Substituent Effects on the Redox Properties of some Bis(*N*-Arylpyrrole-2-carboxaldiminato)-copper(II) Complexes†

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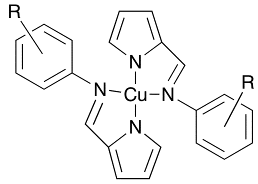
Cyclic voltammetry shows that the reduction of bis(*N-para* and *meta* substituted phenylpyrrole-2-carboxaldiminato)-copper(II) complexes are considered quasireversible and irreversible in the case of *ortho* derivatives, the stereochemical effect being more important than the inductive effect.

The metal chelate complexes of condensed pyrrole ring systems, such as dipyrromethenes, phthalocyanines or porphyrins, which play a crucial role in biological chemistry particularly in the electron transfer processes, have been well known for almost 50 years. However, the complexes with ligands containing a single pyrrole ring are relatively scarce. In a previous study[1] we have shown that the *N*-arylpyrrole-2-aldimine copper(II) compounds are nearly square planar.



Cu(Pim-$C_6H_4R)_2$
R = H, Br, Cl, Me, OMe, OEt or NO_2 (*ortho*, *meta* or *para*)

Electrochemical investigations on the influence of the substituents in a series of the Schiff base ligands on the redox properties of their complexes have been carried out by considering only the *para* position of the substituent group on the aromatic ring.[2–6]

Here we report an investigation carried out by cyclic voltammetry on the reduction of a series of bis(*N*-arylpyrrole-2-aldiminato)copper(II) complexes to assess the influence of the phenyl substituents on the electrochemical behaviour of these compounds, and how their nature and position (*ortho*, *meta* or *para*) modify the electronic effects and the steric constraints.

Attempts to oxidize these compounds chemically were unsuccessful whereas the yellow–green copper(II) complexes were reduced by the action of sodium borohydride. The colourless solutions of copper(I) returned to yellow-green after the bubbling of air. Cyclic voltammograms of the complexes always showed one redox system in the potential range where no oxidation or reduction peaks were observed with all the free ligands. Our results agree with those of Addison *et al.*[2,3] and Holm *et al.*[7] for similar bis(*N*-alkyl or *N-para*-arylpyrrole-2-carboxaldiminato)copper(II) complexes. Moreover, they have coulometrically shown that the observed redox processes involve one electron. The voltammetric curves for three bromo-substituted phenylpyrrole-2-carboxaldimine complexes given in Fig. 1 are typical of the series of bis(*N*-arylpyrrole-2-carboxaldiminato)copper(II) complexes investigated. Voltammograms indicate that the electron transfer process for the reduction of copper(II) to copper(I) can be considered quasi-reversible for *para* and *meta* derivatives; the ΔE_p values being lower than 0.35 V (where $\Delta E_p = E_{p_a} - E_{p_c}$ with E_{p_a} the anodic peak potential and E_{p_c} the cathodic peak potential). On the other hand, the irreversibility for the *ortho* derivatives involves the decrease of the anodic wave because of the larger diffusion duration.

The electrochemical data obtained for all the compounds are given in Table 1. The cathodic peak potentials always follow the same trends:

$(E_{p_c})_{ortho} \leqslant (E_{p_c})_{meta} \approx (E_{p_c})_{para}$, except for Cu(Pim-$C_6H_4$-*m*-OEt$)_2$ and Cu(Pim-C_6H_4-*m*-Me$)_2$ where $(E_{p_c})_{ortho} = (E_{p_c})_{meta}$,

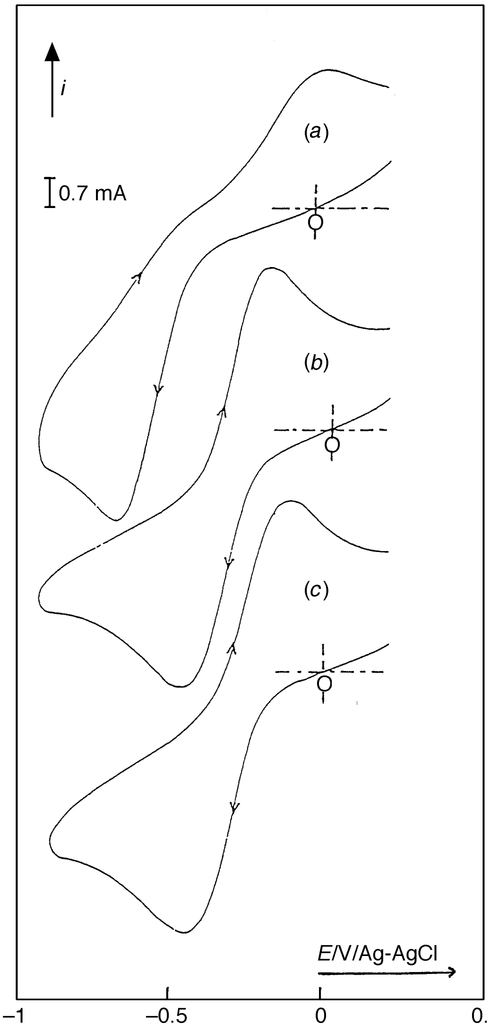


Fig. 1 Cyclic voltammograms of bis(bromo-substituted phenylpyrrole-2-aldimine) copper(II) compounds, 1.5×10^{-3} mol dm^{-3} in MeCN, with 0.1 mol dm^{-3} $Et_4N(ClO_4)$, at 20 °C. Reference electrode: Ag–AgCl–LiCl saturated in MeCN. Sweep rate: 100 mV s^{-1}. (*a*) Cu(Pim-C_6H_4-*o*-Br$)_2$; (*b*) Cu(Pim-C_6H_4-*m*-Br$)_2$; (*c*) Cu(Pim-C_6H_4-*p*-Br$)_2$

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Table 1 Electrochemical data for Cu(Pim-C_6H_4)$_2$ complexes

Compounds	E_{p_c}/V	E_{p_a}/V	$\Delta E_p{}^a$/V	10^5 D^b/cm^2 s^{-1}	$E'_{1/2}{}^c$/V	$i_{p_a}/i_{p}{}^c$
Cu(Pim-Ph)$_2$	–0.500	–0.180	0.320	1.8	–0.340	1.02
Cu(Pim-C_6H_4-*m*-No$_2$)$_2$	–0.430	–0.210	0.220	2.7	–0.320	0.96
Cu(Pim-C_6H_4-*p*-Br)$_2$	–0.440	–0.140	0.300	1.6	–0.290	1.10
Cu(Pim-C_6H_4-*m*-Br)$_2$	–0.450	–0.140	0.310	2.1	–0.280	1.06
Cu(Pim-C_6H_4-*o*-Br)$_2$	–0.675	0.030	0.705	3.2	—	
Cu(Pim-C_6H_4-*p*-Cl)$_2$	–0.400	–0.080	0.320	1.7	–0.240	0.92
Cu(Pim-C_6H_4-*m*-Cl)$_2$	–0.420	–0.100	0.320	2.6	–0.260	0.84
Cu(Pim-C_6H_4-*o*-Cl)$_2$	–0.650	0.020	0.670	2.9	—	
Cu(Pim-C_6H_4-*p*-Me)$_2$	–0.500	–0.180	0.320	2.4	–0.340	0.84
Cu(Pim-C_6H_4-*m*-Me)$_2$	–0.680	–0.210	0.470	1.6	—	0.99
Cu(Pim-C_6H_4-*o*-Me)$_2$	–0.680	–0.070	0.610	3.2	—	
Cu(Pim-C_6H_4-*p*-OMe)$_2$	–0.480	–0.280	0.200	1.4	–0.380	0.84
Cu(Pim-C_6H_4-*m*-OMe)$_2$	–0.480	–0.230	0.250	1.7	—	
Cu(Pim-C_6H_4-*o*-OMe)$_2$	–0.650	–0.200	0.450	2.1	—	
Cu(Pim-C_6H_4-*p*-OEt)$_2$	–0.650	–0.310	0.340	1.7	–0.480	0.92
Cu(Pim-C_6H_4-*m*-OEt)$_2$	–0.680	–0.270	0.410	1.6	–0.475	1.02
Cu(Pim-C_6H_4-*o*-OEt)$_2^d$	–0.680	—	—	—	—	—

[a] $\Delta E_p E_{p_a} – E_{p_c}$; obtained with the sweep rate of 100 mV s^{-1}. [b] D values were determinated from the peak current i_{p_c} obtained from the voltammograms with a potential scan of 10 mV s^{-1} where the process is reversible; [c] The apparent potential $E'_{1/2} = 0.5(E_{p_a} + E_{p_c})$ is only calculated for quasi-reversible process; [d] No reoxidation of the reduction product is obtained for this compounds.

i.e. E_{p_c} (with electron attracting group NO_2) $\approx E_{p_c}$ (with weak electron donor groups) > E_{p_c} (unsubstituted) > E_{p_c} (with strong electron donor groups).

The fact that the electrochemical reactions are practically reversible for small scan rate values (v < 20 mV s^{-1}) allows the determination of the diffusion coefficient D from the peak current equation:[8–10]

$$i_p = 0.4463\, nFAC(nF/RT)^{1/2} v^{1/2} D^{1/2}$$

where n is the number of electrons involved in the electrochemical process (n = 1), A is the area of the working electrode, D is the diffusion coefficient, C is the bulk concentration of the electroactive species and v is the sweep rate.

When t = 20 °C the peak equation i_p becomes:

$$i_p = 2.72 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2}$$

The magnitude of the obtained values is always $[(1–3) \times 10^{-5}]$ cm^2 s^{-1} and always follows the trend $D_{para} < D_{meta} < D_{ortho}$, except for the ethoxy group where $D_{para} \approx D_{meta}$. However, the methyl substituted phenyl complexes have a particular behaviour which was also observed by Sima *et al.*[11,12] in the investigation of Schiff-base thioiminato complexes. These values are slightly greater than those observed for the slightly bulky porphyrin copper(II) complexes.[13]

The chemical parameters E_{p_c}, E_{p_a} and the apparent potential $E'_{1/2}$ obtained for the *para* derivatives are close to those of the *meta* derivatives. As the inductive effect is the same for *para* and *ortho* positions and opposite for the *meta* position, it seems that the electronic effects are not an essential factor in the variation of the cathodic potential E_{p_c}. However, when the substituent group is in the *ortho* position, these complexes can present a greater steric constraint around the metallic ion than the other compounds. The diffusion coefficient D values which are directly related to the species' size ($D_{para} < D_{meta} < D_{ortho}$) confirm this steric effect, as is shown for the diffusion coefficient D of bis(R_2-β-diketiminato)copper(II) compounds which depends on the size of the substituents R.[5,14] These results demonstrate that the electrochemical behaviour of the reduction of copper(II) to copper(I) compounds is more sensitive to stereochemical effects than electronic effects.

Experimental

Preparation of Compounds.—The syntheses of these Schiff base copper complexes with various electron-donor or -withdrawing groups have been described elsewhere.[1] The ligands were obtained by condensation of pyrrole-2-carbaldehyde and the appropriate substituted aniline using ethanol as solvent. A mixture of copper(II) acetate and ligand in a 1:2 molar ratio was stirred at room temperature for 1 h the crude copper(II) complexes were recrystallized from *n*-hexane–methylene chloride (70:30).

Electrochemical Measurements.—The cyclic voltammetry experiments were carried out with a conventional three electrode apparatus using a PRT 40 IX SOLEA potentiostat with a linear sweep generator (PILOVIT-NUM SOLEA) and a KIPP & ZONEN BD 91 X–Y recorder. The working electrode was a 2 mm diameter platinum disk, the counter electrode was a large platinum cylinder and the reference electrode was Ag–AgCl–LiCl saturated in acetonitrile (+0.33 V *vs* SCE).

Acetonitrile was purified by using standard methods[15] while tetraethylammonium perchlorate was recrystallised from water before use.

The complex solutions (1.5×10^{-3} mol dm^{-3}) in acetonitrile, with tetraethylammonium perchlorate (0.1 mol dm^{-3}) as supporting electrolyte, were purged of oxygen by bubbling nitrogen for 15 min and then blanketed with the same gas during the experiments and thermostated at (20.0 ± 0.1) °C. The voltammograms were recorded with a potential scan of 100 mV s^{-1}.

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