] The total energy reported by ZINDO is the amount of energy required to separate the molecule into isolated nuclei and electrons at 0 K. ZINDO uses d orbitals, in contrast to MOPAC, which uses only s and p orbitals and MM2 that does not use orbitals at all. [b] 1 au = 2625.50 kJ/mol.

Discussion

The results (Figures 3 and 4 and Table 2) clearly demonstrate that indeed the methylated ligands L^6, L^8, and L^{10} thermodynamically stabilize copper(I) in aqueous solutions. The common notion is that polydentate-saturated-amine ligands catalyze the disproportionation of monovalent copper ions in aqueous solutions.[30] Thus the results obtained clearly demonstrate that tertiary-polyamine ligands have properties considerably different from those of the corresponding primary- and secondary-polyamine ligands. This conclusion is in accord with the commonly accepted observation that tertiary amines are poorer σ donors than the corresponding primary and secondary amines and, therefore, also poorer ligands. In the following paragraphs the sources of this property of tertiary amines, at least for their complexes with copper ions, are discussed.

Analysis of the data in Table 1 clearly indicates that N-methylation of the ligands caused a tremendous destabilization of the corresponding divalent complexes, $CuL^{i\,2+}$. The binding constants of the non-methylated ligands to Cu(I) cannot be measured, and therefore, only upper limits for them are given in the table. However, it is evident that $K_2(L^5)/K_2(L^6) \gg K_1(L^5)/K_1(L^6)$; $K_2(L^7)/K_2(L^8) \gg K_1(L^7)/K_1(L^8)$; and $K_2(L^9)/K_2(L^{10}) \gg K_1(L^9)/K_1(L^{10})$. The results do not rule out the possibility that the ratio $K_1(L^5)/K_1(L^6)$ and probably also the ratios $K_1(L^7)/K_1(L^8)$ and $K_1(L^9)/K^1(L^{10})$ are smaller than 1. Furthermore the data point out that $K_1(L^8) \sim K_2(L^8)$, in accord with a previous report that $K_1(L^4) \gg K_2(L^4)$ and analogous observations for complexes with other transition metal ions.[14] The latter observation is surprising for ligands which are pure σ donors, as for such ligands $K_2 > K_1$ is expected to be the rule. The observations clearly cannot be attributed only to electronic factors. The large effect of the N-methylation on K_2/K_1 is the

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(29) Kimura, E.; Koike, T.; Kodama, M.; Meyerstein, D. *Inorg. Chem.* **1989**, *28*, 2998.

(30) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 801.

source for the observed thermodynamic stabilization of the monovalent copper complexes, CuL^{i+}. The decrease in the value of K_2/K_1 is mainly due to the effect of N-methylation on K_2.

The red shift induced by the N-methylation of the ligands, of the L → M charge transfer bands (Table 4), can be attributed to one of the following effects:

(1) N-methylation increases the electron density on the nitrogen donor atoms, thus making them better σ donors and decreasing their optical electronegativity.

(2) N-methylation lowers the electrode potential of the central copper ions, in accord with the electrochemical observations.

In principle, the energy of the transition depends also on the solvation of the excited state. However, as both the ground state and the excited state have the same charge though the exited state has a different charge distribution, it is reasonable to assume that both states have approximately the same solvation energy. The observation that N-methylation of the ligands causes also a red shift of the d−d bands (Table 4) clearly points out that the N-methylated ligands are poorer σ donors than the unmethylated ligands, in accord with many reports in the literature.[3a,d,e,6b] Therefore the observed shift of the charge transfer band cannot be attributed, even partially, to an increase in the electron-donating properties of the nitrogen atoms and has to be attributed to the effect of N-methylation on the redox potential.

The effect of N-methylation on the electrode potentials of the copper complexes and on their spectra points out that the tertiary amines are poorer σ donor ligands than secondary amines. This observation is attributed to the effect of the M−N−H••O hydrogen bonds on the σ-donating properties of primary and secondary amines. An alternative explanation for the poor σ-donating properties of the N-methylated ligands could be steric hindrance: the steric hindrance causes an elongation of the M−N bond in the complexes and thus weakens them.[3a] This effect clearly does not explain all the observations, *e.g.* the observation that β_2 for the complexation of Ag^+ by trimethylamine is considerably smaller than that for ammonia and methylamine.[31]

Alternatively the red shift of the d−d bands could be due to a tetrahedral distortion of the coordination sphere of the copper caused by the steric strain induced by the N-methylation. Such a distortion of the coordination sphere would also explain the effect of N-methylation on the electrode potential of the copper complexes. However, the ESR spectra of the complexes (Table 5) indicate that N-methylation has only a minor effect on $A_{\rm II}$. These results suggest that the Cu−N bonds are somewhat elongated by N-methylation, either due to the lowering of the σ-donating properties of the nitrogens or due to steric hindrance, and rule out a considerable tetrahedral distortion of the complex which would reduce the value of $A_{\rm II}$ to <0.01 cm^{-1}. In order to confirm these conclusions, the d−d adsorption transitions and ESR g values were simulated using the angular overlap model;[32] e_σ values were chosen for a trans N_4O_2 coordination geometry to fit the absorption spectra of the unmethylated complexes. The D_q values for the primary and secondary amines are about 15 000−16 000 cm^{-1} for oxygen and 9000 and 14 000 cm^{-1} for tertiary amines. Our calculations point out that the variations in energy of the d−d transitions as well as those of the g values observed upon methylation are better reproduced in terms of a reduction of the e_σ values of the equatorial nitrogens rather than in terms of a tetrahedral distortion of the coordination polyhedron of the metal. These results are in agreement with the idea that methylation causes weakening of the nitrogen−copper bonds. Also the MO calculations of the geometries of the complexes (Table 7) suggest that N-methylation of the ligands causes no tetrahedral distortion, as expressed by the N(1)−N(2)−N(3)−N(4) tetrahedral angle. This simulation suggests that the Cu−N bonds are somewhat elongated (Table 7) due to the steric hindrance caused by the N-methylation.

The optimal geometry of the complexes obtained from the MO calculations suggests that the only significant effect of the N-methylation on the geometry of the complexes is a slight lengthening of the Cu−N bonds due to steric hindrance. It is of interest to note that for L^5 and L^6 all the chelating rings C−N−M−N−C are five-membered ones; this enforces N−M−N angles smaller than 90°. Elongation of the N−M bond by N-methylation further decreases these N−M−N angles. On the other hand a tetrahedral conformation requires N−M−N angles of ~109.5°. The calculations suggest that the N−M−N angle of the unmethylated complexes has an average value of 90°; therefore, the observation that N-methylation does not induce considerable tetrahedral distortions is not surprising.

It should be pointed out that the MO calculations in the gas phase include all the molecular parameters, *i.e.* bond lengths, bond angles, steric hindrance including Van der Waals repulsions, bond torsions, etc. The only parameters not considered in the MO calculations are the interactions with the solvent, *i.e.* hydrogen bonds and outer sphere solvation. The MO calculations (Table 8) suggest that in the gas phase the difference in energy between the mono- and the divalent complexes is larger for the non-methylated ligands. The calculated effect of N-methylation is not large, but it suggests that in the gas phase the reduction of the complexes with the methylated ligands is more endoergic than that with the unmethylated ligands. In other words, in the gas phase, copper(I) is thermodynamically better stabilized by the non-methylated ligands in contrast to the experimental results in aqueous solutions. The MO calculations thus suggest that in the gas phase the tertiary-amine ligands are better σ donors than the corresponding primary and secondary amine ligands, in accord with recent MO calculations using a different theoretical approach.[33] The difference in the effect of N-methylation on the σ-donating properties of the nitrogen atoms in the gas phase and in aqueous solutions is attributed to the role of the hydrogen bonds, of the type Cu−N−H••O, in the latter phase. These hydrogen bonds which clearly contribute energetically more in the divalent complexes increase the electron density on the nitrogen atoms, thus making them better σ donors. It is suggested that the lack of such hydrogen bonds in the complexes of the tertiary-amine ligands is the reason for the lower ligand field splittings caused by these ligands. In less polar solvents the interaction of the complex with the counterions results in a similar effect. These arguments are analogous to those commonly accepted as an explanation to the fact that the pK_a of $HN(CH_3)_3^+$ is lower than that of $H_2N(CH_3)_2^+$ in aqueous solutions, whereas the reverse order is observed in the gas phase.[24]

The lack of the Cu−N−H••O hydrogen bonds in the complexes of the N-methylated ligands means that the charge density on the central copper ion will be larger in these complexes. Indeed the results (Tables 1 and 6) point out that the copper in these complexes is a considerably stronger acid than in the corresponding non-methylated ones. This finding is in accord with reports in the literature for a variety of

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(31) Sillen, L. G.; Martell, A. E. *Stability Constants of Metal Ion Complexes*; Special Publication No. 17; The Chemical Society: London, 1964; pp 358, 392.

(32) (a) Schaffer, C. E. *Struct. Bonding (Berlin)* **1973**, *14*, 69. (b) Bencini, A.; Benelli, C.; Gatteschi, D. *Coord. Chem. Rev.* **1984**, *60*, 131.

(33) Bernhardt, P. V.; Comba, P. *Inorg. Chem.* **1993**, *32*, 2798.

transition metal complexes with methylated and non-methylated polyamine ligands.[14,18,34] It is of interest to note (Table 6) that whereas the stability constants for axial binding to $CuL^{5\ 2+}$ are $I^- > Br^- > F^- \sim N_3^-$ they are for $CuL^{6\ 2+}$ $N_3^- \gg F^- > Br^- > I^-$, *i.e.* the central copper ion is a soft acid in $CuL^{5\ 2+}$ and a hard acid in $CuL^{6\ 2+}$. This finding corroborates the explanation given above. At this stage we have no explanation for the difference in the acidities of the copper in $CuL^{5,6\ 2+}$ compared to $CuL^{7,8\ 2+}$.

A second factor which has to be considered when calculations in the gas phase are compared with the experimental data is the outer sphere solvation energy of the complexes. For complexation reactions of the type

$$M(H_2O)_6{}^{n+}{}_{aq} + L \rightleftharpoons ML(H_2O)_2{}^{n+}{}_{aq} + 4H_2O$$

(where L is a tetradentate ligand) the equilibrium constant depends, on top of the electronic and entropic factors, on the outer sphere solvation energies of $M(H_2O)_6{}^{n+}{}_{aq}$, $ML(H_2O)_2{}^{n+}{}_{aq}$, and L. The outer sphere free energy of solvation, ΔG_s, of the charged complexes can be calculated at first approximation using the Born equation, $\Delta G_s = -686Z^2/R_{eff}$ kJ/mol at 298 K, where Z and R_{eff} are the charge and effective radius of the complex and 686 is constant for aqueous solutions. From our MO calculations we estimate that $R = 3.3$ and 3.8 Å for $CuL^{5\ 2+}$ and $CuL^{6\ 2+}$, respectively; these radii were used as R_{eff}. Using the Born equation and these radii, the decreases in the solvation energy upon N-methylation are 100 and 25 kJ/mol for the copper(II) and copper(I) complexes, respectively (note that 75 kJ/mol would shift the redox potential by 0.7 V). Though the Born equation gives only a rough estimate of solvation energies, this calculation clearly points out that the thermodynamic stabilization of low-valent cations via N-methylation is at least in part due to the effect of N-methylation of the ligands on the outer sphere solvation energy of the complexes. The effect of methylation on the solvation energies calculated by the Born equation could be the major source for the decreased stability constants of the Cu(II)-methylated complexes as compared with the unmethylated ones. The calculated effect of N-methylation on the solvation energies is larger than the observed shift in the redox potential. This is clearly due to a variety of factors contributing to the thermochemical cycles (Figure 11). The entropy change $\Delta S°$, upon reduction of a positively charged complex, includes a large contribution due to the decreased solvation of the reduced complex. Thus, if indeed the N-methylated copper(II) complexes are considerably less solvated than the non−methylated ones, a relatively small $\Delta S°$ for the reduction of the N-methylated complexes is expected. The results in Table 3 corroborate these expections. The considerably larger $\Delta S°$ for the reduction of $Cu(NH_3)_4{}^{2+}$ than that of $Cu^{2+}{}_{aq}$ is due to the release of two NH_3 molecules upon reduction. The reduction of $Cu^{2+}{}_{aq}$ in the presence of CH_3CN is expected to involve very small $\Delta S°$ due to the binding of CH_3CN molecules of Cu(I) to form a mixture of $Cu(CH_3CN)_n{}^+$ ($n = 2, 3$).[35] However, the binding of CH_3CN increases the radius of the complexes, and therefore, its solvation is considerably smaller than that of $Cu^+{}_{aq}$. The two effects seem to cancel each other. The reductions of $CuL^6(H_2O)_2{}^{2+}$ and $CuL^8(H_2O)_2{}^{2+}$ have considerably smaller ΔS^0 than that of $Cu^{2+}{}_{aq}$. As the inner coordination spheres of these complexes are not significantly changed during the redox process; the small $\Delta S°$ values reflect mainly the small shanges in the outer sphere solvation upon reduction. Thus the results corroborate qualitatively the calculations using the Born equation.

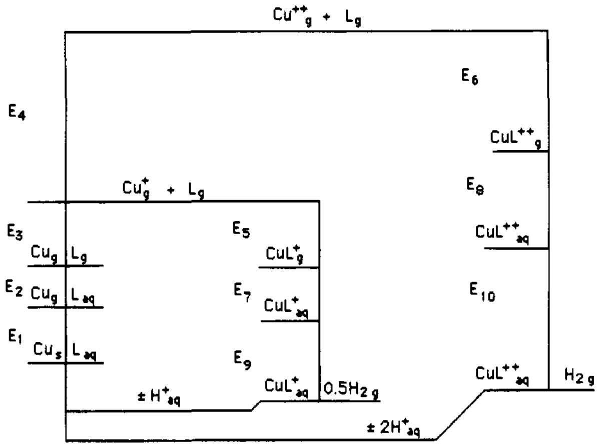

Figure 11. Thermochemical cycles of the redox reactions. (a) E_1, the evaporation energy of the copper; E_3 and E_4, the first and second ionization energies of copper; E_9 (429 kJ/mol) and E_{10} (858 kJ/mol), the energies required to the adaptation for NHE scale. All these energies are independent of the N-methylation of the ligands. (b) E_2, the solvation and evaporation energies of the ligands. N-methylation affects these properties as follows: (1) The MWs of the methylated ligands are larger by 84 g/mol (~50%) than those of the non-methylated ligands. This should increase $\Delta H^0{}_{evap}$; however, the decrease in hydrogen bonding has an opposing effect (compare the boiling temperatures of $NH(CH_3)_2$ and $N(CH_3)_3$); (2) The solvation energies of the non-methylated ligands are larger than those of the methylated ligands due to hydrogen bonding to the aqueous solvent. (c) E_5 and E_6, the complexation energies of the Cu(I) and Cu(II) complexes. These energies are clearly larger for the methylated complexes due to the σ-donating properties of the methyl groups. The complexation energies of the Cu(II), E_6, are clearly larger than those of Cu(I), E_5. (d) E_7 and E_8, the solvation energies of the complexes, larger for the non-methylated complexes as calculated from the Born equation (see text) and due to hydrogen bonding in the former (see text).

Concluding Remarks

The results presented are all in accord with the following conclusions:

(1) Tertiary-tetraazaalkane ligands thermodynamically stabilize monovalent copper ions in aqueous solutions.

(2) The thermodynamic stabilization of the $CuL^{i\ +}$ complexes is mainly due to the considerably lower binding constants of the N-methylated ligands to copper(II). There is also some decrease in the binding constants of the N-methylated ligands to copper(I), but this is minor in comparison with the effect observed for the Cu(II) complexes.

(3) The major factors causing this destabilization of the copper(II) complexes are the following:

(a) The absence of Cu−N−H···O hydrogen bonds to the solvent for the N-methylated complexes.

(b) The lowering of the outer sphere solvation energy of the complexes by N-methylation.

(c) The strain induced by the N-methylation on the ligand skeleton when all the nitrogens are bound to the central copper (this strain is naturally smaller for the Cu(I) complexes than for the Cu(II) complexes).

It is reasonable to propose that these conclusions are of general nature and can be used to explain the following observations:

(1) Tertiary amine ligands are poor σ donor ligands.[3a,d,e,6b,10,14,17]

(2) N-alkylation of ligands thermodynamically stabilizes low-valent transition metal complexes.[3−9,14,17]

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[34] Webb, R. L.; Mino, M. L.; Blinn, E. L.; Pinkerton, A. A. *Inorg. Chem.* **1993**, *32*, 1396.

[35] Zuberbuhler, A. *Helv. Chim. Acta* **1970**, *53*, 473.

(3) N-alkylation of ligands increases their binding constants to large cations while it decreases the binding constants to small cations.[13]

Note Added in Proof: In principle, the subject matter discussed herein is analogous to the problem of "the puzzle of association in aqueous solution" of ligands binding of uncharged molecules.[36] It was recently shown that three factors affect this binding, *i.e.* solute–solute and solute–solvent interactions and solvent reorganization. Clearly for charged species the role of solute–solvent interaction is of major importance.

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Appendix 1

The stability constants K_1 for L^5, L^7, and L^9 can be estimated using the following relations:

$$Cu^+_{aq} + L^i \rightleftharpoons CuL^{i\,+} \qquad K_1 = [CuL^{i\,+}]/[Cu^+_{aq}][L^i]$$

$$Cu^{2+}_{aq} + L^i \rightleftharpoons CuL^{i\,2+} \qquad K_2 = [CuL^{i\,2+}]/[Cu^{2+}_{aq}][L^i]$$

$$Cu^{2+}_{aq} + Cu^0 \rightleftharpoons 2Cu^+ \qquad 10^{-6} = [Cu^+_{aq}]^2/[Cu^{2+}_{aq}] \quad \text{(ref 10)}$$

$$CuL^{i\,2+} + Cu^0 + L^i \rightleftharpoons 2CuL^{i\,+} \qquad K_3 = [CuL^{i\,+}]^2/[CuL^{i\,2+}][L^i]$$

$$K_3 = (K_1[Cu^+_{aq}])^2/K_2[Cu^{2+}_{aq}]$$

$$K_3 = 10^{-6}(K_1)^2/K_2$$

As no comproportionation is observed in the solutions containing L^5, L^7, and L^9, Cu^{2+}_{aq} and Cu^0 at range pH 7–11, clearly $K_3 < 10^{-2}$; therefore

$$10^{-6}(K_1)^2/K_2 < 10^{-2}$$

$$K_1 < 10^2(K_2)^{0.5}$$

$\log K_1 < 12$, < 14, and < 13 for L^5, L^7, and L^9, respectively

Estimation of these constants was also made by giving an upper limit to the Cu(II)/Cu(I) electrode potential of the nonmethylated complexes and using eq 3; the results of this calculation are very similar to the one made above.

Appendix 2

The binding constants of azide to $CuL^{i\,2+}$ were measured by following the dependence of the absorption at 370 nm on $[N_3^-]$ using the following equations:

$$CuL^{i\,2+} + N_3^- \rightleftharpoons CuL^iN_3^+$$

$$K_4 = [CuL^iN_3^+]/[CuL^{i\,2+}][N_3^-]$$

$$K_4/[CuL^iN_3^+] = 1/([CuL^{i\,2+}]_T - [CuL^iN_3^+])[N_3^-]$$

$$[CuL^iN_3^+] = OD/\epsilon l$$

$$1/[N_3^-] = K_4\epsilon l[CuL^{i\,2+}]_T/OD - K_4$$

where $[CuL^{i\,2+}]_T$ is the total concentration of copper, OD the optical density measured, ϵ the molar absorption coefficient of $CuL^iN_3^+$, and l is the optical path.

As the concentration of N_3^- was always considerably larger than that of $CuL^{i\,2+}$, the changes in $[N_3^-]$ due to complexation were negligible. Thus a plot of $1/[N_3^-]$ vs 1/OD gives a straight line with an intercept of $-K_4$; see for example Figure 9.

Appendix 3

The binding constants of halides to $CuL^{i\,2+}$ were measured by competition with azide following the absorption of the $CuL^iN_3^+$ complexes. The following equations have to be taken into account:

$$CuL^{i\,2+} + A^- \rightleftharpoons L^iCuA^+$$

$$K_4 = [CuL^iN_3^+]/[CuL^{i\,2+}][N_3^-]$$

$$K_5 = [L^iCuA^+]/[CuL^{i\,2+}][A^-]$$

$$[L^iCuA^+]/K_5[A^-] = [CuL^iN_3^+]/K_4[N_3^-]$$

$$[L^iCuA^+] = [CuL^{i\,2+}]_T - [CuL^{i\,2+}] - [CuL^iN_3^+]$$

$$[A^-]/[[N_3^-] = K_4\{[CuL^{i\,2+}]_T - [CuL^{i\,2+}] - [CuL^iN_3^+])/K_5[CuL^iN_3^+]\}$$

$$[CuL^iN_3^+] = OD/\epsilon l$$

$$[A^-]/[N_3^-] = -K_4/K_5 + K_4\{[CuL^{i\,2+}]_T - [CuL^{i\,2+}]\}\epsilon l/K_5OD$$

As $[CuL^{i\,2+}]$ is negligible within the experimental conditions

$$[A^-]/[N_3^-] = -K_4/K_5 + K_4\epsilon[CuL^{i\,2+}]_T/K_5OD$$

A plot of $[A^-]/[N_3^-]$ vs 1/OD gives a straight line with an intercept of $-K_4/K_5$.

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