

# Electrochemical studies of copper(II) complexes with Schiff-base ligands

Santiago Zolezzi <sup>a</sup>, Evgenia Spodine <sup>a,b</sup>, Antonio Decinti <sup>a,\*</sup>

<sup>a</sup> *Departamento de Química Inorgánica y Analítica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233 Santiago, Chile*

<sup>b</sup> *Facultad de Ciencias Químicas y Farmacéuticas, Centro de Investigación Interdisciplinaria Avanzada en Ciencias de los Materiales, Universidad de Chile, Casilla 233 Santiago, Chile*

---

## Abstract

The electrochemical reduction of copper(II) complexes with salen Schiff-base ligands derived from ethylenediamine or (*R,R*) or (*S,S*)-1,2-diphenylethylenediamine and 5-methoxy, 5-bromo and 5-nitrosalicylaldehyde have been studied by cyclic voltammetry in the potential range +1 to -2.3 V in dimethyl sulfoxide (DMSO) as a solvent. The resulting voltammograms consist of a single quasi-reversible one-electron transfer attributable to the couple [Cu(II)L]/[Cu(I)L]<sup>-</sup>. Trends in cathodic peak potential ( $E_{pc}$ ) values are observed which can be correlated with the electronic effects of the 5-substituents of the Schiff-base ligands. Changes in the basicity of the ligand groups are determinant for such electrochemical trends.

*Keywords:* Salen Cu(II) complexes; Schiff-base ligands; Cyclic voltammetry; Hammett substituent constants

---

## 1. Introduction

Transition metal complexes with tetradentate Schiff-base ligands have been extensively investigated as catalysts for a number of organic redox reactions and electrochemical reduction processes [1–5]. Salen complexes have also been recently used as catalytically active materials to develop surface-modified electrodes for sensing applications [6,7]. Cyclic voltammetry has been a useful tool to investigate the mechanisms of catalysis by Schiff-base metal complexes as well as to study the structure–reactivity relationships in these compounds [3,5,8]. We have previously studied the syntheses and spectroscopic characterisation of copper(II) complexes of salen Schiff bases derived from ethylenediamine, (1*R*,2*R*)- and (1*S*,2*S*)-1,2-diphenylethylenediamine, and 5-nitro, 5-bromo and 5-methoxysalicylaldehyde [9]. Electronic spectra of these complexes in the d–d region suggest that the ligand field strength varies as a function of the 5,5'-sub-

stituents according to the sequence NO<sub>2</sub> < Br < H < OCH<sub>3</sub>. Hence, it should be expected that the thermodynamic stabilities of such complexes follow a similar order which, in turn, should influence both their electrochemical properties and potential catalytic behaviour. Properties of these complexes, as potential catalysts for epoxidation of olefins are being tested at present in our laboratory. In connection with such studies, herein, we report an electrochemical study of the above mentioned Schiff-base ligands and their respective copper(II) complexes in dimethyl sulfoxide (DMSO) as a solvent. Copper(II) complexes whose electrochemical characterisation has been reported previously [10,11] have been included in this report in order to parallel both Schiff-base ligand series, the ethylenediamine and the 1,2-diphenylethylenediamine derivatives.

## 2. Experimental

Reagent grade chemicals were obtained from Aldrich and were used as provided. HPLC grade DMSO was

---

\* Corresponding author. Tel.: +56-2-6782851; fax: +56-2-7370567.

*E-mail address:* [mroa@ciq.uchile.cl](mailto:mroa@ciq.uchile.cl) (A. Decinti).

dried over molecular sieve previously dried at 105 °C under vacuum, redistilled and stored under N<sub>2</sub> over molecular sieve before use. The Schiff bases and copper(II) complexes under study have been prepared previously [9]. For comparative purposes, the redox couple Cu(II)/Cu(I) of Cu(ClO<sub>4</sub>)<sub>2</sub> in DMSO was also considered. Moreover, in the cases of sparing solubility in DMSO, dimethylformamide (DMF) was used. Cyclic voltammetry was carried out under pure dry nitrogen in a three-electrode cell with a vitreous carbon working electrode, a platinum counter electrode and an aq. saturated AgCl/Ag reference electrode ( $E = -0.0474$  V vs. the saturated calomel electrode). Supporting electrolyte was 0.05 M *n*-Bu<sub>4</sub>NClO<sub>4</sub> (TBAP). Cyclic voltammograms were scanned at room temperature (r.t.) in the potential range of +1 to -2.3 V, at sweep rates ( $v$ ) between 25 and 1000 mV s<sup>-1</sup>, and were recorded with a Metrohm VA-693 potentiostat equipped with a VA-694 stand and connected to a personal computer. Oxidative CV measurements were not performed because, according to literature data on copper(II) complexes with similar coordination spheres [8], the CV wave for the process Cu(II)/Cu(III) falls at potentials near +1.48 V, i.e. outside the potential range allowed by the electrode-solvent system here used. Coulometric measurements were carried out at

r.t., under pure dry nitrogen, with a Princeton Applied Research (PARC) model 173 potentiostat coupled to a PARC model 179 digital coulometer, with a platinum mesh working electrode, a platinum coil counter electrode and an aq. saturated AgCl/Ag reference electrode. Controlled-potential electrolysis measurements were performed at r.t., under pure dry nitrogen, with a Wenking POS 88 potentiostat, using an electrochemical cell modified for spectrophotometric measurements (optical path length, 1 cm). Here a platinum coil working electrode, a platinum coil counter electrode and an aq. saturated AgCl/Ag reference electrode were used. Absorption spectra were recorded in the visible region on a UV3 Unicam spectrometer.

### 3. Results and discussion

The ligands and metal complexes under study were labelled as shown in Table 1 by use of the atom-labelling scheme given in Fig. 1. The voltammetric parameters obtained for the ligands and their respective copper(II) complexes are listed in Table 2. Moreover, typical voltammograms of a given ligand and its respective copper(II) complex are shown in Fig. 2.

#### 3.1. Schiff-base ligands

For all Schiff-base ligands studied, except compounds **4** and **4R** (nitro derivatives), cyclic voltammograms at 100 mV s<sup>-1</sup> consist of a single cathodic peak at potentials ranging from -1.6 to -2.0 V; no anodic wave occurs in the reverse scan. This behaviour was observed for a wide range of scan rates from 25 to 1000 mV s<sup>-1</sup>. Hence, such a reduction process should correspond to a totally irreversible electron transfer. Voltammograms of compounds **4** and **4R** show the above-mentioned cathodic peak at -1.13 V (Table 2). Additionally, they exhibit CV waves in the range -1.4 to -1.8 V, which may be ascribed to the reduction of the nitro groups [15]. Coulometric measurements of compound **2** in DMSO indicate that the cathodic wave observed corresponds to a two-electron transfer. In fact, the shapes of the cathodic waves suggest that they would consist of two overlapped one-electron processes. A similar result has previously been reported for this compound in DMF, but in the presence of 2 equiv. of acetic acid [12]. Such a requirement would arise from the fact that both the dielectric constant and the dipole moment of DMF are smaller than those of DMSO. For all Schiff bases under study, this irreversible reduction peak would be ascribed to an intramolecular reductive coupling of the two imine groups to yield a piperazine [12–14]. Such a process would involve self-protonation reactions where the phenolic hydroxyl groups act as proton donors.

Table 1  
Labelling for the Schiff-base ligands and their copper(II) complexes

Ligand	Complex	Substituents	
		5,5'	8,8'
<i>Ethylenediamine derivatives</i>			
<b>1</b>	Cu1	OCH <sub>3</sub>	H
<b>2</b>	Cu2	H	H
<b>3</b>	Cu3	Br	H
<b>4</b>	Cu4	NO <sub>2</sub>	H
<i>1,2-Diphenylethylenediamine derivatives</i>			
<b>1R</b>	Cu1R	OCH <sub>3</sub>	( <i>R,R</i> )C <sub>6</sub> H <sub>5</sub>
<b>1S</b>	Cu1S	OCH <sub>3</sub>	( <i>S,S</i> )C <sub>6</sub> H <sub>5</sub>
<b>2R</b>		H	( <i>R,R</i> )C <sub>6</sub> H <sub>5</sub>
<b>2S</b>	Cu2S	H	( <i>S,S</i> )C <sub>6</sub> H <sub>5</sub>
<b>3R</b>	Cu3R	Br	( <i>R,R</i> )C <sub>6</sub> H <sub>5</sub>
<b>4R</b>	Cu4R	NO <sub>2</sub>	( <i>R,R</i> )C <sub>6</sub> H <sub>5</sub>

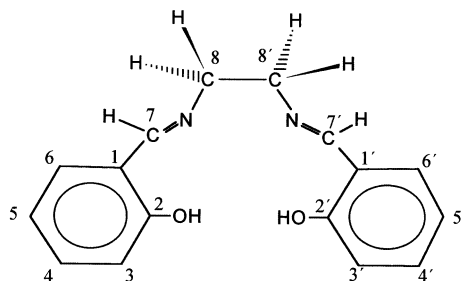


Fig. 1. Atom labelling scheme for salen copper(II) complexes.

Table 2  
Cyclic voltammetric parameters for the Schiff-base ligands and their copper(II) complexes, and calculated values for  $\Delta \log \beta = \log \beta(\text{Cu(II)L}) - \log \beta(\text{Cu(I)L}^-)$

Ligand	Complex						
	$E_{\text{pc}}$ (V)		$E_{\text{pc}}$ (V)	$E_{1/2}$ (V)	$\Delta E_{\text{p}}$ (mV)	$i_{\text{pa}}/i_{\text{pc}}$	$\Delta \log \beta$
<i>Ethylenediamine derivatives</i>							
<b>1</b>	−1.97	Cu1	−1.26	−1.19	130	0.50	21.4
<b>2</b>	−1.79	Cu2	−1.23	−1.17	115	0.73	20.9
<b>3</b>	−1.62	Cu3 <sup>a</sup>	−1.14	−1.07	140	0.46	19.4
<b>4</b>	−1.13	Cu4	−0.91	−0.86	111	0.27	15.6
<i>1,2-diphenylethylenediamine derivatives</i>							
<b>1R</b>	−1.87	Cu1R	−1.28	−1.21	113	0.96	21.8
		Cu1S	−1.28	−1.23	100	1.01	21.8
<b>2R</b>	−1.85	Cu2S	−1.22	−1.17	101	0.97	20.9
<b>3R</b>	−1.69	Cu3R	−1.08	−1.05	91	0.80	18.5
<b>4R</b>	−1.13	Cu4R	−0.95	−0.91	94	0.88	16.3
Cu(ClO <sub>4</sub> ) <sub>2</sub> <sup>b</sup>			0.01	0.05	91	0.97	

<sup>a</sup> For Cu3, the solvent was DMF.

<sup>b</sup> CV parameters of Cu(ClO<sub>4</sub>)<sub>2</sub> correspond to the couple Cu(II)/Cu(I). For the couple Cu(I)/Cu<sup>0</sup>  $E_{\text{pc}} = -0.57$  V and  $E_{1/2} = -0.26$  V.

On the other hand, in each series of ligands, the cathodic peak potential ( $E_{\text{pc}}$ ) corresponding to the intramolecular reductive coupling of the imine groups varies as can be expected from the electronic effects of the substituents at positions 5,5'. Thus,  $E_{\text{pc}}$  becomes less negative according to the sequence  $\text{OCH}_3 < \text{H} < \text{Br} < \text{NO}_2$ , i.e. in order of an increase in both electron-withdrawing and  $\pi$ -acceptor qualities of the substituents. In fact, for both ethylenediamine and 1,2-diphenylethylenediamine derivatives, Hammett type relationships were found between the  $E_{\text{pc}}$  values and the appropriate *para*-substituent parameters [16]. Such correlations are shown in Fig. 3. However, since the substituents at positions 5,5' are indeed *para*- to the respective phenolic hydroxyl groups, the occurrence of these Hammett type correlations would indicate that the  $E_{\text{pc}}$  for the reductive coupling of the imine groups actually varies as a function of the acidity of the hydroxyl group through the ligand series. This fact agrees with a mechanism involving self-protonation reactions for the electrochemical reduction of the imine groups in the Schiff bases under study.

### 3.2. Copper(II) complexes

The cyclic voltammetric curves for the electrochemical reduction of the studied copper(II) complexes (Table 2) exhibit a redox couple at potentials in the range of  $-0.91$  to  $-1.28$  V, which can be attributed to the reduction of the metal centre [10,11]. Voltammograms of complexes Cu4 and Cu4R show additional CV waves in the range of  $-1.5$  to  $-1.8$  V, which correspond to the reduction of the nitro groups. Moreover, for all complexes studied, the cathodic wave

corresponding to the irreversible two-electron reduction of the imino groups is no longer observed. This fact indicates that, owing to the lack of transferable hydroxylic protons, the reduction potentials of the dianionic ligands have been shifted beyond the lower limit of the potential interval considered in the experimental measurements [12].

On the other hand, the  $\Delta E_{\text{p}}$  data listed in Table 2, though being much larger than the theoretical value for an electrochemically reversible one-electron process, at least suggest that the reduction of copper(II) in the complexes under study should correspond to a one-electron charge transfer. Actually, this possibility has been corroborated through coulometric measurements on the system Cu2 in DMSO. The exceedingly large  $\Delta E_{\text{p}}$  val-

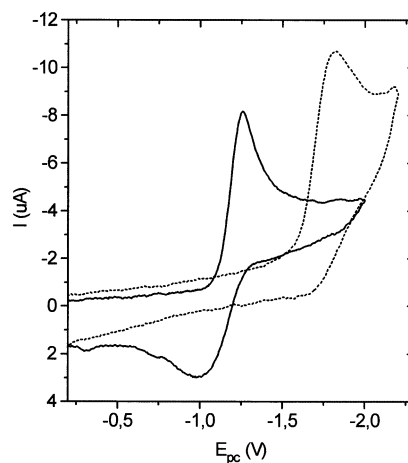


Fig. 2. Cyclic voltammograms recorded for the reduction of 1.0 mM ligand **2** (----) and 1.0 mM complex Cu2 (—) at a vitreous carbon electrode in DMSO containing 0.05 M TBAP. Scan rate, 0.1 V s<sup>-1</sup>.

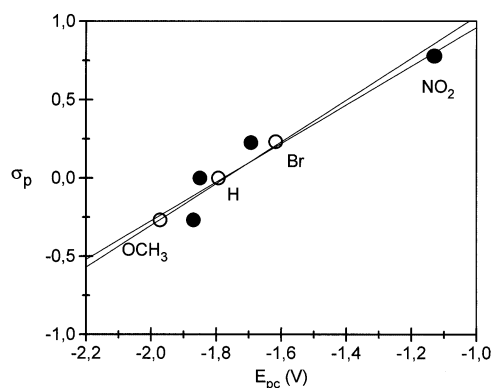


Fig. 3. Correlation between the  $E_{pc}$  values for Schiff-bases and the respective  $\sigma$  substituent constants (for  $p$ -substitution). Ethylenediamine derivatives ( $\circ$ )  $r = 0.998$ ; 1,2-diphenylethylenediamine derivatives ( $\bullet$ )  $r = 0.960$ .

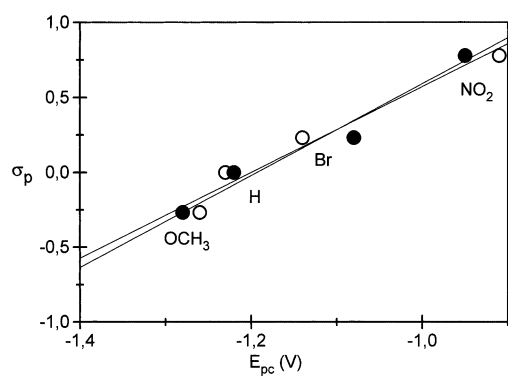


Fig. 4. Correlation between the  $E_{pc}$  values for copper(II) complexes with Schiff-base ligands and the respective  $\sigma$  substituent constants (for  $p$ -substitution). Ethylenediamine derivatives ( $\circ$ )  $r = 0.982$ ; 1,2-diphenylethylenediamine derivatives ( $\bullet$ )  $r = 0.983$ .

ues for the electrochemical reduction of copper(II) in these complexes would be due to both a quasi-reversible behaviour of the couple  $[\text{Cu(II)L}] + e^- = [\text{Cu(I)L}]^-$  under the  $v$  conditions here adopted and the non-aq. nature of the systems [8,17]. For all complexes, CV measurements at different  $v$ , in the range 25–1000  $\text{mV s}^{-1}$ , indicate that the  $E_{pc}$  values are only slightly dependent upon the  $v$ . Furthermore, in all cases a linear relationship between the cathodic peak current ( $i_{pc}$ ) and the square root of the  $v$  ( $v^{1/2}$ ) was observed. This fact implies that these electrochemical processes are mainly diffusion-controlled.

As can be noticed in Table 2, the  $E_{pc}$  and  $E_{1/2}$  values for the copper complexes are more negative by 1.1–1.7 V compared with the respective values for the  $\text{Cu}(\text{ClO}_4)_2$  couple in DMSO. This indicates that, for the Schiff-base ligands herein studied, the chelates of copper(II) are considerably more stable than the respective chelates of copper(I). Accordingly, the differences between the logarithms of the formation constants ( $\beta$ ) of these complexes were estimated through the expression:

$$\begin{aligned} \Delta \log \beta &= \log \beta(\text{Cu(II)L}) - \log \beta(\text{Cu(I)L}^-) \\ &= (E^{\circ'} - E)/0.059 \end{aligned}$$

where  $E^{\circ'}$  stands for the reduction potential of the reference  $\text{Cu(II)/Cu(I)}$  redox couple and  $E$  for the reduction potential of the couple  $[\text{Cu(II)L}]/[\text{Cu(I)L}]^-$ . In such calculations, the approximation  $E^{\circ'} - E = E_{pc}[\text{Cu}(\text{ClO}_4)_2] - E_{pc}[\text{Cu(II)L}]$  was taken. The parameters  $\Delta \log \beta$  thus calculated are included in Table 2. As can be seen in this table,  $E_{pc}$  becomes less negative in the sequence  $\text{OCH}_3 < \text{H} < \text{Br} < \text{NO}_2$  and, hence,  $\Delta \log \beta$  decreases according to  $\text{OCH}_3 > \text{H} > \text{Br} > \text{NO}_2$ , i.e. in a sequence of increasing electron-withdrawing effects of the substituents at positions 5,5'. Similar results have been reported previously for analogous copper(II) and nickel(II) systems, and have been interpreted by assuming that the strong electron-withdrawing effects stabilise the lower oxidation state [8]. However, another possibility would be that, owing to the decrease in donor ability of the ligand groups (mainly the phenoxy groups) the stabilities of both  $[\text{Cu(II)L}]$  and  $[\text{Cu(I)L}]^-$  decrease through the above mentioned sequence, but for the latter to a lesser extent. This would be a consequence of an increase in the flexibility of the coordination sphere over such a series, which should favour the stability of the copper(I) complex. Moreover, for both metal complex series, Hammett type relationships were found between  $E_{pc}$  and the appropriate  $para$ -substituent parameters [16] which reflect the variation of the electrode potential as a function of the electron-withdrawing ability of the substituents at positions 5,5'. Such correlations are shown in Fig. 4. These results indicate that the decrease in basicity of the phenoxy group through the sequence  $\text{OCH}_3 > \text{H} > \text{Br} > \text{NO}_2$  would be determinant for the electrochemical trends observed.

On the other hand, since the  $\Delta \log \beta$  data indicate that, for each system the  $\text{Cu(II)}$  complex should be considerably more stable than the  $\text{Cu(I)}$  one, a less negative electrode potential for the couple  $[\text{Cu(I)L}]^-/\text{Cu}^0$  than for the couple  $[\text{Cu(II)L}]/[\text{Cu(I)L}]^-$  should be expected. Hence, it should also be expected that the electrochemical reduction of the copper(II) complexes occurs through a two-electron charge transfer, i.e. by an EE or EC mechanism. Reduction of  $[\text{Cu(II)L}]$  to  $\text{Cu}^0$  has not been observed, not even in the coulometric experiments. Thus, the copper(I) complexes would behave as kinetically inert to both cathodic heterogeneous charge transfer and disproportionation. Nevertheless, if the solution resulting from the coulometric experiment on the complex Cu2 is allowed to stand overnight under pure dry nitrogen, a partial recovery of its original colour is observed. This suggests that, at least for the mentioned complex, disproportionation of  $[\text{Cu(I)L}]^-$  occurs to a some extent. This fact has been confirmed by means of spectroelectrochemical measure-

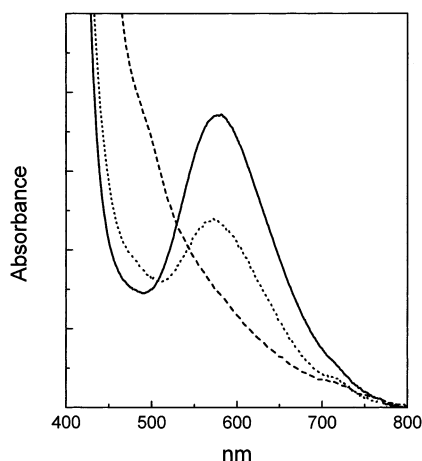


Fig. 5. Absorption spectrum in the d–d band region of 1 mM Cu<sub>2</sub> in DMSO containing 0.05 M TBAP, (—) before electrochemical reduction; (---) after reduction; and (···) allowed to stand for 15 h after reduction, under pure dry nitrogen, at r.t.

ments on the complexes Cu<sub>2</sub> and Cu<sub>4</sub>. Results obtained for Cu<sub>2</sub> are shown in Fig. 5. Such results can be related with the  $i_{pa}/i_{pc}$  data listed in Table 2. Accordingly, for complexes with 8,8'-diphenyl substituted Schiff-base ligands the ratio of  $i_{pa}/i_{pc}$  takes values close to one, as required for a reversible or quasi-reversible charge transfer without coupled chemical reactions. Instead, for complexes with Schiff-base ligands derived from ethylenediamine  $i_{pa}/i_{pc} < 1$  is always observed. This fact suggests that the electrochemical reduction of these complexes involves an EC mechanism consisting of a reversible or quasi-reversible one-electron heterogeneous charge transfer followed by an irreversible chemical reaction, i.e. the disproportionation of [Cu(I)L]<sup>-</sup>. It has previously been suggested that the ratio  $i_{pa}/i_{pc}$  smaller than unity observed for complex Cu<sub>2</sub> in DMF can be attributed to the presence of traces of water in the solvent-supporting electrolyte [10]. Accordingly, additional experiments performed in our laboratory have shown that, on increasing the water concentration of the CuIS system from traces to 5 M, the peak-current ratio decreases from 1.01 to 0.87. However, as can be seen in Table 2, peak-current ratios for complexes with Schiff-base ligands derived from ethylenediamine are smaller than 0.87. Thus, the somewhat different behaviour of copper(II) complexes with 8,8'-diphenyl substituted Schiff-base ligands can be ascribed to a greater

kinetic inertness to disproportionation of the respective copper(I) complexes. Since the disproportionation reaction of Cu(I) complexes should involve a bimolecular process, it could be assumed that such a greater kinetic inertness arises from the occurrence of steric hindrance effects involving the phenyl substituents in the transition state.

### Acknowledgements

Financial support from FONDAP, project 11980002, is gratefully acknowledged.

### References

- [1] L. Canali, D.C. Sherrington, *Chem. Soc. Rev.* 28 (1998) 85.
- [2] A.A. Isse, A. Gennaro, E. Vianello, *J. Electroanal. Chem.* 444 (1998) 241.
- [3] D. Pletcher, H. Thompson, *J. Electroanal. Chem.* 464 (1999) 168.
- [4] T. Okada, K. Katou, T. Hirose, M. Yuasa, I. Sekine, *J. Electrochem. Soc.* 146 (1999) 2562.
- [5] L.J. Klein, K.S. Alleman, D.G. Peters, J.A. Karty, J.P. Reilly, *J. Electroanal. Chem.* 481 (2000) 24.
- [6] P.H. Aubert, A. Neudeck, L. Dunsch, P. Audebert, P. Capdevielle, M. Maumy, *J. Electroanal. Chem.* 470 (1999) 77.
- [7] L. Mao, K. Yamamoto, W. Zhou, L. Jin, *Electroanalysis* 12 (2000) 72.
- [8] E.G. Jäger, K. Schuhmann, H. Görls, *Inorg. Chim. Acta* 255 (1997) 295.
- [9] S. Zolezzi, A. Decinti, E. Spodine, *Polyhedron* 18 (1999) 897. (Owing to typing errors in the original manuscript, in this reference, page 900, right-hand column, line 18, it says: "... NO<sub>2</sub> > Br > H > OCH<sub>3</sub>. Hence, the π-donor character...". It should say: "... NO<sub>2</sub> < Br < H < OCH<sub>3</sub>. Hence, the σ-donor character...". Moreover, in page 903, figure 5, in the wave number-axis it says: '17000' and '18000'; it should say: "17" and "18").
- [10] M.J. Samide, D.G. Peters, *J. Electroanal. Chem.* 443 (1998) 95.
- [11] M.M. Bhadbhade, D. Srinivas, *Inorg. Chem.* 32 (1993) 6122.
- [12] A.A. Isse, A. Gennaro, E. Vianello, *Electrochim. Acta* 42 (1997) 2065.
- [13] T. Shono, N. Kise, E. Shirakawa, H. Matsumoto, E. Okazaki, *J. Org. Chem.* 56 (1991) 3063.
- [14] N. Kise, H. Oike, E. Okazaki, M. Yoshimoto, T. Shono, *J. Org. Chem.* 60 (1995) 3980.
- [15] J.A. Squella, G. Jimenez, S. Bollo, L.J. Núñez-Vergara, *Electrochim. Acta* 42 (1997) 2305.
- [16] H.H. Jaffé, *Chem. Rev.* 53 (1953) 191.
- [17] C.L. Bailey, R.D. Bereman, D.P. Rillema, R. Nowak, *Inorg. Chem.* 23 (1984) 3958.