Study of electrochemical oxidation of nickel catecholate complexes with bis(diphenylphosphino)ethane by cyclic voltammetry and ESR

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One- and two-electron electrochemical oxidation of the (dppe)Ni(Cat) complexes (dppe is bis(diphenylphosphino)ethane, Cat is the sterically hindered catechol dianion) was studied. The transfer of the first electron proceeds reversibly to give paramagnetic species; parameters of their EPR spectra attest to a square planar geometry of one-electron oxidation products. The transfer of the second electron is irreversible because of co-proportionation of radical cations involving the initial complexes and the generated dications.

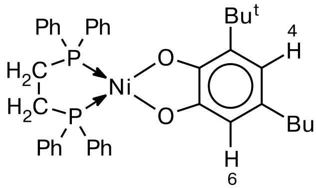
Key words: (diphosphine)nickel(catecholate), radical cation, dication, electron transfer, electron spin resonance, cyclic voltammetry, co-proportionation.

In recent years, metal coordination compounds with paramagnetic ligands, including *o*-semiquinone ligands, have attracted considerable attention of researchers. The molecules of these compounds can contain several paramagnetic centers of various nature, whose sign and energy of exchange interactions are determined by the electronic structure and geometric features.[1—3] Paramagnetic ligands are often electrochemically active; the electrochemical reduction or oxidation of complexes may involve not only transformations of the central metal ion but also ligand transformations, which change the magnetic properties of the ligands and the system as a whole.

By combining electrochemical methods with ESR spectroscopy, one can gain additional information about the electrode processes, electronic structure, geometry, and reactivity of depolarizers. In some cases, using the ESR spectrum of a paramagnetic substrate, one can identify the localization region of the unpaired electron and the geometry of magnetic nuclei.

Methods for simultaneous recording of ESR signals and electrochemical characteristics using an electrolytic cell—ESR in a cavity of the ESR spectrometer in a potentiostatic mode, by chronopotentiomety, and cyclic voltammetry (CV) are known.[4,5] However, direct comparison of CV curves and ESR signal levels is not entirely valid, because the current is the first derivative of the charge that has passed through the cell, while the ESR signal level is proportional to the proper charge related to the depolarizer under study.

Currently a new method, electron spin resonance-detected voltammetry (V—ESR) is being developed. This method comprises two traditional methods, voltammetry and ESR, which are combined by an original three-electrode electrolytic ESR cell[6] (El—ESR) for investigation of paramagnetic species and a computer controlling the ESR spectrometer and the electrochemical setup consisting of a programming device and a potentiostat. The method allows simultaneous recording of usual voltammetric curves $i(E)$ and also dependences of the ESR signal intensity ($s(E)$) and its first derivative ($s'(E)$) on the potential. In this work, the V—ESR technique was used to study nickel catecholate complexes **1** and **2** with bis(diphenylphosphino)ethane (dppe).



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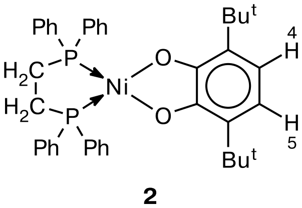

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Experimental

Complexes **1** and **2** were prepared at the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences (Nizhny Novgorod) by the reaction of nickel tetracarbonyl with dppe and the corresponding *o*-quinone taken in an equimolar ratio according to a publication.[7] The complexes recrystallized from a toluene—dichloromethane mixture (10 : 1) are dark-green crystals. Yield 53%. Found (%): C, 73.82; H, 7.44; Ni, 7.62; P, 8.04. $C_{47}H_{52}NiO_2P_2$. Calculated (%): C, 73.37; H, 6.76; Ni, 7.64; P, 8.07. IR (mineral oil), ν/cm^{-1}: 1595, 1485, 1440 s, 1410, 1275, 1255, 1190, 1110 s, 1035, 980, 940, 880, 830, 795, 745, 725 s, 710 s, 690 s, 660, 540, 480, 450.

Acetonitrile was purified by threefold distillation from $KMnO_4$ and P_2O_5; $NaBF_4$ was dried for 2 days *in vacuo* at 100 °C. Liquid samples were freed from oxygen by liquid nitrogen freezing—evacuation—thawing cycle repeated three times. An inert atmosphere was created in the El—ESR cell by supplying helium therein under normal pressure. The concentration of the complexes was 0.005 mol L^{-1}, that of the supporting salt was 0.3 mol L^{-1}. The working an auxiliary electrodes were made of platinum, and $Ag/AgNO_3$ (0.01 *M* solution) was used as the reference electrode.

The measurements were carried out on a hardware/software unit assembled from an analog electrochemical setup with a PI-50-1 potentiostat, a Pr-8 programming device, an RE1306 X-range ESR spectrometer, an ADC module, an E14-440 DAC (L-Card), a generation IV computer, and an original three-electrode electrolytic spiral cell. The temperature was maintained by a B-VT-1000 temperature control unit (Bruker) connected to an RE1306 spectrometer.

ESR spectra were processed by a WinSim (NIEH/NIH) program, which allows one to determine the key parameters of the experimental isotropic spectrum by simulating the spectrum and automatic fitting of the simulated spectrum to the experimental one.

Results and Discussion

At the first-peak potential of the electrochemical oxidation of complexes **1** and **2** (0.6 and 0.7 V, respectively), ESR signals appear. The ESR spectra of radical cations $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ recorded at room temperature in acetonitrile are shown in Fig. 1, while the magnetic resonance parameters obtained by automatic fitting with the assumption of a Lorentzian line shape are in Table 1.

Table 1. Parameters of the ESR spectra of radical cations $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$

Compound	a_P	a_H	Line width	*g*-Factor
	mT			
$\mathbf{1}^{\bullet+}$	0.255	0.369 (H(4)), 0.069 (H(6))	0.105	2.004
$\mathbf{2}^{\bullet+}$	0.257	0.366 (H(4), H(5))	0.050	2.004

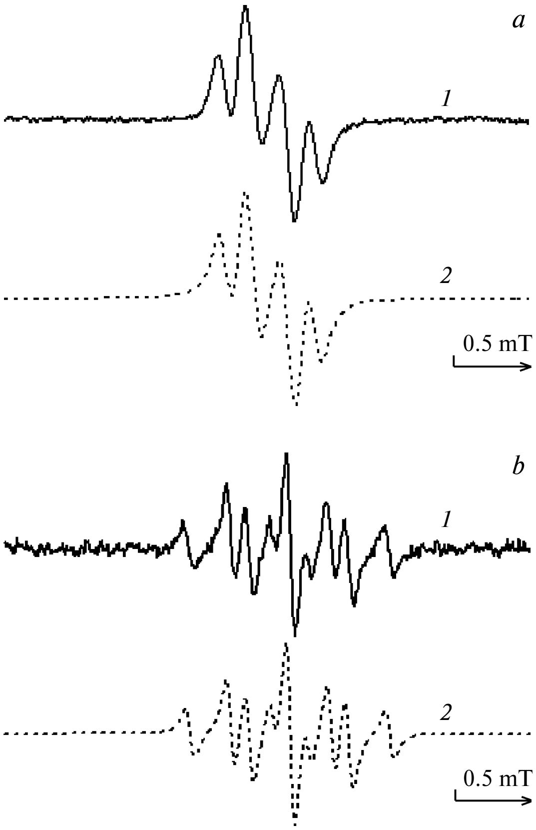

Fig. 1. Experimental (*1*) and simulated (*2*) ESR spectra of radical cations $\mathbf{1}^{\bullet+}$ (*a*) and $\mathbf{2}^{\bullet+}$ (*b*) electrochemically generated in acetonitrile at 293 K in the potentiostatic mode at the first-wave potential.

The ESR spectrum of radical cation $\mathbf{1}^{\bullet+}$ (see Fig. 1, *a*) is a quartet with a single line width of 0.105 mT caused by the HFC of the unpaired electron with two equivalent P nuclei of the diphosphine ligand with the constant a_P = 0.255 mT and with protons in positions 4 and 6 of the *o*-semiquinone ring with the constants $a_{H(4)}$ = 0.369 mT and $a_{H(6)}$ = 0.069 mT.

The spectrum of radical cation $\mathbf{2}^{\bullet+}$ (see Fig. 1, *b*) with a single line width of 0.05 mT was better resolved. The HFC of the unpaired electron with two equivalent P nuclei of the diphosphine ligand, a_P = 0.257 mT, and with two protons, equivalent to within the linewidth, in positions 4 and 5 of the *o*-semiquinone ring, $a_{H(4)} = a_{H(5)}$ = 0.366 mT, are observed.

The parameters of the isotropic ESR spectra (small line width, the values of *g*-factors, HFC constants with the ligand protons and ^{31}P magnetic isotopes of the diphosphine ligand) are typical of metal complexes containing a paramagnetic *o*-semiquinone ligand. The HFC parameters that we determined for the radical cations derived from complexes **1** and **2** are consistent with published data[7] on the electrochemical oxidation of analogous nickel catecholate complexes. The low HFC

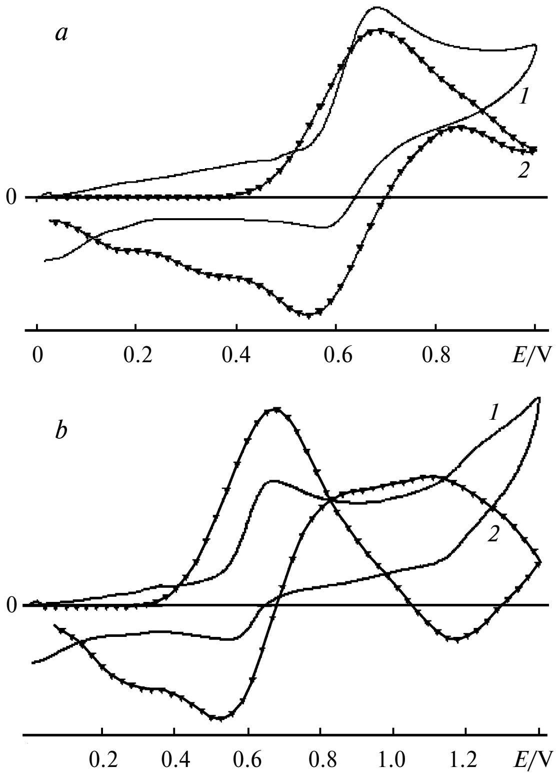

Fig. 2. Cyclic voltammetry ($i(E)$, *1*) and CV—ESR ($s'(E)$, *2*) curves of complex **1** ($5 \cdot 10^{-3}$ mol L^{-1}) in acetonitrile in the presence of a $3 \cdot 10^{-1}$ *M* solution of $NaBF_4$ at potential sweep from 0 to 1.0 V (*a*) and from 0 to 1.6 V (*b*). The potential sweep rate was 0.5 V s^{-1}, 293 K.

constants with the phosphorus magnetic nuclei (0.255—0.257 mT) in the diphosphine ligand attest to a square planar geometry of the resulting cations.[7,8]

The CV ($i(E)$) and CV—ESR ($s'(E)$) curves for compound **1** are shown in Fig. 2, *a*. The CV curve shows the final current immediately after application of the potential and its gradual growth before the oxidation potentials of the depolarizer are attained, which is mainly due to charging of the double electric layer and oxidation of impurities. No substantial increase in $s'(E)$ is noted before attaining the oxidation potentials of the depolarizer. This is attributable to the fact that the CV—ESR technique measures the rate of variation of the ESR signal intensity. This change is due only to depolarizer electrolysis, while the currents of the double electric layer charging, the adsorption component of the current, and the currents of impurities do not contribute to the $s'(E)$ dependence. The CV—ESR curve mainly follows the CV curve, although does not reproduce its shape in detail. The $s'(E)$ dependence reflects better the reversibility of the first electron transfer. The reversible intramolecular electron transfer related to the catecholate—semiquinone transition is well known.[9—11]

$$\mathbf{1} \xrightleftharpoons{-\mathrm{e}} \mathbf{1}^{\cdot +} \tag{1}$$

The CV ($i(E)$) and CV—ESR ($s'(E)$) curves for compound **1** in a broader potential range, *i.e.*, including the heterogeneous transfer of the second electron, are shown in Fig. 2, *b*. According to CV data, the first oxidation wave is reversible, while reversibility of the second wave is not manifested in the voltammogram under the experimental conditions. The first oxidation wave $i(E)$ corresponds to the $s'(E)$ wave related to the formation of the radical cation by reaction (1). The second wave (1.3 V) corresponds to the oxidation of the radical cation to give the dication

$$\mathbf{1}^{\cdot +} \xrightarrow{-\mathrm{e}} \mathbf{1}^{2+}, \tag{2}$$

as is clearly seen from the shape of the $s'(E)$ curve, which is lower in intensity. The $s'(E)$ CV—ESR curve explains why the second oxidation wave is irreversible. After the second oxidation wave is reached, $s'(E)$ starts to increase. This implies that some additional process, resulting in radical cations, occurs after the dication formation potentials are attained. As a result, the rate of formation of radical cations is higher than the rate of their consumption according to reaction (2). This third process is the co-proportionation of radical cations with participation of the initial compound **1** and its dication $\mathbf{1}^{2+}$.

$$\mathbf{1} + \mathbf{1}^{2+} \rightleftharpoons 2\,\mathbf{1}^{\cdot +} \tag{3}$$

The increase in the rate of formation of radical cations continues also after the change in the direction of potential sweep: the intensity of the $s'(E)$ curve starts to decrease at first-wave potentials to reach a minimum at the cathodic peak.

The oxidation pattern of compound **2** (Fig. 3) does not differ much from that of complex **1**. The first and second oxidation waves (0.7 and 1.4 V, respectively) are shifted by ~0.1 V to more anodic potentials compared to the waves of complex **1** and the first-wave return peak is less intense.

Thus, complexes **1** and **2** undergo two-electron electrochemical oxidation. The transfer of the first electron is a reversible process affecting the catecholate ligand giving rise to paramagnetic *o*-semiquinone complexes $\mathbf{1}^{\cdot +}$ and $\mathbf{2}^{\cdot +}$ whose ESR are easily recorded by the hardware/soft-

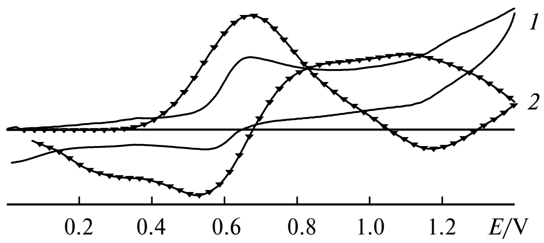

Fig. 3. Cyclic voltammetry ($i(E)$, *1*) and CV—ESR ($s'(E)$, *2*) curves of complex **2** ($5 \cdot 10^{-3}$ mol L^{-1}) in acetonitrile in the presence of a $3 \cdot 10^{-1}$ *M* solution of $NaBF_4$. The potential sweep rate was 0.5 V s^{-1}, 293 K.

ware unit we designed. The ESR spectral parameters of radical cations $\mathbf{1}^{\bullet +}$ and $\mathbf{2}^{\bullet +}$ attest to a square planar geometry of the one-electron oxidation products. The application of electron spin resonance-detected cyclic voltammetry clarified the nature of the processes involved in the heterogeneous transfer of the second electron. The irreversibility of this transfer is due to co-proportionation of radical cations involving the initial complexes and their dications.

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