# Model Complexes for Biologically Active Copper[1]

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## Abstract

*In regard to the understanding of copper at the active site of "blue" proteins a series of open chain and macrocyclic $N_2S_2$-ligands have been studied potentiometrically, spectrophotometrically and voltammetrically. $Cu^{2+}$ forms the species $CuL^{2+}$ and sometimes $CuLOH^+$, whereas $Cu^+$ gives $Cu(an)LH_2^{3+}$ (an = $CH_3CN$), $CuLH^{2+}$ and $CuL^+$. From the stabilities of the $Cu^{2+}$ and $Cu^+$ species the redox potentials have been calculated and compared to the values obtained from cyclic voltammetry. The redox potentials for the open chain complexes are between 250 - 280 mV against SHE. The complexes with the macrocyclic ligands span a range of 340 mV, going from 80 to 420 mV against SHE, or six order of magnitude in relative stability reflecting the importance of subtle differences in steric requirements. This is exemplified through the X-ray structure of the $Cu^+$ complex with one of the 16-membered macrocycles, which reveals a tetrahedral coordination geometry typical for the cuprous ion. A comparison between open chain and cyclic ligands shows that a macrocyclic effect is found for $Cu^{2+}$, but not for $Cu^+$. The ligand field strength is very different for the two types of ligands and the redox potentials are nearly independent of the chain length of the open chain ligands, but strongly depend on the ring size of the macrocycles.*

## Introduction

Ligands with an $N_2S_2$-donor set have been widely used as models for copper at the active site of "blue" proteins [1] [2], since the structure determination of plastocyanine in its oxidized and reduced form have shown that both $Cu^{2+}$ and $Cu^+$ (at high pH) are

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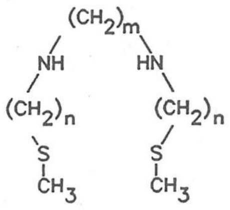
[1] Abstract of a plenary lecture hold at the VI Meeting of the Portuguese Electrochemical Society, 7. - 10. October 1992, Vila Real Portugal

*Portugaliæ Electrochimica Acta, 10 (1992) 109-120*

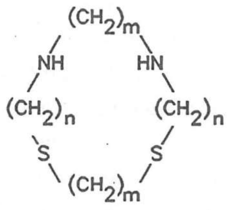
tetrahedrally coordinated by two imidazole nitrogens, a methionine thioether and a cysteine thiolate sulfur [3].

Most of these studies are related to mimicking the spectroscopic properties of the natural systems. So the position and the high molar absorptivity of the "blue" band have been the subject of many theoretical [4 - 6] and experimental [6] investigations. The correlation between spectral properties and the geometry of the $Cu^{2+}$ coordination sphere have been amply discussed [7]. Other studies have tried to understand the unusually low $A_{\parallel}$ values found in the EPR spectra of "blue" copper proteins [8]. Relatively little is known, however, about the stability of $Cu^{2+}$ and especially $Cu^{+}$ complexes with ligands having the $N_2S_2$ donor set.

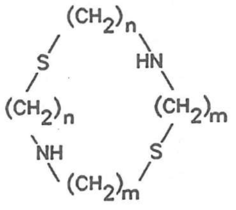
Since an actual copy of the active centre in "blue" copper proteins, with two imidazoles, one cysteine and one methionine would be very difficult to achieve, we have used open chain and cyclic ligands with two amino nitrogen and two thioether sulfur atoms to study their $Cu^{2+}$ and $Cu^{+}$ complexes. With open chain chelates one can change the length of the chain (ligand **1** - **4**), whereas with cyclic compounds one can systematically modify the ring size and/or the arrangement of the donor atoms, since one has the possibility of a *cis*- (ligand **5** - **7**) and a *trans* (ligand **8** - **10**) arrangement.



**1** n = m =2
**2** n = 2, m = 3
**3** n = 3, m = 2
**4** n = m = 3



**5** n = m = 2
**6** n = 3, m = 2
**7** n = m = 3



**8** n = m = 2
**9** n = 2, m = 3
**10** n = m = 3

The present study was undertaken to investigate a series of fundamental questions in this respect: 1) What are the absolute and relative stabilities of the $Cu^{+}$ and $Cu^{2+}$ complexes with $N_2S_2$ ligands; 2) Is there an effect of the length or the ring size; 3) Are the expected complexes $CuL^{+}$ and $CuL^{2+}$ the only species formed by these ligands; 4) How does $Cu^{+}$, which prefers a linear arrangement of aliphatic amino groups, adjust to the steric restrictions imposed by the *cis*-ligands; 5) How closely do redox potentials calculated from the stability constants of the $Cu^{+}$ and $Cu^{2+}$ complexes correlate with those obtained from cyclic voltammetry? For this purpose a series of open chain [9] and cyclic [10] compounds were synthesized.

**Spectroscopic Properties of the $Cu^{2+}$ complexes**

The $Cu^{2+}$ complexes were prepared by mixing the free ligand and an equimolar amount of $Cu(ClO_4)_2 \cdot 6H_2O$ in MeOH or EtOH [10]. The UV-VIS spectra in the solid state, in $H_2O$ and in $CH_3CN$ solution are collected in *Table 1.*

*Table 1.* Absorption maxima (nm) and molar absorptivities ($M^{-1}cm^{-1}$) of the $Cu^{2+}$ complexes with the macrocycles **5** - **10**.

| Ring | Ligand | Solid [b)] | $CH_3CN$ | $H_2O$ |
|---|---|---|---|---|
| 12 | 5 | 630, 346 | 620(803),343(4800) | 620(610),356(4600),270(2000) |
| | 8 | 630, 385 | 620(727),390(4800) | 620(505),375(4800),295(1500) |
| 14 | 6 | 506, 346 | 527(435),336(8900) | 533(386),335(8900),300(2800) |
| | 9 | 530, 382 | 554(465),373(9600) | 565(400),370(8900),300(2800) |
| 16 | 7 | 530, 353 | 584(467),370(7200) | 607(500),362(5500),280(2000) |
| | 10 | 540, 365, 320sh | [a)] | 625(550),360(5000),320(3200) |

a) The solution is not stable. b) Using the nujol technique [23].

The three bands observed in aqueous solution at 270 - 320 nm, 335 - 372 nm and 530 - 625 nm can be assigned, by comparison to the $CuN_2S_2$ chromophore as described in [4] [5] [11], to the $N \rightarrow Cu^{2+}$ LMCT (ligand to metal charge transfer), to the $S \rightarrow Cu^{2+}$ LMCT and to the ligand field (LF) bands, respectively. The energy differences between the $N \rightarrow Cu^{2+}$ and $S \rightarrow Cu^{2+}$ LMCT range in our complexes between 6500 and 8100 $cm^{-1}$, which is reasonable [11]. A comparison of the LF-bands in the series of the 14-membered $N_4$- (512 nm) [12], *cis*-$N_2S_2$- (533 nm), *trans*-$N_2S_2$- (565 nm) and $S_4$-macrocycle (570 nm) [13] indicates that the thioether sulfur fits into the spectrochemical series very well, since it has a ligand field splitting somewhat smaller than an amino nitrogen [14]. Interesting is also the gradual increase of the molar absorptivity for this band: for the $Cu^{2+}$ complex with the 14-membered $N_4$-ligand 100 $M^{-1}cm^{-1}$, for that with the analogous *cis*-$N_2S_2$-ligand 386 $M^{-1}cm^{-1}$ and for that of the analogous $S_4$-ligand 1900 $M^{-1}cm^{-1}$. This might indicate that the pure LF (d-d*) transition gains intensity by mixing with CT contribution when

N-donors are replaced with S-donors.

The $E_{1/2}$ values for the $Cu^{2+}/Cu^{+}$ couple, determined by cyclic voltammetry (CV) in $CH_3CN$, are given in *Table 2* and one experiment is shown in *Figure 1* [10]. The CV of the 12-membered *cis* and *trans* ligands **5** and **8** are nearly reversible as indicated by the peak to peak separation $\Delta E$ of 84 - 88 mV under conditions in which the internal standard ferrocenium/ferrocene gives 64 mV. The other criteria for reversibility are also fulfilled: so $i_a/i_c = 1$ and the peak separation remains constant for scan rates between 5 and 30 mV $s^{-1}$. On the other hand the $Cu^{2+}$ complexes of the 14- and 16-membered macrocycles are quasi reversible: the peak to peak separation is over 120 mV, although $i_a/i_c$ is still about 1. Hence it appears that in the case of the 12-membered ligands little or no rearrangement takes place when $Cu^{2+}$ is reduced to $Cu^{+}$. This might be due to the non-planarity of these $Cu^{2+}$ complexes, since the 12-membered rings being to small cannot encircle the metal ion. The larger macrocycles, however, can encompass the $Cu^{2+}$ ion, so that the typical square planar geometry for $Cu^{2+}$ can be achieved Since this is not ideal for $Cu^{+}$, a structural rearrangement is necessary after the electron transfer. The $E_{1/2}$ values of the 16-membered rings **7** and **10** are the highest ones, followed by those of the ligands **5**, **8** and **9**, whereas the $Cu^{2+}$ complex with **6** has the lowest one. Comparing the $E_{1/2}$ values for the macrocycles with a $N_4$-, a $N_2S_2$- and a $S_4$-donor set the sequence is $E_{1/2}$ $(N_4) < E_{1/2}$ $(N_2S_2) < E_{1/2}$ $(S_4)$ for each ring size (*Table 2*).

*Table 2.* Redox potentials from CV in $CH_3CN$ for the $Cu^{2+}$ complexes with the macrocycles **5** - **10** and the parent compounds with $N_4$- and $S_4$-donor set .

| Ring | $N_4$-donor | $N_2S_2$-donor$^{d)}$ | | $S_4$-donor | |
|---|---|---|---|---|---|
| | $E_{1/2}$ $^{a)}$ | $E_{1/2}$ $^{a)}$ | $\Delta E$ $^{b)}$ | $E_{1/2}$ $^{a)}$ | $\Delta E$ $^{b)}$ |
| 12 *cis* | -379 [24] | 164 | 84 | 64 [22] | 72 |
| 12 *trans* | | 132 (40) $^{c)}$ | 88 (70)$^{c)}$ | | |
| 14 *cis* | -474 [24] | 12 (76)$^{c)}$ | 120 (181)$^{c)}$ | 600 [22] | 63 |
| 14 *trans* | | 172 | 148 | | |
| 16 *cis* | | 368 | 160 | 771 [22] | 70 |
| 16 *trans* | | 484 | 146 | | |

a) All values in mV against SHE; b) Potentials difference between the cathodic and anodic peak in mV; c) In $H_2O$ from [25] and [22]; d) In $CH_3CN$ with 0.1 M $LiClO_4$.

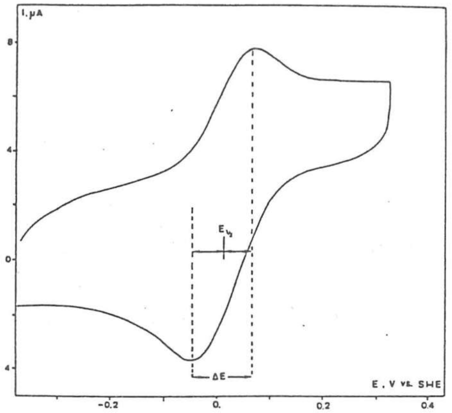


*Figure 1.* Cyclic voltammogram of the $Cu^{2+}$ complex ($4 \cdot 10^{-4}$ M) with **6** in $CH_3CN$ at 10 $mVs^{-1}$. The parameters $E_{1/2}$ and $\Delta E$ are defined in the text.

The $A_{\parallel}$ and $g_{\parallel}$ values determined from the EPR-spectra of the $Cu^{2+}$ complexes measured in a $EtOH/H_2O$ glass at -120° are given in *Table 3* [10]. The values are typical for $N_2S_2$-ligands and show a rough correlation between $g_{\parallel}$ and $A_{\parallel}$, as previously observed by other authors. From the low $g_{\parallel}$ (2.145) and the high $A_{\parallel}$ value ($170 \cdot 10^{-4} cm^{-1}$) for the $Cu^{2+}$ complex with **6**, one would expect the lowest distortion from square planar geometry for this compound. This is also in accordance with the highest ligand field as

*Table 3.* ESR Results for the $Cu^{2+}$ with the macrocycles **5** - **10** and the parent compounds with $N_4$- and $S_4$-donor set

| Ligand | $g_{\parallel}$ | $A_{\parallel} \cdot 10^4 cm^{-1}$ |
|---|---|---|
| **5** | 2.174 | 152 |
| **6** | 2.145 | 170 |
| **7** | 2.172 | 151 |
| **8** | 2.171 | 145 |
| **9** | 2.162 | 161 |
| **10** | a) | a) |
| [14]ane$N_4$ $^{b)}$ | 2.186 | 205 |
| [14]ane$S_4$ $^{c)}$ | 2.100 | 165 |

a) The spectrum is an overlap of two species; b) From [24]; c) From [22] shown by its LF-band (Table 1). The 12-membered ligands being to small to encircle the $Cu^{2+}$ ion and the 16-membered macrocycles, being to large and to flexible, probably give distorted geometries. The 14-membered *trans*-$N_2S_2$-macrocycle **9**, having the chelate ring sequence [5,5,6,6] gives a less strong ligand field than the *cis*-ligand **6** with the ideal ring sequence [5,6,5,6].

## Equilibrium studies in aqueous solution

The complexation of the open chain and cyclic $N_2S_2$-ligands with $Cu^{2+}$ and $Cu^+$ was studied by spectrophotometric and pH-titrimetric techniques [9] [15]. The results are collected in *Table 4* and the definitions of the constants can be taken from *eqn. 1 - 5.*

*Table 4.* Stability constants of the $Cu^{2+}$ and $Cu^+$ complexes with the open chain and cyclic $N_2S_2$-ligands at 20° and I = 0.2 M ($Na_2SO_4$).

| Ligand | log $K^{II}_{CuL}$ | log $K^{II}_{CuLOH}$ | log $K^{I}_{CuL}$ | log $K^{I}_{CuLH}$ | log $K^{I}_{CuL(an)LH_2}$ |
|---|---|---|---|---|---|
| 1 | 12.62 | 9.72 | 14.33 | 8.92 | 3.16 |
| 2 | 12.97 | 11.40 | 14.46 | 9.35 | 3.17 |
| 3 | 10.98 | 10.22 | 13.02 | 8.25 | 3.57 |
| 4 | a) | a) | 12.56 | 8.28 | 3.48 |
| 5 | 13.95 | 11.08 | 13.14 | 7.00 | b) |
| 6 | 15.85 | b) | 13.39 | 7.73 | b) |
| 7 | 10.15 | a) | 14.35 | b) | b) |
| 8 | 11.69 | b) | 12.33 | 6.49 | b) |
| 9 | 12.89 | a) | 14.20 | 9.46 | b) |
| 10 | 10.25 | b) | 13.95 | 10.17 | b) |

a) Precipitate of $Cu(OH)_2$; b) Not observed.

$$Cu^{2+} \quad + \quad L \quad \rightleftharpoons \quad CuL^{2+} \quad ;K^{II}_{CuL} \qquad (1)$$

$$CuL(OH)^{+} \quad + \quad H^{+} \quad \rightleftharpoons \quad CuL^{2+} \quad ;K^{II}_{CuLOH} \qquad (2)$$

$$Cu^{+} \quad + \quad L \quad \rightleftharpoons \quad CuL^{+} \quad ;K^{I}_{CuL} \qquad (3)$$

$$Cu^{+} \quad + \quad LH^{+} \quad \rightleftharpoons \quad CuLH^{2+} \quad ;K^{I}_{CuLH} \qquad (4)$$

$$Cu(CH_3CN)^{+} \quad + \quad LH_2^{2+} \quad \rightleftharpoons \quad Cu(CH_3CN)LH_2^{3+} \quad ;K^{I}_{Cu(an)LH_2} \qquad (5)$$

All ligands except **4** give with $Cu^{2+}$ the species $CuL^{2+}$. The 16-membered cyclic ligands **7** and **10** forming the less stable complexes have a tendency to hydrolyse to $Cu(OH)_2$ at pH > 7. The log $K^{II}_{CuL}$ values increase in the order **4** << **7** < **10** < **3** < **8** < **9** < **2** < **6** and span more than 5 log units. That the weakest complexes are formed by ligands which only form six-membered chelate rings, is not surprising, since at least the cyclic ligands **7** and **10** are to large for $Cu^{2+}$. The most stable complex is formed by **6**, which has the *cis*-$N_2S_2$ donor set and the ideal ring sequence [5,6,5,6], which is known to be optimal [16]. Interesting is also the observation that the *cis* arrangement gives more stable complexes than the *trans* one, except for **7** and **10**. In general the stability constants are 1 - 2 log units higher for the macrocycles than for the corresponding open chain ligands, which can be rationalized by the macrocyclic effect.

To describe the stability of the $Cu^+$ species the equilibria *(3) - (5)* are necessary. Whereas $CuL^+$ does not interact with $CH_3CN$ (an), the species $CuLH^{2+}$ sometimes and $CuLH_2^{3+}$ always form ternary complexes with $CH_3CN$, since the amino groups are not available to form coordinative bonds. Interesting is that the cyclic as well as the open chain ligands all give $CuLH^{2+}$, whereas $Cu(an)LH_2^{3+}$ is only formed with the open chain ligands. The stability constants of $CuL^+$ show a less broad scattering from 12.33 to 14.46 than those of the analogous $Cu^{2+}$ species. This indicates that for $Cu^+$ the ring size and the structural properties have a weaker effect on the stability constants and there is no typical trend. Interesting is, that the 16-membered cyclic ligand **7** forms one of the most stable $Cu^+$ complexes, but gives in turn the less stable $Cu^{2+}$ complex of all cyclic ligands. The very different requirements of $Cu^+$ and $Cu^{2+}$ are also clearly exemplified by the complexation with **6**. This compound forms by far the most stable $Cu^{2+}$ complex of the whole series, but it forms a relatively weak $Cu^+$ species.

The second point of difference between the complexation with $Cu^{2+}$ and $Cu^+$ concerns the formation of additional species beside the 1:1 complexes. With $Cu^+$ protonated complexes with relatively high stabilities are formed. The effect is most prominent with the smallest ring **5** and **8**, for which $CuLH^+$ is practically formed at pH 4, and for the open chain ligand for which $Cu(an)LH_2^{3+}$ is also formed at low pH. The protonated species, in which the ligand is bound mostly or only by S-atoms, often are ternary species in which one $CH_3CN$ is also bound.

The redox potentials can be obtained either by cyclic voltammetry or from the stability constants of the $Cu^+$ and $Cu^{2+}$ complexes according to *eqn. 6.*

$$E_{1/2}(CuL^{2+}/CuL^{+}) = E_{1/2}(Cu^{2+}/Cu^{+}) - 0.059 \log (K^{II}_{CuL}/K^{I}_{CuL}) \qquad (6)$$

Taking 160 mV for the redox potential $E_{1/2}$ $(Cu^{2+}/Cu^+)$ of the free ions [17], the values calculated from the stability constants were determined (*Table 5*) and are plotted in *Figure 2.* Calculated and experimental values differ by ± 20 mV, which could be due to the only quasi reversibility of the voltammograms measured in aqueous solution or to problems with the junction potential. In the case of **6** the difference is 69 mV or more than one order of magnitude in the relative stabilities. The reason of this large difference may be related to the very slow complex formation of this ligand with $Cu^{2+}$ and to the stronger irreversible character of its cyclic voltammogram. So, inspite of single specific problems $E_{1/2}$ from cyclic voltammetry appears to be a good way to obtain a guess of the redox potential even though some of the electrode reactions are not strictly reversible. The other possibility to use $E_{1/2}$ and log $K^{II}_{CuL}$ to calculate log $K^{I}_{CuL}$, which often is more difficult to obtain experimentally, allows to obtain a guessed value within a factor of 2 in stability. However, it has the disadvantage that this method does not indicate whether other species beside $CuL^+$ are present.

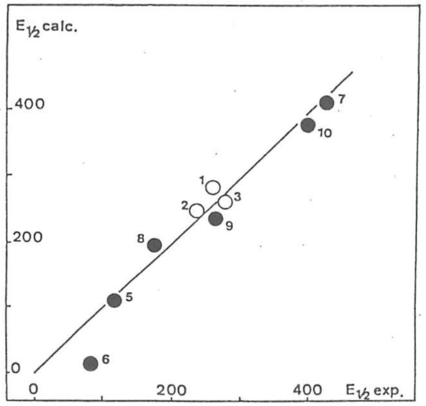


*Figure 2.* Correlation between the calculated (according to *eqn. 6*) and experimentally determined $Cu^{2+}/Cu^+$ potentials for open chain (O) and cyclic (●) $N_2S_2$-ligands.

*Table 5.* Absorption spectra, molar absorptivities and redox potentials of the copper complexes with **1** - **10** in aqueous solution.

| Ligand | VIS-spectrum | | $E_{1/2}$ (mV)$^{a)}$ | |
|---|---|---|---|---|
| | (nm) | $(M^{-1}cm^{-1})$ | calc.$^{c)}$ | exp. |
| 1 | 580 | 378 | 260 | 277 |
| 2 | 563 | 355 | 247 | 230 |
| 3 | 570 | 395 | 279 | 258 |
| 4 | b) | b) | b) | b) |
| 5 | 620 | 610 | 112 | 116 |
| 6 | 533 | 386 | 15 | 84 |
| 7 | 607 | 500 | 409 | 424 |
| 8 | 620 | 505 | 198 | 172 |
| 9 | 565 | 400 | 237 | 262 |
| 10 | 625 | 550 | 397 | 396 |

a) Against SHE; b) Not stable; c) Calculated from *Eqn. 6.*

### Structure of the $Cu^+$ complex with 7

During our studies on $Cu^{2+}$ and $Cu^+$ complexes with $N_2S_2$ ligands we were able to crystallize the $Cu^+$ complex of 7, which is relatively stable towards dioxygen [18]. The X-ray structure shows a $Cu^+$ ion surrounded in a slightly distorted tetrahedral arrangement by two amino nitrogens and two thioether sulfurs (*Figure 3*) [19]. The bond lengths Cu-N (2.05 - 2.06 Å) are in the usual range, whereas the Cu-S bonds are relatively short (2.25 - 2.26 Å), compared to examples taken from the *Cambridge Structural Database*, which range from 2.23 to 2.46 Å. Whereas the angles S(1)-Cu-N(1) and S(2)-Cu-N(2) are distinctly larger (117 - 121°) than the tetrahedral ones, the others are somewhat smaller. The dihedral angle between the two planes S(1)-Cu-N(1) and S(2)-Cu-N(2) is 89.6(2)°, so that a pseudo $C_2$ axis is present. The macrocycle is in the *ttt* configuration, in which all of the six-membered chelate rings adopt the twist configuration, as was found in the structure of the $Cu^{2+}$ complex with the $N_2S_2$ macrocycle 3,3,7,7,11,11,15,15-octamethyl-1,9-dithia-5,13-diazacyclohexadecane [20].

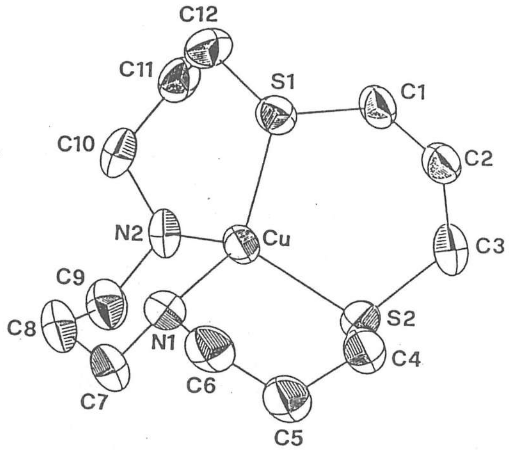


*Figure 3.* ORTEP plot of the $Cu^+$ complex with **7** and atomic numbering scheme.

## Conclusions

The $N_2S_2$ donor set is equally well suited for the complexation of $Cu^+$ and $Cu^{2+}$. This is unexpected considering the results for the $N_4$-macrocycles which strongly favour the cupric state [21] and for the $S_4$-analogues, which form only weak $Cu^{2+}$ complexes but greatly stabilize the $Cu^+$ state [22].

The first point to mention is the large difference between open chain and cyclic $N_2S_2$-ligands. For $Cu^{2+}$ the well known macrocyclic effect is observed, whereas for $Cu^+$ this is not the case. The open chain ligands despite their different chain lengths give a relatively constant ligand field, as can be seen from the absorption spectra of their $Cu^{2+}$ complexes (*Table 5*). This contrasts strongly with the macrocycles and is probably a consequence of the more rigid structures found in the macrocyclic complexes, which do not adapt themselves to the geometrical requirements of the metal ion, but impose their geometry onto the coordinated metal ion.

The second fact concerns the redox potential. Whereas it remains relatively constant for the open chain ligands, it changes by about 340 mV in the case of the macrocycles. Especially interesting are the high values for the 16-membered ligands **7** and **10**, which indicates a good stabilization of the cuprous state. As shown in the X-ray structure this is possible since the 16-membered ring is flexible enough to assume the typical tetrahedral geometry preferred by $Cu^+$.

In these studies considerable effort was put in the direct determination of the stability constants of the $Cu^+$ complexes by potentiometric titrations and into the control of the correlation between measured and calculated redox potentials. From our results three main conclusions can be put forward: 1) In most of the systems here studied a reasonable correlation between the results from cyclic voltammetry and from equilibrium measurements is obtained. Deviations are in the order of ± 20 mV or roughly 0.3 log units in relative stability. 2) However, relatively high discrepancies between the two methods are possible even when the cyclic voltammogram is quasi reversible. This is the case for ligand **6** with a difference of 69 mV in redox potential or 1.2 log units in relative stability. 3) The combination of cyclic voltammetry and equilibrium studies of the $Cu^{2+}$ complexes does not allow to determine other than the $CuL^+$ species. Specifically the protonated complexes $CuLH^{2+}$ and $Cu(an)LH_2^{3+}$ would not have been observed.

## Acknowledgements

This work was supported by the *Swiss National Science Foundation* (Project 20-32137.91) and this is gratefully acknowledged.

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# The Characterisation of Solvents using the Kamlet-Taft Solvatochromic Parameters

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For many years, solvent effects on kinetic and thermodynamic properties and processes were interpreted using single solvent parameters. For example, solvent effects on nonelectrolytes could be studied in terms of the cohesive energy density (CED) of the solvent, as $\delta_H^2$ where $\delta_H$ is the so-called Hildebrand solubility parameter. The CED is defined through equation 1,

$$\delta_H^2 = (\Delta Hv - RT)/V_1 \tag{1}$$

where $\Delta Hv$ is the enthalpy of vaporisation of the solvent at 298K, and $V_1$ is the solvent molar volume. Then the Raoults law activity coefficient of a solute, $\gamma_2$, is given by

$$RT\ln\gamma_2 = V_2(\delta_{H2} - \delta_H)^2 \tag{2}$$

where $V_2$ is the solute molar volume and $\delta_{H2}$ is the solute solubility parameter.[1] Since the Gibbs energy of transfer of the solute from some standard solvent A to any other solvent B is given by

$$\Delta G_t^o = RT\ln\ \gamma_2(A)/\gamma_2(B) \tag{3}$$

then equation (2) is equivalent to an equation for the solvent effect on the given nonelectrolyte, cf. equation (3).

For a dipolar solute, Kirkwood[2] calculated the electrostatic contribution to the Gibbs energy of transfer from a solvent medium of dielectric constant unity to one of dielectric constant $\Sigma$, as

$$\Delta G_e^o = RT\ln\gamma_2 = \frac{\mu_2^2}{r_2^3}\ \frac{\varepsilon - 1}{2\varepsilon + 1} \tag{4}$$

where the dipolar species is considered as a dipole of moment $\mu_2$ in a sphere of radius $r_2$. Although the Kirkwood equation (4) has seldom been used to study Gibbs energies of transfer as such, it has been employed from time to time in the study of solvent effects on rate constants.[1]

The situation with ionic species is quite different because the Born equation[3] has very often been used to analyze solvent effects on the Gibbs energy of ions or of pairs of dissociated ions,

$$\Delta G_e^o = \frac{Z^2}{2}\ \frac{1}{\varepsilon r} - \frac{1}{r} \tag{5}$$

Here, $\Delta G_e^o$ is again the electrostatic contribution to the Gibbs energy of transfer of an ion of charge Z and radius r from a dielectric of $\varepsilon=1$ to a dielectric continuum of $\varepsilon$. Equation(5) as such is not quantitatively very successful and has been amended on numerous occasions in order to obtain agreement with experiment, notably by adjusting the ionic radius r to some arbitrary

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[*] Plenary lecture held at the VI Meeting of the Portuguese Electrochemical Society, 7-10 October, 1992, Vila Real, Portugal.

*Portugaliæ Electrochimica Acta, 10 (1992) 121-134*