The Stabilization of Monovalent Copper Ions by Complexation with Saturated Tertiary Amine Ligands in Aqueous Solutions. The Case of 2,5,9,12-Tetramethyl-2,5,9,12-tetraazatridecane

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The complex of copper(I) ions with 2,5,9,12-tetramethyl-2,5,9,12-tetraazatridecane in aqueous solutions is stable in the absence of oxygen; this observation indicates that the stabilization of low valent transition metal cations by tertiary tetraazamacrocyclic ligands is due to the hydrophobic nature of these ligands.

Recent studies point out the *N*-methylation of the tetraazamacrocyclic ligands **1** and **3** stabilizes the low valent complexes of Ni^{I},[1] Cu^{I},[2] Pd^{I}[3] and Cr^{II},[4] with these ligands.

Four tentative explanations for this effect of *N*-methylation have been proposed.

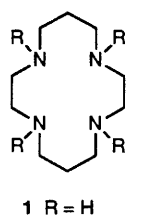
(*i*) *N*-Methylation causes an increase in the size of the cavity of the macrocyclic ligand thus stabilizing the low valent complexes.[5] Though this effect clearly occurs a comparison of the redox potentials of $[Ni\mathbf{1}]^{2+}$, $[Ni\mathbf{2}]^{2+}$ and [1,4,8,12-tetraazacyclopentadecane–nickel(II)]$^{2+}$ clearly indicates that this effect has only a minor contribution to the effect observed.[6]

(*ii*) The redox potentials of a large group of $[NiL]^{2+/+}$ couples were shown to be linearly correlated to 10 Dq for the $[NiL]^{2+}$ complexes, *i.e.* to the ligand field splitting due to the ligand.[1,5,7] *N*-Methylation decreases 10 Dq[6] though methyls are known to be electron-donating groups. It is, therefore, surprising that tertiary amine ligands are considered to the poor σ-donating groups.[5] A plausible explanation of this observation is that *N*-methylation inhibits the effect of hydrogen bonding to the solvent, *via* $M^{n+}:N\text{–}H\cdots OH_2$, which contributes to the σ-donating properties of the nitrogen. In aprotic solvents the counter anions are expected to have a similar effect.

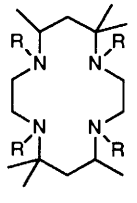
(*iii*) *N*-Methylation increases considerably the hydrophobic nature of the complexes thus relatively stabilizing the lower valent complexes.[1,6] (The effect of hydrogen bonding on the σ-donating properties, discussed above, is a part of this effect).

(*iv*) *N*-Methylation causes in some cases considerable stereochemical distortions of the complex, *i.e.* pyramidal and/or tetrahedral distortions, which stabilize the low valent complexes.[3]

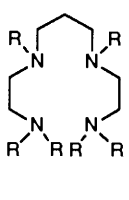
If arguments (*ii*) and/or (*iii*) are the dominant factors in the stabilization of the low valent complexes, then one would expect that *N*-methylation of polydentate-open chain amines will have a similar effect. Indeed, *N*-methylation of ethylene-



1 R = H
2 R = Me



3 R = H
4 R = Me



5 R = H
6 R = Me

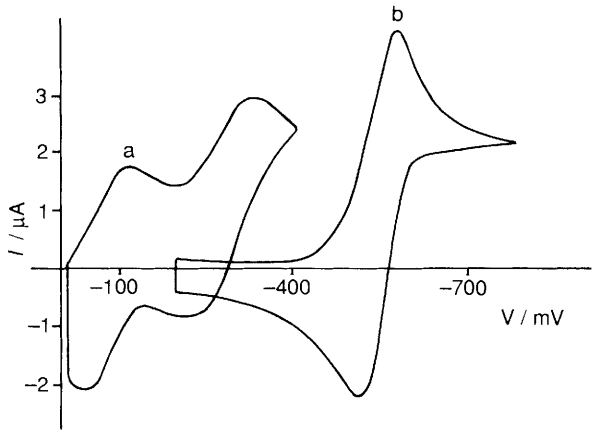


Fig. 1 Cyclic voltammogram, HMDE *vs.* SCE, rate 5 mV s^{-1} $[Cu^{II}]$ = 0.001 $[ClO_4^-]$ = 0.8 mol dm^{-3} pH = 10 (*a*) [**6**] = 0.002 mol dm^{-3} (*b*) [**5**] = 0.002 mol dm^{-3}

diamine and diethylenetriamine is known to shift the redox potentials of $[RuL_n]^{3+/2+}$ [8] and $[CuL]^{2+/+}$ [9] in the expected direction. It seemed, therefore, reasonable to expect that the complex [2,5,9,12-tetramethyl-2,5,9,12-tetraazatridecane–copper(I)]$^+$, $[Cu\mathbf{6}]^+$, should be stable towards disproportionation in aqueous solutions, though it is commonly accepted that saturated polyamine ligands catalyse the disproportionation of $Cu^+(aq)$.[10]

The ligand **6** was synthesized by *N*-methylation of 1,9-diamino-3,7-diazanonane, **5**, with HCO_2H, CH_2O in analogy to a procedure described in the literature.[11]

The UV–VIS spectra of $[Cu\mathbf{6}]^{2+}$ and $[Cu\mathbf{5}]^{2+}$ at pH 10.0 in solutions containing an excess of L, revealed two absorption bands for each complex. For $[Cu\mathbf{6}]^{2+}$ the bands are at 636 nm (ε_{max} = 36.0 mol^{-1} m^2) and 312 nm (ε_{max} = 1300 mol^{-1} m^2) and for $[Cu\mathbf{5}]^{2+}$ at 526 nm (ε_{max} = 13.0 mol^{-1} m^2) and 224 nm (ε_{max} = 1100 mol^{-1} m^2).

The red shift of the d–d band upon *N*-methylation points out that the ligand field splitting of $[Cu\mathbf{6}]^{2+}$ is smaller than in $[Cu\mathbf{5}]^{2+}$. This observation might stem from the fact that tertiary amines are worse σ donors than secondary amines though methyls are electron-donating substituents. Alternatively the lack of hydrogen bonding in the tertiary amine complex causes this effect. A contribution of a tetrahedral distortion, caused by steric hindrance in $[Cu\mathbf{6}]^{2+}$ cannot be ruled out.

The red shift of the charge transfer band upon *N*-methylation suggests that either the tertiary amine is a better electron donor than the secondary amine and/or that the Cu ion is a stronger oxidant in $[Cu\mathbf{6}]^{2+}$ than in $[Cu\mathbf{5}]^{2+}$. The effect of the *N*-methylation on the d–d indicates that the second argument is the correct one.

Typical cyclic voltammograms of $[Cu\mathbf{6}]^{2+}$ and $[Cu\mathbf{5}]^{2+}$ on a hanging mercury electrode (HMDE) are shown in Fig. 1. The results indicate the following points.

(*i*) $[Cu\mathbf{5}]^{2+}$ is reduced in a single two-electron process at −540 mV *vs.* SCE (saturated calomel electrode), as expected for copper complexes with chelating saturated amine ligands.

(*ii*) $[Cu\mathbf{6}]^{2+}$ is reduced at a less cathodic potential. Furthermore, it is reduced in two single electron processes at −70 and −270 mV *vs.* SCE.

The latter result clearly indicates that $[Cu\mathbf{6}]^+$ is stable towards disproportionation. Indeed, when a deaerated solution of $Cu^I(NCCH_3)_4PF_6$ in methanol is added to a deaerated solution of an excess of **6** at pH 10 no disproportionation is observed during several days whereas the disproportion reaction occurs within minutes in the presence of **5**.

Furthermore, when a copper wire is added to a stirred deaerated solution of $[Cu\mathbf{6}]^{2+}$ in the presence of an excess of **6** at pH 10 the solution turns colourless within hours. When oxygen is bubbled through the latter solution it turns blue and its spectrum reveals that the concentration of $[Cu\mathbf{6}]^{2+}$ was doubled during this process, *i.e.* the reactions shown in eqns. (1) and (2) are being observed.

$$[Cu\mathbf{6}]^{2+} + \mathbf{6} + Cu^0 \rightarrow 2[Cu\mathbf{6}]^+ \quad (1)$$
(a conproportionation reaction)

$$2[Cu\mathbf{6}]^+ + 1/2O_2 + 2H^+ \rightarrow 2[Cu\mathbf{6}]^{2+} + H_2O \quad (2)$$

The equilibrium constant for the ligation reaction eqn. (3)

$$Cu^{2+}(aq) + \mathbf{6} \leftrightharpoons [Cu\mathbf{6}]^{2+} \; pK\,([Cu\mathbf{6}]^{2+}) = 17.1 \pm 0.3 \quad (3)$$

was derived from the results of a potentiometric titration. This value indicates that **6** is a weaker ligand than **5**, eqn. (4)[12] in accord with expectations. From the electrochemical data and the redox potential of $Cu^{2+/+}(aq)$ one calculates $K([Cu\mathbf{6}]^+)/K([Cu\mathbf{6}]^{2+})$ = 5 *i.e.* that **6** is a better ligand to Cu^+ than to Cu^{2+}.

$$Cu^{2+}(aq) + \mathbf{5} \leftrightharpoons [Cu\mathbf{5}]^{2+} \; pK\,([Cu\mathbf{5}]^{2+}) = 23.9 \quad (4)$$

The fact that the stability constant for complexation of Cu^+ by **6**, a pure σ donor, is larger than that for complexation of Cu^{2+} by **6** suggests that the major factor causing the stabilization of low valent transition metal complexes by *N*-methylation of polydentate saturated amine ligands is the increase in the hydrophobic nature of the *N*-methylated ligands. A contribution of a stereochemcial distortion, caused by steric hindrance in $[Cu\mathbf{6}]^{2+}$, to the observed effect cannot be ruled out. However, as the effect of *N*-methylation was observed for a variety of central cations, *e.g.* Ni^I,[1] Cu^I,[2] Pd^I,[3] Ru^{II} [8] and Cr^{II},[4] which prefer different coordination geometries the major expected steric contribution is the plausible M–N bond lengthening in the complexes of the *N*-methylated ligands. This bond lengthening, if it occurs, is caused in part by the absence of hydrogen bonds as discussed above.

Finally the results clearly point out that saturated tertiary amine ligands stabilize monovalent copper ions in aqueous solutions contrary to the expected notions. This finding suggests a new approach to the design of ligands for the complexation of low valent cations in aqueous solutions.

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