Design of Ligands That Stabilize Cu(I) and Shift the Reduction Potential of the $Cu^{II/I}$ Couple Cathodically in Aqueous Solutions

Nadav Navon,[†] Gilad Golub,[†] Haim Cohen,[†,‡] Piero Paoletti,[§] Barbara Valtancoli,[§] Andrea Bencini,[§] and Dan Meyerstein*[†,||]

The Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel, Nuclear Research Centre Negev, Beer-Sheva, Israel, The College of Judea and Samaria, Ariel, Israel, and Chemistry Department, University of Florence, Florence, Italy

Received October 13, 1998

The ligands $R_2NCH_2CH_2N(R)CH_2CH_2N(R)CH_2CH{=}CH_2$, where R = H, CH_3, were synthesized. The stability constants of their complexes with Cu(II) and Cu(I) in aqueous solutions were determined. Both ligands stabilize Cu(I) in aqueous solutions, though the reduction potentials of both $(CuL^i)^{2+/+}$ couples are shifted cathodically in comparison to the $Cu^{2+/+}{}_{aq}$ couple. These properties indicate that these complexes should be good catalysts for a variety of processes that are catalyzed by Cu(I).

Introduction

The redox properties of copper complexes explain their role as catalysts of a large variety of processes. Thus in biological systems copper enzymes are involved in dioxygen transport, in monooxygenases, in dioxygenases, in oxidases, and in electron transfer processes.[1−3] Also a large variety of organic reactions, e.g., the Ullmann reaction,[4] the Sandmeyer reaction,[5] the Meerwein reaction,[6] and the addition of polyhalides to alkenes,[7] are catalyzed by Cu^0/Cu(II) and/or by Cu(I) salts. Many of these reactions are initiated by a redox process, i.e., the copper(I) redox properties are crucial to these processes. However, due to the low solubility of Cu(I) salts, e.g., CuCl, CuBr, and CuOH, and due to the disproportionation reaction of $Cu^+{}_{aq}$,

$$2Cu^+{}_{aq} \rightleftharpoons Cu^{2+}{}_{aq} + Cu^0 \qquad K_{disp} = 10^6\ M^{-1} \text{ [8]} \tag{1}$$

the concentration of Cu(I) in these solutions is very small and usually unknown. It is possible to increase the concentration of Cu(I) species in the solutions by adding ligands that stabilize it, e.g., alkenes,[9] CH_3CN,[10] and NH_3.[11] In principle adding such ligands to a catalytic system containing Cu^0/Cu(II) is expected to increase the rate of the catalytic process due to the increase in the concentration of the Cu(I)-containing species in the system. However, these ligands clearly affect also the reactivity of the Cu(I), i.e., the Cu(I) becomes a poorer reducing agent the higher the concentration of the stabilizing ligand.

However, in principle, ligands can be designed which will shift equilibrium 1 to the left while shifting the redox potential of the $Cu^{II}L_n/Cu^{I}L_m$ cathodically. This stems from

$$2Cu^IL_n \rightleftharpoons Cu^{II}L_m + Cu^0 + (2n - m)L \tag{1'}$$

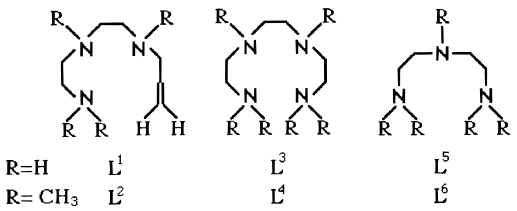
$$K_{disp'} = \frac{[Cu^{II}L_m][L]^{2n-m}}{[Cu^IL_n]^2} = \frac{K^{II}[Cu^{2+}{}_{aq}][L]^m[L]^{2n-m}}{(K^I[Cu^+{}_{aq}][L]^n)^2} = \frac{K^{II}}{(K^I)^2}\frac{[Cu^{2+}{}_{aq}]}{[Cu^+{}_{aq}]^2} = 10^6\frac{K^{II}}{(K^I)^2}$$

where

$$K^{II} = \frac{[Cu^{II}L_m]}{[Cu^{2+}{}_{aq}][L]^m} \quad \text{and} \quad K^I = \frac{[Cu^IL_n]}{[Cu^+{}_{aq}][L]^n}$$

i.e., equilibrium 1′ will be shifted to the left if $(K^I)^2 > K^{II}$ whereas the redox potential of the $Cu^{II}L_m/Cu^IL_n$ couple is shifted cathodically if $K^{II} > K^I$. Thus, the addition of ligands for which both of these criteria are fulfilled to a mixture of $Cu^{2+}{}_{aq}$ and Cu^0 should improve the catalytic properties of the mixture.

Copper(I) is known to form relatively stable d−π^* complexes with alkenes in aqueous solutions.[9] Therefore it was decided to synthesize the ligands L^1 and L^2 and to study the properties of their Cu(I) and Cu(II) complexes.



The choice of these ligands was based on the following assumptions:

1. Tridentate and tetradentate ligands are expected to form stable Cu(II) and Cu(I) complexes without too large steric constraints toward approaching substrates.

[†] Ben-Gurion University of the Negev.

[‡] Nuclear Research Centre Negev.

[§] University of Florence.

[||] The College of Judea and Samaria.

(1) Karlin, K. D.; Lee, D. H.; Obias, H. V. *Pure Appl. Chem.* **1998**, *70*, 855.
(2) Karlin, K. D.; Kaderli, S.; Zuberbuhler, A. D. *Acc. Chem. Res.* **1997**, *30*, 139.
(3) Tolman, W. B. *Acc. Chem. Res.* **1997**, *30*, 227.
(4) (a) Weingarten, H. *J. Org. Chem.* **1964**, *29*, 3624. (b) Schwartz, M. A.; Crowell, J. D.; Musser, J. H. *J. Am. Chem. Soc.* **1972**, *94*, 4363.
(5) (a) Kochi, J. K. *J. Am. Chem. Soc.* **1955**, *77*, 5090. (b) Kochi, J. K. *J. Am. Chem. Soc.* **1956**, *78*, 1228.
(6) Rondestvedt, C. S., Jr. *Org. React.* **1976**, *24*, 225.
(7) Bellus, D. *Pure Appl. Chem.* **1985**, *57*, 1827.
(8) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980.

10.1021/ic9812048 CCC: $18.00

Table 1. Basicity of the Ligands and Stability Constants of Their Copper Complexes in Aqueous Solutions

	log *K*					
reaction	L^1	L^2	$L^{3\,a}$	$L^{4\,a}$	$L^{5\,a}$	$L^{6\,a}$
$L + H^+ \rightleftharpoons LH^+$	9.73	9.06	9.74	9.23	9.84	9.22
$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	8.87	8.09	9.07	8.47	9.02	8.41
$LH_2^{2+} + H^+ \rightleftharpoons LH_3^{3+}$	4.11	2.13	6.56	5.36	4.23	2.09
$LH_3^{3+} + H^+ \rightleftharpoons LH_4^{4+}$			3.25	1.68		
$L + Cu^{2+} \rightleftharpoons CuL^{2+}$	15.16	11.45	20.1	12.60	15.9	12.16
$L + Cu^+ \rightleftharpoons CuL^+$	11.94[b]	10.52[b]	<12	11.0	<10	<8
$CuL^{2+} + L \rightleftharpoons CuL_2^{2+}$	2.13				4.6	
$CuL^{2+} + H^+ \rightleftharpoons CuLH^{3+}$			3.6	6.16		
$CuL^{2+} + OH^- \rightleftharpoons CuLOH^+$	4.54	4.74	3.3	6.43	4.83	5.14

[a] The data of copper(II)/L^i ($i = 3-6$) were taken from the literature.[13] [b] The values for L^1 and L^2 were calculated from the electrochemical data.

2. The complex $(CuL^6)^+$ is stabilized in aqueous solutions in the presence of π-acid ligands, e.g., CH_3CN and CO.[12]

3. The $-CH_2CH{=}CH_2$ group is not expected to decrease significantly the stability constant of the Cu(II) complexes whereas it is expected to stablilize considerably the Cu(I) complexes.

4. N-Alkylation stabilizes Cu(I) complexes relative to the nonmethylated ligands.[13]

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. L^1 was prepared by adding dropwise 0.58 mol of allyl bromide, in 200 mL of ethanol, into 1.75 mol of L^5, in 500 mL of ethanol. The temperature was kept below 15 °C. KOH was added to neutralize the HBr formed. The salt and the excess base were filtered, the solvent was evaporated, and the mixture was distilled in a vacuum, 1.1 mmHg; the product was collected at 87 °C. The product was crystallized as its HCl salt and identified by C,H,N analysis. Anal. for the ratio C:N in $C_7H_{20}N_3Cl_3$ calculated (found) 2.00 (2.01). The product was identified also by ^1H NMR and ^{13}C NMR measurements. ^{13}C NMR (D_2O): ($CH_2{-}\underline{C}H{=}CH_2$) δ 128.31, ($CH_2{-}CH{=}\underline{C}H_2$) 126.15, ($N{-}\underline{C}H_2{-}CH{=}CH_2$) 51.58, 4($N{-}CH_2{-}$) 46.27, 45.10, 43.89, 37.13. The ligand L^2 was prepared by *N*-methylation of the unmethylated ligand L^1, using formaldehyde and formic acid according to a procedure described in the literature.[14] The product was crystallized as its HCl salt and identified by C,H,N analysis. Anal. for the ratio C:N in $C_{11}H_{28}N_3Cl_3$ calculated (found) 3.14 (3.21). The product was identified also by ^1H NMR and ^{13}C NMR measurements. ^{13}C NMR (D_2O): ($CH_2{-}\underline{C}H{=}CH_2$) δ 127.52, ($CH_2{-}CH{=}\underline{C}H_2$) 124.98, ($N{-}\underline{C}H_2{-}CH{=}CH_2$) 58.96, 2(N−Me) 40.03, 39.70, ($N{-}Me_2$) 43.23, 4($N{-}CH_2{-}$) 49.73, 50.97, 51.08, 52.05.

Electrochemical measurements were carried out using an EG&G potentiostat/galvanostat model 263. The working electrode was EG&G parc model 303A SMDE. The reference electrode was Ag/AgCl in a KCl/AgCl solution separated by a frit from the bulk solution. The electrode potential is 0.222 V vs NHE (this was checked against the $Cu_{aq}^{II/0}$ couple as in ref 9b). The software used was EG&G model 270/250 research electrochemistry 4.00. The results were shown to be independent of [L] as expected for chelating ligands.

The pH was measured with a Corning 220 pH meter.

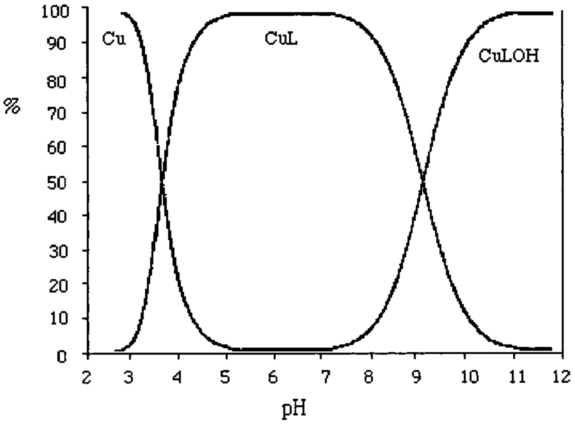


Figure 1. Distribution diagrams of the species formed as a function of pH in the system Cu^{2+}/L^1 in a 0.15 M $NaClO_4$ solution at 25 °C; $[Cu^{II}] = [L] = 1 \times 10^{-3}$ M.

Potentiometric measurements were carried out in solutions of 0.15 M $NaClO_4$ (C. Erba ACS grade) and purified according to a procedure described earlier.[15] Standardized CO_2-free solutions of NaOH, used in the potentiometric titrations, were prepared by following the procedure described.[16] The potentiometric titrations were carried out by using equipment (potentiometer, buret, stirrer, cell microcomputer, etc.) that has been fully described.[17] The computer program HYPERQUAD[18] was used to process the data and calculate both basicity and stability constants.

NMR measurements were carried out using a Bruker DMX-500 operating at 500 MHz for protons.

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

Results and Discussion

Potentiometric titrations were performed by using L^1:Cu(II) or L^2:Cu(II) molar ratios varying from 1:1 to 1:2, to obtain a detailed characterization of the species in the solutions used in this study. The results obtained are summed up in Table 1 and in Figures 1, 2, and 3. For comparison purposes, data concerning the ligands L^3, L^4, L^5, and L^6 and their copper complexes were added to the table. The results presented in Table 1 indicate that L^1 is more basic than L^2 in accord with the effect of *N*-methylation on other aliphatic amines.[13,19] This observation is attributed to the lower solvation energy of tertiary ammonium ions.[13,19]

---

(9) (a) Meyerstein, D. *Inorg. Chem.* **1975**, *14*, 1716. (b) Navon, N.; Masarwa, A.; Cohen, H.; Meyerstein, D. *Inorg. Chim. Acta* **1997**, *261*, 29.

(10) Mi, L.; Zuberbuhler, A. D. *Helv. Chim. Acta* **1991**, *74*, 1679.

(11) Braish, T. F.; Duncan, R. E.; Harber, J. J.; Steffen, R. L.; Stevenson, K. L. *Inorg. Chem.* **1984**, *23*, 4072.

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

(13) (a) Golub, G.; Cohen, H.; Paoletti, P.; Bencini, A.; Messori, L.; Bertini, I.; Meyerstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 8353. (b) Golub, G.; Cohen, H.; Paoletti, P.; Bencini, A.; Meyerstein, D. *J. Chem. Soc., Dalton* Trans. **1995**, 2055. (c) Golub, G.; Cohen, H.; Meyerstein, D. *J. Chem. Soc., Chem. Commun.* **1992**, 398.

(14) Icke, R. N.; Wisegarver, B.; Alles, G. A.; Synder, H. R. *Org. Synth.* **1941**, *3*, 723.

(15) Micheloni, M.; May, P. M.; Williams, D. R. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1209.

(16) Micheloni, M.; Sabatini, A.; Vacca, A. *Inorg. Chim. Acta* **1977**, *25*, 41.

(17) Bianchi, A.; Bologni, L.; Dapporto, P.; Micheloni, M.; Paoletti, P. *Inorg. Chem.* **1984**, *23*, 1201.

(18) Gans, P.; Sabatini, A.; Vacca, A. *Talanta* **1996**, *43*, 1739.

(19) Huheey, J. E. *Inorganic Chemistry*; Harper & Row: New York, 1972; p 218.

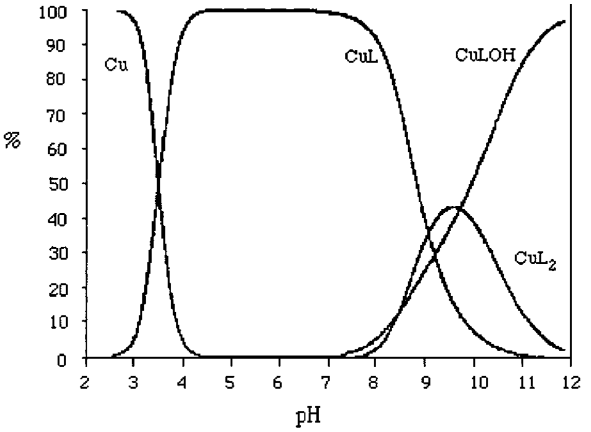


Figure 2. Distribution diagrams of the species formed as a function of pH in the system Cu^{2+}/L^1 in a 0.15 M NaClO$_4$ solution at 25 °C; [Cu^{II}] = 1 × 10^{-3} M, [L] = 2 × 10^{-3} M.

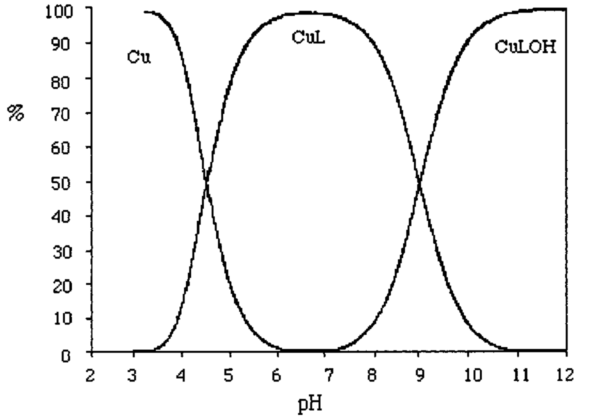


Figure 3. Distribution diagrams of the species formed as a function of pH in the system Cu^{2+}/L^2 in a 0.15 M NaClO$_4$ solution at 25 °C; [Cu^{II}] = [L] = 1 × 10^{-3} M.

The stability constant of the (CuL^1)$^{2+}$ complex is similar to that of the (CuL^5)$^{2+}$, and analogously, the stability constant of (CuL^2)$^{2+}$ is similar to that of (CuL^6)$^{2+}$. These observations are in accord with the expectation that the alkene group is not coordinated to the Cu(II) in both (CuL^1)$^{2+}$ and (CuL^2)$^{2+}$.

The binding constants of OH$^-$ to (CuL^i)$^{2+}$, $i = 1$ and 2, were measured. The results (Table 1) point out that there is a minor difference in the binding constants of OH$^-$ in these complexes. The effect is similar to that reported for (CuL^5)$^{2+}$ and (CuL^6)$^{2+}$ and is attributed to the lack of Cu−N−H···O hydrogen bonds in the solutions of complexes with the N-methylated ligands, which results in a larger charge density on the central copper ion, thus increasing the binding constant of the OH$^-$ to the copper(II) complex. This effect is smaller for the complexes of L^2 and L^6 than for L^4 since in the latter complex there are only axial aquo ligands bound to the central copper ion. It is assumed that the ligation site of OH$^-$ to (CuL^i)$^{2+}$ (i = 1, 2, 5, and 6) is in the plane of the nitrogens and not in the axial position as in (CuL^i)$^{2+}$, i = 3 and 4.

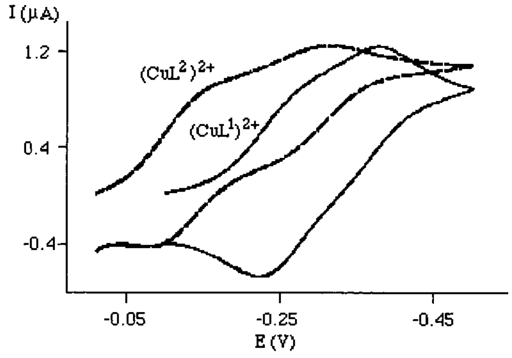


Figure 4. Cyclic voltammogram, HMDE vs Ag/AgCl; scan rate = 5 mV/s; [Cu^{2+}] = 0.001 M; [L] = 0.002 M; pH = 6.0; [ClO$_4^-$] = 0.5 M.

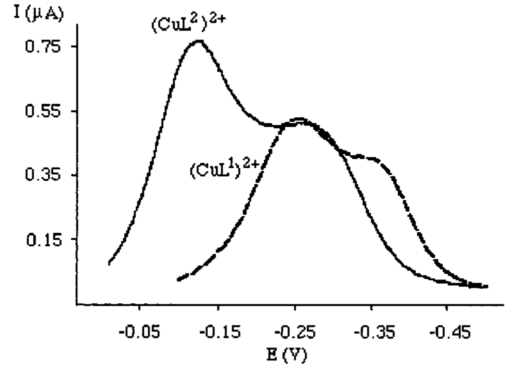


Figure 5. Square wave voltammogram, HMDE vs Ag/AgCl: frequency = 5 Hz; [Cu^{2+}] = 0.001 M; [L] = 0.002 M; pH = 6.0; [ClO$_4^-$] = 0.5 M.

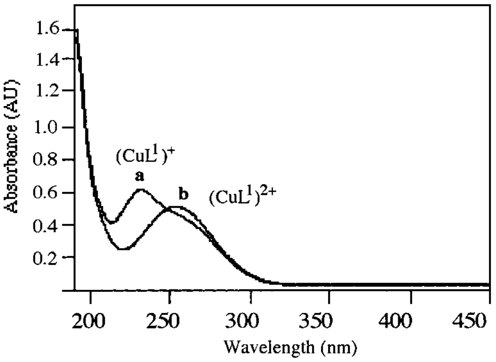


Figure 6. Spectra of (CuL^1)$^+$ and (CuL^1)$^{2+}$: (a) 0.08 mM (CuL^1)$^+$ pH 6.0; (b) solution of spectrum a exposed to air, 0.08 mM (CuL^1)$^{2+}$.

Electrochemistry. The redox properties of the copper complexes with L^1 and L^2 were studied using cyclic and square wave voltammetry. The results, Figures 4 and 5, clearly point out that both (CuL^1)$^{2+}$ and (CuL^2)$^{2+}$ are reduced via two consecutive single-electron processes. The first step involves reduction of Cu(II) to Cu(I), and the second step involves reduction of Cu(I) to elemental copper. Thus the results indicate that both L^1 and L^2 thermodynamically stabilize Cu(I). The redox potentials of the copper complexes vs NHE are Cu^{II}L^1/Cu^{I}L^1 −0.035 V, Cu^{I}L^1/Cu^0 + L^1 −0.12 V, Cu^{II}L^2/Cu^{I}L^2 0.095 V, and Cu^{I}L^2/Cu^0 + L^2 −0.040 V. Indeed, when solid copper is added to deaerated solutions containing CuSO$_4$ and excess of these ligands at pH 6, the blue color of the solutions disappears within several hours, indicating that the comproportionation reaction 2 occurs (Figure 6). When these solutions are then aerated, reaction 3 occurs and the observed concentration of (CuL^i)$^{2+}$ is double that in the original solutions.

$$(\mathrm{CuL}^i)^{2+} + \mathrm{Cu}^0 + \mathrm{L}^i \rightleftharpoons 2(\mathrm{CuL}^i)^+ \qquad (2)$$

$$2(\mathrm{CuL}^i)^+ + 0.5\mathrm{O}_2 + 2\mathrm{H}_3\mathrm{O}^+ \rightleftharpoons 2(\mathrm{CuL}^i)^{2+} + 3\mathrm{H}_2\mathrm{O} \qquad (3)$$

The comproportionation process, reaction 2, does not occur in solutions containing the ligands L^3, L^5, and L^6.[12,13]

The stability constants of the complexes, (CuL^1)$^+$ and (CuL^2)$^+$, were calculated using the electrochemical data and the stability constants of the respective $(CuL^i)^{2+}$ complexes, and the results are included in Table 1.

Since neither L^5 nor L^6 stabilizes Cu(I), it is concluded that the stabilization of Cu(I) by L^1 and L^2 is due, as expected, to the allyl substituent on these ligands. It is well-known that double bonds form $d-\pi^*$ bonds with Cu(I).[8,9] Since the only difference between L^1, L^2 and L^5, L^6 is the allyl group, it is suggested that, together with the three nitrogen atoms, it binds Cu(I) to form the tetradentate complexes, $(CuL^1)^+$ and $(CuL^2)^+$. Indeed ^1H NMR studies indicate that binding of Cu(I) to L^1 causes an upfield shift, though a small one, of the peaks due to the $-CH{=}CH_2$ group whereas binding of Cu(II) to L^1 causes a downfield shift of the same peaks. The NMR spectra of the Cu(I) complexes cannot be analyzed in detail due to the very fast ligand exchange of alkenes on Cu(I)[9a] which causes a broadening of the observed peaks.

Alternatively the properties of the copper complexes with L^1 and L^2 can be compared with those with L^3 and L^4, respectively, assuming that L^1 and L^2 are tetradentate ligands.[20] Such a comparison leads to the conclusion that the replacement of a tertiary nitrogen by an alkene group does not affect considerably the stability of the Cu(II) and Cu(I) complexes while replacing a primary nitrogen by an alkene group is accompanied by a significant decrease in the stability of the Cu(II) complex and probably by an increase in the stability constant of the Cu(I) complex. This conclusion is analogous to that obtained for the exchange of a primary or a secondary aliphatic nitrogen by a sulfur in open chain[21] and macrocyclic[22] tetradentate ligands.

The results can also be analyzed using Addison's empirical relationship[23]

$$E_{1/2} = E^\circ_{aq} + \Sigma(n\Delta E_L) \tag{4}$$

where E°_{aq} is the potential of the aqueous Cu(II/I) redox couple, ΔE_L represents the change in the Cu(II/I) potential caused by various ligand features, such as type of donor atom, and n represents the number of times the feature occurs for a specific ligand species. Using the data for the $Cu^{II}L^4/Cu^IL^4$ couple, one calculates $\Delta E_L = 0.018$ V for an aliphatic tertiary nitrogen, and from the data for the $Cu^{II}L^2/Cu^IL^2$ couple, $\Delta E_L = 0.031$ V for an alkene group. These values indicate again that the stabilization of Cu(I) by tertiary nitrogens and alkenes is similar and significantly smaller than by thioether groups.[23] The results clearly demonstrate that ΔE_L for tertiary nitrogens is significantly more positive than for primary and secondary ones. However, using the data for the $Cu^{II}L^1/Cu^IL^1$ couple and ΔE_L for the alkene, one obtains $\Delta E_L = -0.026$ V for the nitrogens in L^1. This result differs considerably from $\Delta E_L = -0.075$ V for each primary and secondary aliphatic nitrogen.[23] This discrepancy probably stems from the fact that L^1 and L^2 are only tridentate, and not tetradentate, ligands in the Cu(II) complexes. It was suggested that the stabilization of Cu(I) and other low-valent transition metal complexes by *N*-methylation is due to the considerable decrease in the stability constants of the corresponding divalent complexes, whereas the stability constants of monovalent complexes are considerably less affected by *N*-methylation.[13] The results of the present study corroborate this suggestion, i.e., the stability constant of $(CuL^2)^{2+}$ is considerably smaller than that of $(CuL^1)^{2+}$, whereas the stability constant of $(CuL^1)^+$ is only somewhat larger than that of $(CuL^2)^+$.

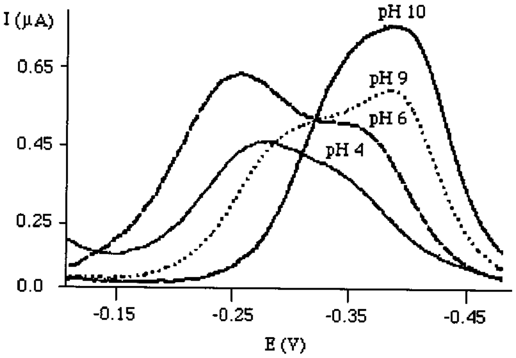


Figure 7. Square wave voltammogram, HMDE vs Ag/AgCl: frequency = 5 Hz; $[Cu^{2+}] = 0.001$ M; $[L^1] = 0.002$ M; $[ClO_4^-] = 0.5$ M.

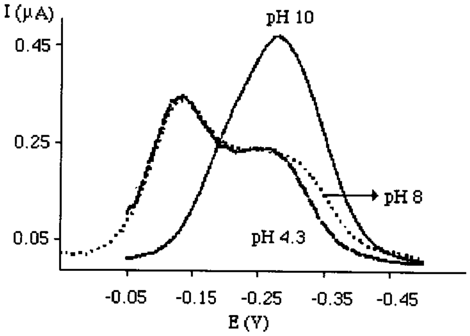


Figure 8. Square wave voltammogram, HMDE vs Ag/AgCl: frequency = 5 Hz; $[Cu^{2+}] = 0.001$ M; $[L^2] = 0.002$ M; $[ClO_4^-] = 0.5$ M.

Table 2. 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})
1	254	6250	612	97
2	294	5000	686	250
3[a]	258	4650	568	140
4[a]	302	5250	636	210
5	246	4200	614	81
6	292	5000	670	220

[a] Solution composition: $[Cu^{II}] = 0.00025$ M, [L] = 0.001 M, for the charge-transfer bands $l = 1$ cm, for the d−d bands $l = 5$ cm, pH 7.0. Error limits ±2 nm and ±10% for the molar absorption coefficients. [a] Data taken from ref 13.

The pH dependence of the electrode potentials of the $(CuL^i)^{2+/+}$ couples (Figures 7 and 8), is in accord with the formation constants of the different species present in the solution (Table 1 and Figures 1−3). The data for the $(CuL^1)^{2+/+}$ couple at pH < 4 are attributed to the presence of a mixture of Cu^{2+}_{aq} and $(CuL^1)^{2+}$ in the solutions, whereas the data at pH > 8 are attributed to the effect of the formation of $(CuL^1OH)^+$ and $(CuL^1_2)^{2+}$ on the electrode potential. The data for the $(CuL^2)^{2+/+}$ couple at pH < 5 are attributed to the presence of a mixture of Cu^{2+}_{aq} and $(CuL^2)^{2+}$, whereas the data at pH > 8 are attributed to the effect of the formation of $(CuL^2OH)^+$ on the electrode potential.

UV−Vis Spectra. The UV−vis spectra of $(CuL^i)^{2+}$ ($i = 1$, 2, 5, 6) were measured, and the results are summed up in Table 2. For comparison purposes Table 2 contains also data concerning the spectra of $(CuL^3)^{2+}$ and $(CuL^4)^{2+}$. The results point out that N-methylation of the ligands causes a red shift of both the charge transfer bands and the d−d bands of the Cu(II)

---

(20) We thank one of the reviewers for pointing out this plausible comparison.

(21) Kaden, T. A.; Kaderli, S.; Sager, W.; Siegfrid-Hertli, L. C.; Zuberbuhler, A. D. *Helv. Chim. Acta* **1986**, *69*, 1216.

(22) Bernardo, M. M.; Heeg, M. J.; Schroeder, R. R.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1992**, *31*, 191.

(23) Addison, A. W. *Inorg. Chim. Acta* **1989**, *162*, 217.

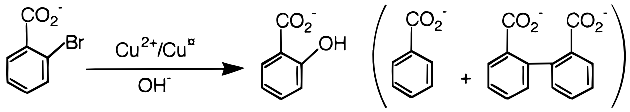
complexes. This result is in accord with previous results[13] and is attributed to the effect of N-methylation on the redox potential of the copper complexes which cause the red shift of the charge transfer bands and to the lower ligand field splitting induced by the N-methylated ligands which cause the shift of the d−d bands.[13]

The considerable similarity between the spectra of $(CuL^1)^{2+}$ and $(CuL^5)^{2+}$ and between the spectra of $(CuL^2)^{2+}$ and $(CuL^6)^{2+}$ suggests that the nature of the corresponding Cu(II) complexes is similar. These results support the conclusion, see above, that L^1 and L^2 are tridentate ligands in these Cu(II) complexes and that the alkene group in L^1 and L^2 does not interact with Cu(II).

The shift to the UV of the LMCT band upon reduction of the $(CuL^i)^{2+}$ complexes, Figure 6, is in accord with earlier observations.[13]

Concluding Remarks

The results obtained clearly demonstrate that tridentate amine ligands with a substituent which does not bind to Cu(II) but binds to Cu(I) stabilize Cu(I) in aqueous solutions. Furthermore, the Cu(I) complexes with such ligands are stronger reducing agents than Cu^{+}_{aq}; this is especially true for $(CuL^1)^+$. Therefore one expects that $(CuL^i)^+$ ($i = 1, 2$), will be good catalysts for a variety of processes. Indeed these complexes were shown[24] to improve considerably the rate and selectivity of the following Ullmann reaction:



Acknowledgment. This study was supported in part by The Israel Science Foundation administered by The Israel Academy of Sciences and Humanities and by a grant from the Budgeting and Planning Committee of The Council of Higher Education and the Israel Atomic Energy Commission. D.M. wishes to express his thanks to Mrs. Irene Evens for her ongoing interest and support.

IC9812048

---

(24) Saphier, M.; Navon, N.; Cohen, H.; Meyerstein, D. To be published.