

## Ligand-Structure Effect on Electrochemical Reduction of Copper(II) Complexes\*\*

Ján Labuda<sup>1,\*</sup>, Pavol Tarapčík<sup>1</sup>, Adela Kotočová<sup>2</sup>, and Jozef Šima<sup>2</sup>

<sup>1</sup> Department of Analytical Chemistry, Slovak Technical University, CS-81237 Bratislava, Czechoslovakia

<sup>2</sup> Department of Inorganic Chemistry, Slovak Technical University, CS-81237 Bratislava, Czechoslovakia

**Summary.** Half-wave potentials for a one-electron reduction of copper(II) complexes containing polydentate ligands can be calculated using the equation  $E_{1/2} = E^0(\text{Cu}^{2+/+}) + \sum_i \sum_j \Delta E_i$  where  $\Delta E_i$  are contributions related to the electronic and steric properties of the ligands. The values of 18  $\Delta E_i$  contributions are presented and explained, and the effect of the solvents on the half-wave potentials is exemplified.

**Keywords.** Copper(II) complexes; Electrochemical reduction; Electronic and steric properties; Half-wave potential; Polydentate ligands.

### Einfluß der Ligandenstruktur auf die elektrochemische Reduktion von Kupfer(II)-Komplexen

**Zusammenfassung.** Die Halbwellenpotentiale einer Einelektronenreduktion von Kupfer(II)-Komplexen mit polydentaten Liganden kann mit der Gleichung  $E_{1/2} = E^0(\text{Cu}^{2+/+}) + \sum_i \sum_j \Delta E_i$  berechnet werden, wobei  $\Delta E_i$  die Beiträge sind, die mit den elektronischen und sterischen Eigenschaften der Liganden in Zusammenhang stehen. Es werden die Werte von 18  $\Delta E_i$ -Beiträgen präsentiert, außerdem wird der Lösungsmittelleffekt auf die Halbwellenpotentiale an Beispielen diskutiert.

### Introduction

One of the main aims in chemistry is the ability to predict properties of chemical compounds. To fulfill this aim a number of structure-property relationships have been found, and various empirical and theoretical approaches have been used.

A large number of chemical processes are redox reactions involving coordination compounds. The redox behaviour of such compounds is a complex function of mutually influenced parameters, from which the following are to be mentioned: a) the radius and the bonding ability of the central atom (particularly the energy and the symmetry of its redox orbitals), b) the electronic and steric properties of coordinated ligands (their bonding properties, electronic effects of their peripheral

\*\* Dedicated to Prof. Dr. Viktor Gutmann to his 70th birthday

substituents, rigidity), c) the structure of the chromophore, d) the properties of the reacting complex environment (donor-acceptor and dielectric constants of solvent, ionic strength).

Copper complexes, besides iron compounds, belong to the industrially and biochemically most important redox active species. As a consequence, there are attempts to find such structure-redox property interrelations that would allow to "tailor" the complex composition and structure with required redox properties.

Three main approaches have been used in calculations and predictions of the redox potential values for the complexes. The approach reviewed by Bursten and Green [1] relates the half-wave potentials of substituted carbonyls and organometallics to the HOMO and LUMO energies of the ligands. The authors discuss the additivity of electronic effects of individual ligands in the calculation of the  $E^0$  values.

Analyzing the experimental redox potentials and ligand properties in some dozens of copper(II) complexes, Addison proposed a method for the calculation of the half-wave potentials in his two successive papers [2, 3]. Addison suggested 6 contributions related to certain ligand parameters which should be taken into account when the potential of the Cu(II) complexes is to be obtained. This approach takes into consideration both the electronic and steric properties of the bonded ligands. It has exhibited its validity for the one-electron processes with the charge change localized predominantly on the copper central atom. Later on we re-elaborated and enlarged Addison's approach and succeeded in obtaining further contributions characterizing the polydentate ligand parameters [4].

Pavlishchuk [5] analyzed the changes in the  $E_{1/2}$  values for the Cu(II) complexes containing tetradentate macrocyclic ligands due to a different tetrahedrality of the ligands. He focused his attention on the stereochemical consequences for the redox potential values.

In this paper we present and rationalize a more complete set of the ligand contributions to the half-wave potential values obtained by the investigation of 134 copper(II) complexes with tetra-, penta-, and hexadentate ligands, point out the influence of solutions for the potential values, and indicate the possibility to employ such knowledge for tuning the redox properties of the copper(II) complexes.

## Experimental Part

Cu(II) complexes with the macrocyclic as well as the open-chain polydentate ligands of polyaza, aza-oxa, aza-thia, and polythia donor sets have been investigated. The values of  $E_{1/2}$  were determined by cyclic voltammetry [ $E_{1/2} = (E_{pc} + E_{pa})/2$ ] or direct current polarography in our laboratory as well as by other authors and are given in the literature [4, 6]. Various working electrodes (mainly platinum and mercury ones) and reference electrodes were used in the experiments, therefore all potential values have been recalculated to the potential of the standard hydrogen electrode (SHE).

A standard method of multiple linear regression analysis (robust variant) was used for the mathematical treatment of the experimental  $E_{1/2}$  data based on the equation

$$E_{1/2} = E^0(\text{Cu}^{2+/+}, \text{H}_2\text{O}) + \sum_i \sum_j \Delta E_i \quad (1)$$

where  $E^0(\text{Cu}^{2+/+}, \text{H}_2\text{O}) = 155 \text{ mV vs. SHE}$ ,  $i$  is the ligand parameter and  $j$  its frequency.

## Results and Discussion

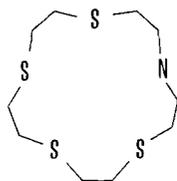
There is a great number of Cu(II) chelates described in the literature [6] which have been characterized voltammetrically in various solvents. However, the solvent

molecules can enter the primary coordination sphere of the complex particle and change substantially its redox properties as it is documented by data in Table 1. Therefore, it was necessary for the evaluation of the ligand-structure effect on  $E_{1/2}$  to select and transfer the data into one solvent scale. In this work the  $E_{1/2}$  values were obtained in three media (water, methanol, and acetonitrile); values recalculated to the aqueous scale have been taken into consideration.

The values of  $E_{1/2}$  measured in methanol were transferred to the aqueous scale by the subtraction of 60 mV which corresponds to the difference between the standard potential values of free solvated cations:  $E^0(\text{Cu}^{2+/+}, \text{CH}_3\text{OH}) = 215 \text{ mV}$  and  $E^0(\text{Cu}^{2+/+}, \text{H}_2\text{O}) = 155 \text{ mV}$ . For the conversion of the  $E_{1/2}$  values measured in acetonitrile to the water medium the correlation equation

$$E_{1/2}(\text{Cu}^{\text{II/I}}, \text{H}_2\text{O}) = 0.77 E_{1/2}(\text{Cu}^{\text{II/I}}, \text{CH}_3\text{CN}) \quad (2)$$

( $E_{1/2}$  values are in V vs. SHE) was obtained by the comparison of 23 half-wave potential data determined both in water and in acetonitrile.



For the evaluation of  $\Delta E_i$  contributions of the individual ligand parameters, the complexes were divided into two groups according to their ligand composition and structure: In the first group (53 complexes) the polydentate ligands could be characterized by small number of the basic parameters (No. 1, 2, 8–12 in Table 2) with high repetition rate. The values of these parameters were calculated only from this group of compounds. Other  $\Delta E_i$  contributions (No. 3–7, 13–18) were obtained from the second group of complexes (81 compounds) using the  $\Delta E_i$  values of the basic parameters as constants. The calculated values of all  $\Delta E_i$  contributions, their standard deviations as well as the significance of their determinations are listed in Table 2.

The value of the redox potential  $E^0$  for a  $\text{Cu}^{\text{II/I}}$  couple is, in general, determined by three factors:

1. the difference in Gibbs energy of solvation for the reactant and the product of an electrochemical process ( $\Delta G_{\text{out}}$ ),
2. the change in Gibbs energy accompanying the transformation of composition and structure of the reactant in its transition to the product ( $\Delta G_{\text{in}}$ ),
3. the electron affinity of the Cu(II) complex [for a process of Cu(II) reduction] or the ionization energy of the Cu(I) complex [for a process of Cu(I) oxidation].

Solvents exhibit several mutually related properties and in a particular case the redox behavior of complexes can be influenced predominantly by one of them [9]. It is manifested by two examples of the copper(II) compounds studied in our laboratory (Table 1). The value of  $E_{1/2}(\text{Cu}^{\text{II/I}})$  for the copper(II) complex with a tetraaza macrocyclic ligand,  $\text{Cu}(\text{TAAB})^{2+}$ , correlates in the best way with Gutmann's donor number. On the other hand, the  $E_{1/2}$  value for the N,N'-ethylene-bis(thioacetylacetoiminato) copper(II) complex,  $\text{Cu}(\text{sacacen})$ , depends mainly on the dielectric constant of the solvent used.

**Table 1.** Effect of solvent on the Cu(II)/Cu(I) redox potential

Solvent	DN <sup>a</sup>	$\epsilon$	$E_{1/2}$ , V vs. SHE	
			Cu(TAAB) <sup>2+</sup> , <sup>b</sup>	Cu(sacacen) <sup>c</sup>
Nitrobenzene	4.4	34.8	0.48	—
Acetonitrile	14.4	36.0	0.37	-0.87
Propandiol-1,2 carbonate	15.1	69.0	—	-0.83
Water	18.0	81.0	0.29	—
Methanol	19.0	32.6	0.35	—
Ethanol	20.0	24.3	0.33	—
N-methylformamide	—	182.4	—	-0.71
Dimethylformamide	26.6	36.1	0.29	—
Dimethylsulphoxide	29.8	45.0	0.21	-0.85
Hexamethylphosphortriamide	38.8	29.6	—	—

<sup>a</sup> DN donor number in kcal mol<sup>-1</sup> [9]

<sup>b</sup> Ref. [7]

<sup>c</sup> Ref. [8]

The determination of the exact value of  $\Delta G_{\text{out}}$  is, however, a complicated task. Moreover, such a value can hardly be related to the empirical  $\Delta E_i$  contributions. Since we will discuss processes associated with the same changes in charge for the complexes with similar structural properties, for the investigated series of the complexes, the  $\Delta G_{\text{out}}$  value may be regarded as roughly similar and its contribution to the changes in the  $E_{1/2}$  values will be omitted.

The most characteristic chromophore structure of the Cu(II) complexes in the solid state and solutions is elongated tetragonal-bipyramidal. The coordination number can be expressed as 4 + 2. The copper(I) complexes prefer the tetrahedral structure of their polyhedra. The rigidity of the coordination sphere in the above mentioned structures and the energy needed for their mutual changes ( $\Delta G_{\text{in}}$ ) are parameters determining substantially the  $E^0$  value for the reduction of Cu(II) to Cu(I) complex. The empirically found values  $\Delta E_i$  for the parameters No. 10–14 can be taken as a measure of  $\Delta G_{\text{in}}$ . Qualitatively speaking, a stronger rigidity of the square-planar tetradentate ligand in tetragonal-bipyramidal coordination bonded to the central atom of Cu(II) causes a higher stabilization of Cu(II) (more negative  $\Delta E_i$  contribution). By contrast, a greater ability of the tetradentate (generally polydentate) ligand to adopt the tetrahedral coordination causes a higher stabilization of Cu(I), (more positive  $\Delta E_i$  contribution). The ability of a polydentate ligand to undergo stereochemical changes depends on its cyclic (non-cyclic) character (parameter No.10), internal structure (5-membered metallo-rings linked in a chelate, parameter No. 11), size of the cavity (14-membered macroring is most suitable for Cu(II), parameter No. 12) and the presence of unsaturated bonds system (parameter No. 13). The stereochemical contributions  $\Delta E_i$  can be related to Pavlishchuk's parameter of tetrahedrality [5] or to the  $\lambda_{\text{in}}$  term in Marcus' theory. It should be mentioned that the parameter concerning conjugate bonds (No. 13)

**Table 2.** The contributions  $\Delta E_i$  of polydentate ligands to the half-wave reduction potential of Cu(II) complexes

No.	Parameter	Number of data	$\Delta E_i$ , mV	Significance, %
1.	-NH- aliphatic	149	$-105 \pm 10$	99.98
2.	-N= aliphatic	70	$-63 \pm 15$	99.98
3.	N (pyridine, quinoline)	56	$-2 \pm 5$	45
4.	N (pyrrole)	6	$-246 \pm 19$	99.98
5.	N (imidazole)	4	$26 \pm 26$	60
6.	N (pyrazole)	8	$106 \pm 16$	99.98
7.	O <sup>-</sup>	14	$-326 \pm 30$	99.98
8.	COO <sup>-</sup>	30	$-57 \pm 17$	99.9
9.	-S- (-SH)	133	$140 \pm 5$	99.98
10.	macrocycle	32	$-87 \pm 43$	95
11.	5-membered metallo-rings linked in chelate	46	$-71 \pm 16$	99.98
12.	difference of atomicity from 14	78	$70 \pm 12$	99.98
13.	conjugated system	4	$352 \pm 40$	99.98
14.	octahedral geometry	6	$-463 \pm 46$	99.98
15.	CH <sub>3</sub> group on N donor	15	$102 \pm 17$	99.98
16.	CH <sub>3</sub> group on S donor	6	$49 \pm 18$	98
17.	CH <sub>3</sub> group on $\alpha$ -carbon	69	$-33 \pm 10$	99.9
18.	CH <sub>3</sub> group on $\beta$ -carbon	14	$61 \pm 16$	99.9

expresses both the stereochemical and electronic influences of unsaturated polydentate ligands on the  $E_{1/2}$  value.

The electron affinity of the Cu(II) complexes or the ionization energy of the Cu(I) complexes depend on several mutually related factors, such as:

- the electronic properties of the central atom itself (for Cu(II) complexes the redox orbital  $\text{Cu}3d_{x^2-y^2}$  is localized in the equatorial plane formed by a polydentate ligand),

- the symmetry of the complex chromophore and the ligand field strength (these factors determine the splitting of Cu3d orbitals and the energy of the redox orbital),

- the donor-acceptor properties of the coordinated ligands (including the presence of unoccupied  $\pi^*$  orbitals allowing a delocalization of the redox orbital),

- the peripheral groups exhibiting various electron-donating and electron-withdrawing effects.

All these factors, though to a different extent, contribute to the changes in the  $E^0$  values in comparison with  $E^0$  for free solvated ions.

Based on the available experimental data, the contributions listed in Table 2 (parameters No. 1-9) are related predominantly to the third of the above factors, i.e. to the bonding properties of coordinated polydentate ligands. The effect of a certain donor atom on the electronic system of the central atom is conditioned by its electronegativity and bonding mode within the ligand framework. This is a reason for the different contributions  $\Delta E_i$  for the same donor atom. For oxygen

donor atoms we have obtained negative values of the  $\Delta E_i$  contributions, i.e. these atoms stabilize Cu(II). Surprisingly the high negative  $\Delta E_i$  value for the phenol-like oxygen (parameter No. 7) can be understood by its hardness and the negative charge in the ligands of the *acacen* and *salen* type. Sulphur atoms, due to their softness and ability of originally vacant S3d orbitals to interact with Cu3d orbitals, stabilize Cu(I). Based on the available data, the effect of sulphur donor atoms does not seem to depend substantially on the bonding mode of these atoms.

Nitrogen donor atoms exhibit both the stabilizing and the labilizing effects on the oxidation state II of copper. The nitrogen donor atoms, as a part of pyrroles, Schiff bases or aliphatic amines, stabilize Cu(II). In other cases, Cu(I) is stabilized (pyrazole can serve as an example). Being a part of pyridine, quinoline or imidazole, the nitrogen donor atoms do not change the redox potential of the Cu<sup>II/I</sup> redox couple to a significant extent. The reason for such a behaviour might be in different HOMO energy and symmetry as well as in a steric availability for the interaction with the copper central atom.

The energy of the redox orbital localized on the central atom (and thus the  $E^0$  value of the complexes) can be tuned by the peripheral substituents of polydentate ligands. The real impact on the  $E^0$  value will be dependent on two factors:

- the nature of the substituent itself (its electron donating or withdrawing properties) which can be characterized by the Hammett or Taft parameters,
- the position of the substituent in a polydentate ligand skeleton.

The importance of the second factor is clearly shown in Table 2 (parameters No. 15–18). It follows from the data that the ability of a CH<sub>3</sub>-group to influence the central atom is modified by the position of this group. The positive value of some  $\Delta E_i$  contributions (parameters No. 15, 16, and 18) indicate that in these cases the effect of the ligand methylation on the redox potential is connected with structural and geometric consequences rather than the inductive influence of the CH<sub>3</sub>-group. Such effect was ascribed to weaker solvation of methylated species which leads to destabilization of the copper(II) complexes [10].

The quantitative evaluation of peripheral substituent effects needs a large number of experimental data for the complexes with a variety of modified structures of ligands. It should be pointed out that in all effects discussed above, the properties of the central atoms play a significant role. The values of the  $\Delta E_i$  contributions can be used for the calculation of the redox potential of the mutual conversion Cu(II)  $\rightleftharpoons$  Cu(I) only. They are neither applicable for another type of reactions (e.g. for the reaction Cu(III)  $\rightleftharpoons$  Cu(II)) nor for reactions of other central atom complexes.

We tested our method by the comparison of experimental and calculated  $E_{1/2}$  values for the Cu(II) complexes which have been appeared lately in the literature. The potential data measured in acetonitrile solutions were transferred to the water scale according to Eq. (2). The results obtained are summarized in Table 3.

The following example demonstrates the type of the ligand structure of the complexes involved as well as our approach in the calculation of the  $E_{1/2}$  values. The macrocyclic ligand [15]*aneNS*<sub>4</sub> (Fig. 1) contains one aliphatic nitrogen donor atom (parameter No. 2), four thiaether donor atoms (parameter No. 9) and it consists of one macroring (parameter No. 10) which forms the 5-membered metallo-rings linked within the Cu(II) chelate structure (parameter No. 11). The cavity of the ligand is determined by the size of the macroring (equal to 15) which differs by one atom (parameter No. 12) from the most stable 14-membered cycle. Using

**Table 3.** Comparison of experimental and calculated  $E_{1/2}$  values for some recently prepared complexes

Complex	$E_{1/2}$ , exptl. <sup>a</sup>	$E_{1/2}$ , water-based <sup>a</sup>	$E_{1/2}$ , calcd. <sup>a</sup>
Cu([15]aneNS <sub>4</sub> ) <sup>2+</sup>	0.74 <sup>b</sup>	0.57	0.52
Cu(biquinen) <sup>2+,c</sup>	0.22 <sup>d</sup>	0.17	0.17
Cu(biquidien) <sup>2+,c</sup>	-0.06 <sup>d</sup>	-0.04	-0.01

<sup>a</sup> All potential values in V vs. SHE

<sup>b</sup> In acetonitrile solution, Ref. [11]

<sup>c</sup> Prepared and kindly supplied by Prof. H. Elias, Darmstadt University, Ref. [12]

<sup>d</sup> In acetonitrile solution, 0.1 M NaClO<sub>4</sub>, mercury electrode, own results

the  $E_i$  contributions given in Table 2, the  $E_{1/2}$  value for the Cu([15]aneNS<sub>4</sub>)<sup>2+</sup> complex (see formula) in the aqueous medium can be calculated according to Eq. (1):

$$E_{1/2} = 155 + \Delta E^2 + 4 \Delta E^9 + \Delta E^{10} + \Delta E^{11} + \Delta E^{12} = 523 \text{ mV vs. SHE.}$$

From Table 3 it is obvious that the agreement of the experimental and calculated  $E_{1/2}$  values is within the experimental error. This fact allows us to propose the use of our  $\Delta E_i$  contributions both for the calculation of the redox potential (based on a known chromophore structure) and vice versa for the prediction of ligand structure and composition in order to design required redox properties.

Moreover, the proposed approach seems to be suitable for the estimation of the Cu(II) complex chromophore structure in solution. The complex Cu([15]aneNS<sub>4</sub>)<sup>2+</sup> can serve as an example. The comparison of the experimental  $E_{1/2}$  value (0.57 V) with the calculated values for the complex chromophores CuNS<sub>4</sub> (0.52 V), CuS<sub>4</sub> (0.63 V) and CuNS<sub>3</sub> (0.38 V) allow us to formulate the chromophore composition as being CuNS<sub>4</sub> in solution. This result is in accordance with spectral measurements [11].

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Received September 9, 1991. Revised October 10, 1991. Accepted December 3, 1991