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Electrochemical Oxidation of Cu(II) and Co(II) Complexes with Substituted *N,N'*-ethylenebis(*p*-R-benzoylacetoneimines)

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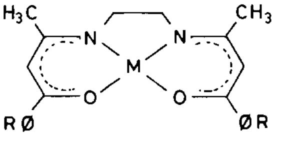
Abstract

The electrochemical oxidation of the Cu(II) and Co(II) complexes with a series of substituted *N,N'*-ethylenebis(*p*-R-benzoylacetoneimines) $[H_2N_2O_2(\phi R)_2]$, where R = OCH_3, CH_3, H, F, Cl, Br and NO_2, was investigated by cyclic voltammetry in acetonitrile at a platinum electrode. The anodic peak potentials for the copper complexes varied linearly with the Hammett substituent constants, whereas for the cobalt complexes no relationship between the mentioned data was observed. The one-electron oxidation process is in both complex types coupled with a following chemical reaction. In the presence of triphenylphosphine the oxidation process of cobalt complexes is preceded by its coordination. Triphenylphosphine has a catalytic effect during copper complex oxidation.

Introduction

The main aspect in our preceding papers [1–5] was the study of the redox properties of the nearly square-planar Cu(II) and Co(II) complexes with tetradentate ligands of Schiff-base types. Our attention in these studies was focussed on the axial and equatorial interactions of the mentioned complexes.

Because some electrode reactions are coupled with chemical reactions, we decided in further studies to try and characterize these chemical reactions. Studied were complexes of the type further on denoted as



$MN_2O_2(\phi R)_2$, where during electrode oxidation we observed a significant influence of the following chemical reactions.

This work apart from the investigation of the axial and equatorial interactions of the complexes, deals mainly with a qualitative analysis of the chemical reactions coupled to the electrode oxidation of these complexes.

Experimental

The complexes $CuN_2O_2(\phi R)_2$ and the ligands $H_2N_2O_2(\phi R)_2$, where R = OCH_3, CH_3, H, F, Cl, Br and NO_2, were prepared according to the literature method [6]. Analyses for carbon, hydrogen and nitrogen were in accordance with the calculated values. The cobalt complexes were prepared directly in an electrolyzed compartment.

Commercially available triphenylphosphine (TPP) was purified by double recrystallization from ethanol. Tetrabutylammonium perchlorate (TBAP) was synthesized from perchloric acid and tetrabutylammonium hydroxide. Acetonitrile was purified by a standard procedure.

Electrochemical measurements were made on a polarographic analyzator PA 3 (Laboratory Instruments, Prague), utilizing three-electrode geometry consisting of a platinum-wire working electrode, a platinum-foil auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE). The SCE was separated from the test solution by a bridge filled with the solvent and the supporting electrolyte.

Voltammograms of the complexes were done on acetonitrile solution (0.05 mol dm^{-3} TBAP) at room temperature with scan rates 20, 50, 100, 200 and 500 mV s^{-1}. The maximal content of the added triphenylphosphine in the system did not exceed the five-fold amount of the measured complex.

Results and Discussion

$CuN_2O_2(\phi R)_2$

The one-electron oxidation potentials of the studied complexes are summarized in Table I, as differences in E_{pa}, anodic peak potentials between the $CuN_2O_2(\phi R)_2$ and $CuN_2O_2(\phi H)_2$ complexes. Cyclic

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TABLE I. Change of the Redox Properties of $CuN_2O_2(\phi R)_2$ Complexes Dependent on Remote Substituent R and in the Presence of TPP

R	ΔE_{pa} [a] (V)	ΔE_{pa}^{TPP} [b]	σ_p [c]	σ_p^+ [c]
OCH_3	−0.07	0.00	−0.21	−0.78
CH_3	−0.02	−0.02	−0.17	−0.31
H	0.00	−0.02(5)	0.00	0.00
F	0.01(5)	−0.01(5)	0.06	−0.07
Cl	0.02(5)	−0.00(5)	0.23	0.11
Br	0.04(5)	−0.02(5)	0.23	0.15
NO_2	0.11(5)	–	0.78	0.79

[a] $\Delta E_{pa} = E_{pa}^{CuN_2O_2(\phi R)_2} - E_{pa}^{CuN_2O_2(\phi H)_2}$. [b] $\Delta E_{pa}^{TPP} = E_{pa}^{CuN_2O_2(\phi R)_2 + TPP} - E_{pa}^{CuN_2O_2(\phi R)_2}$. [c] Hammett substituent constants.

voltammograms were evaluated according to a theory published in the literature [7].

Anodic peak potentials were dependent on the inductive properties of the remote substituent R, as shown in Table I. From the values it is evident, that with increasing Hammett substituent constants σ_p and σ_p^+, respectively, ΔE_{pa} values also increase, *i.e.* the electron density on the reaction centre of the complex was influenced by the inductive properties of the remote substituent R. The magnitude of substituent interaction with the reaction centre, *i.e.* influence of electron-donating or electron-withdrawing character of the substituent, may be quantified by a Hammett linear free energy relationship [8]

$$\Delta E_{pa} = \rho \Sigma \sigma_R \tag{1}$$

ΔE_{pa} is the difference in E_{pa}, anodic peak potentials, between the $CuN_2O_2(\phi R)_2$ and $CuN_2O_2(\phi H)_2$ complexes; $\Sigma\sigma_R$ is the total substituent constant representing the sum of the constants characteristic of the electronic properties of substituent R ($\Sigma\sigma_R = 2\sigma_R$); and ρ is the reaction constant, characteristic of the reaction centre as well as expressing the reaction sensitivity of charge transfer to substituent influence.

According to eqn. (1) between ΔE_{pa} values of $CuN_2O_2(\phi R)_2$ complex oxidation and the sum of Hammett substituent constants σ_R, a close correlation was found ($r = 0.96$) with a ρ value of 0.006 V. When a mesomeric interaction was considered (σ_R^+) a better correlation was found ($r = 0.99$) with a reaction constant value, $\rho = 0.018$ V.

The above results show that during electrode oxidation of copper(II) complexes mesomeric substituent effects occur too, and the linear relationship ΔE_{pa} *versus* σ_R and σ_R^+, respectively, confirms an identical mechanism of electrode process in the investigated series of complexes. Changes of the anodic peak potentials in the presence of triphenylphosphine ΔE_{pa}^{TPP} expressed as potential differences in anodic peak potentials of complexes with and without TPP are given in Table I. In all cases a shift of the anodic peak potential to more negative values was observed.

Analysis of voltammograms shows that the studied complexes present a "kinetic case", *i.e.* a homogeneous chemical reaction is coupled to the electrode process. By using appropriate diagnostic criteria comparing the rate of chemical reaction with time necessary to carry out the experiment ($i_p v^{-1/2}$ *versus* v, $i_{pc}(i_{pa})^{-1}$ *versus* v, ΔE_{pa} *versus* v) [7] it was qualitatively found that the one-electron oxidation of the studied complexes was followed by a reversible chemical reaction, belonging to E_rC_r mechanism

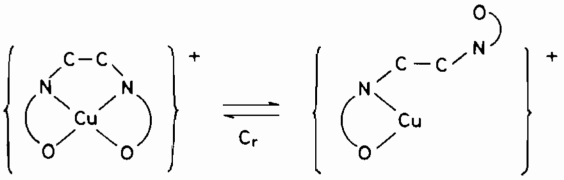
$$CuN_2O_2(\phi R)_2 \underset{E_r}{\overset{-e}{\rightleftharpoons}} \underset{2}{\{CuN_2O_2(\phi R)_2\}^+} \underset{C_r}{\rightleftharpoons} \underset{3}{Y}$$

TABLE II. Dependence $i_{pc}(i_{pa})^{-1}$ and E_{pa} *versus* v for $CuN_2O_2(\phi H)_2$ Complex

v (mV s^{-1})	$i_{pc}(i_{pa})^{-1}$	E_{pa} (V)[a]
20	0.77	0.71
50	0.48	0.71
100	0.38	0.72
200	0.35	0.73
500	0.32	0.75

[a] Measured against SCE.

The decreasing value of the ratio of the cathodic to anodic peak currents on increasing potential scan rate v (Table II) indicated that the product **2** created during electrode oxidation undergoes a reversible chemical reaction. The rate of this reaction was fast enough so that at higher scan rates it was possible to identify only a small amount of non-reacted substance **2**. As the chemical reaction is reversible, the backward process becomes more important with lower potential scan rates, where a larger amount of product **2** was identified (a higher value of the ratio $i_{pc}(i_{pa})^{-1}$), than with higher potential scan rates, where mainly the creation of product **3** is important. The product of the chemical reaction might be the original substance, where after electrode oxidation breaking of one half of the Cu–N and Cu–O bonds and a negligible rotation around the C–C bond occurred.



The above-mentioned explanation is corroborated by kinetic studies of substitution exchange reactions of central atoms in complexes of similar types [10], where metal substitution proceeds through a binuclear intermediate with a ligand partially bound to a substituted (original) and substituting (entering the complex) metal as well. Formation of the binuclear complex was explained by breaking of the Cu–O and Cu–N bonds and by rotation of the ligand part around the C–C bond, possible in highly asymmetrical ligands.

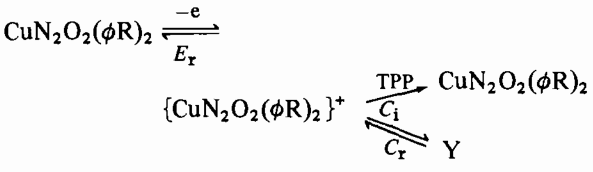
In the studied complexes it was observed (Table II), that an increase of potential scan rate caused an anodic shift of the anodic peak potential, confirming the aforesaid E_rC_r mechanism diagnosed already by another criterion [7, 9]. The dependence of E_{pa} on ν induces the significance of the equilibrium constant of the reversible chemical reaction [7].

TABLE III. Dependence of the Anodic Peak Potential of $CuN_2O_2(\phi H)_2$ Complex, E_{pa}^{TPP}, the Current Ratio $i_{pa}^{TPP}(i_{pa})^{-1}$ and the Ratio of the Cathodic to Anodic Peak Current $i_{pc}^{TPP}(i_{pa}^{TPP})^{-1}$ on Polarization Scan Rate in the Presence of TPP

ν (mV s^{-1})	E_{pa}^{TPP} (V)	$i_{pa}^{TPP}(i_{pa})^{-1}$	$i_{pa}^{TPP}(i_{pa}^{TPP})^{-1}$
20	0.71	1.75	0.71
50	0.72	1.71	0.53
100	0.73	1.74	0.37
200	0.74	1.41	0.32
500	0.77	1.26	0.30

The presence of TPP in the system caused an increase of the anodic peak current of the studied complexes (Table III). These data are a qualitative proof of the catalytic chemical reaction following the electrode oxidation of the complexes. The change in the anodic peak potential of the copper complexes in the presence of TPP E_{pa}^{TPP} with a change of potential scan rate (anodic schift, Table III) confirms the catalytic effect of TPP in the system.

Ratios of anodic to cathodic peak current are not equal to one, as would result from the observed reaction mechanism [7], but with increasing potential scan rate it decreases (Table III), as in the case of copper complex oxidation in the absence of TPP. This points to the fact that besides a catalytic reaction, a reversible chemical reaction observed without TPP takes place. That is, after electrode oxidation of the copper complexes in the presence of TPP two chemical reactions proceed in parallel – a catalytic and a reversible chemical reaction



$$CuN_2O_2(\phi R)_2 \underset{E_r}{\overset{-e}{\rightleftharpoons}} \{CuN_2O_2(\phi R)_2\}^+ \quad \xrightarrow[C_i]{TPP} CuN_2O_2(\phi R)_2 \quad \underset{C_r}{\rightleftharpoons} Y$$

TABLE IV. Change of the Redox Properties of $CoN_2O_2(\phi R)_2$ Complexes in Dependence on Remote Substituent R and in the Presence of TPP

R	ΔE_{pa} [a] (V)	ΔE_{pa}^{TPP} [b]	σ_p [c]	σ_p^+ [c]
OCH_3	0.04	−0.17	−0.21	−0.78
CH_3	0.03	−0.22	−0.17	−0.31
H	0.00	−0.17	0.00	0.00
Cl	0.05	−0.18	0.23	0.11
Br	0.03	−0.17	0.23	0.15

[a] $\Delta E_{pa} = E_{pa}^{CoN_2O_2(\phi R)_2} - E_{pa}^{CoN_2O_2(\phi H)_2}$. [b] $\Delta E_{pa}^{TPP} = E_{pa}^{CoN_2O_2(\phi R)_2 + TPP} - E_{pa}^{CoN_2O_2(\phi R)_2}$. [c] Hammet substituent constants.

TABLE V. Dependence $i_{pc}(i_{pa})^{-1}$ and E_{pa} *versus* ν for $CoN_2O_2(\phi H)_2$ Complex

ν (mV s^{-1})	$i_{pc}(i_{pa})^{-1}$	E_{pa} [a] (V)
50	0.89	0.13
100	0.78	0.13
200	0.69	0.14
500	0.63	0.16

[a] Measured against SCE.

$CoN_2O_2(\phi R)_2$

The redox properties of the $CoN_2O_2(\phi R)_2$ complexes were investigated similarly to the above case and their redox potentials were compared with those of $CoN_2O_2(\phi H)_2$. The results, summarized in Table IV, show that the measured values of anodic peak potentials are independent of the electronic properties of the substituents.

In the presence of TPP a marked shift of anodic peak potential to lower values was observed, again without a significant dependence on the electronic properties of the substituents.

Using identical diagnostic criteria as with the preceding copper complexes, it was found that the process of one-electron oxidation of the cobalt complexes was followed by a reversible chemical reaction, corresponding to the E_rC_r mechanism.

$$CoN_2O_2(\phi R)_2 \underset{E_r}{\overset{-e}{\rightleftharpoons}} \{CoN_2O_2(\phi R)_2\}^+ \underset{C_r}{\rightleftharpoons} Z$$

This mechanism was identified by a decreasing dependence of peak current ratios on potential scan rate and also by anodic peak potential shift to more positive values with increasing potential scan rate (Table V). It was assumed that the product Z of this reversible chemical reaction might be the original oxidized substance where, similar to the copper complexes, breaking of one half of the Co–N and Co–O bonds and slight rotation around C–C bond had occurred.

TABLE VI. Dependence of the Anodic Peak Potential of $CoN_2O_2(\phi H)_2$ Complex E_{pa}^{TPP}, the Ratio of the Cathodic to Anodic Peak Current $i_{pc}^{TPP}(i_{pa}^{TPP})^{-1}$ on Potential Scan Rate in the Presence of TPP

ν (mV s^{-1})	E_{pa}^{TPP} (V)	$i_{pc}^{TPP}(i_{pa}^{TPP})^{-1}$
50	−0.10	1.07
100	−0.10	1.07
200	−0.09	1.07
500	−0.07	1.01

The presence of TPP in this system caused a significant shift of the anodic peak potential to more negative values (Table IV). According to diagnostic criteria (Table VI) it was found that TPP enters the coordination sphere of the complex, and only this one undergoes the electrode oxidation. That is, in the presence of TPP, oxidation of cobalt complexes realizes according to the C_rE_r mechanism, *i.e.* the reversible electrode process is preceded by a reversible chemical reaction.

$$CoN_2O_2(\phi R)_2 \xrightleftharpoons[C_r]{+TPP} [CoN_2O_2(\phi R)_2TPP] \xrightleftharpoons[E_r]{-e} \{CoN_2O_2(\phi R)_2TPP\}^+$$

The ratio of anodic to cathodic peak current dependent on polarization scan rate equals the value of about one (Table VI), which points to an electrode process uncomplicated by a chemical reaction and confirms the correctness of a reaction mechanism during the oxidation of cobalt complexes in the presence of TPP.

In summary, this paper deals with the one-electron process of copper and cobalt complexes with substituted N,N'-ethylenebis(p-R-benzoylacetoneimines) in dependence on the electronic properties of R substituents on the benzene ring characterized by Hammett substituent constants. With copper complexes an obvious dependence was observed whereas with cobalt complexes such a dependence was missed.

The electrode process with both complex types was significantly influenced by the following chemical reaction. In the presence of TPP, cobalt complex oxidation occurred only after its entry into the coordination sphere, however, during electrode oxidation of the copper complexes in the presence of TPP catalytic effects take place but no coordination. In this case oxidation of the complex proper is accompanied by a parallel catalytic reaction with a following chemical reaction.

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