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Electronic Structures of the Palladium(II) Complexes with Redox-Active *o*-Phenylenediimines

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Abstract—The electronic structures and the character of the electron density redistribution in the palladium complexes with the redox-active ligands in the oxidized and nonoxidized forms are studied by X-ray photoelectron spectroscopy. According to the photoelectron spectroscopic data, the redox-active ligands exist in different oxidation states due to the redox process proceeding "at ligand." It is shown that the transition from the neutral to oxidized semiquinone form (from $[\mathrm{Pd}(\mathrm{L}_{\mathrm{Me}})_2]\cdot2\mathrm{Cl}\cdot\mathrm{H_2O}$ to $[\mathrm{Pd}(\mathrm{L}_{\mathrm{Ph}}^{\mathrm{ISQ}})_2]$) occurs in the ligand and involves no palladium ions, and the oxidation state of palladium remains unchanged: Pd(II). A significant difference in the photoelectron spectroscopic characteristics obtained for the oxidized *trans*-complex at 298 and 153 K indicates a specific electronic lability of this complex.

Keywords: X-ray photoelectron spectroscopy, pivalate complexes, binding energy, palladium(II), electron density, atomic concentration

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INTRODUCTION

Metal complexes are unique objects exhibiting functionally useful properties, such as optical, electrochemical, magnetic, catalytic, and others. Active studies in the area of coordination and organometallic compounds containing redox-active ligands are caused by interest of researchers in controlling chemical and magnetic properties that manifest redox isomerism (intramolecular electron transfer) [1–3]. This is determined by the fact that the orbitals of the transition metals and frontier orbitals of the ligands are close in energy. These orbitals are strongly mixed, and the assignment of the oxidation state of individual components, metal, and ligand is difficult in some cases. *o*-Benzoquinones, *o*-benzoiminoquinones, and *o*-benzoquinonediamines can be distinguished among the organic ligands forming similar metallocycles with transition metal ions, since their electronic and geometric properties can substantially change during the electron transfer. The *o*-benzosemiquinonediimine systems are the product of the one-electron oxidation of *o*-phenylenediamines and are restrictedly studied, although interest in these complexes is fairly high due to prospects of their use in electrocatalysis and as bioactive additives or units of molecular electronic devices owing to a comparatively easy transfer of electrons [4–6]. The synthesis of the transition metal complexes with *o*-phenylenediamine and its derivatives can afford complexes with the oxidation products of the corresponding diamines. For the redox processes occurring in the complex, if the reduction (oxidation) processes involve "ligands," then the ligands considered can exist in various states (redox-active ligands), the redox orbitals of the metal participate weakly in these processes, and the state of the metal changes slightly. The body of the main factors, electronic form of the ligand, and oxidation state of the metal determine the structure and physicochemical properties of the complex [7]. It is not too difficult to interpret the electronic structures of the complexes with phenylenediamine in the nonoxidized form that are formed at the initial stage of the process. The subsequent transition to the semiquinonediimine derivatives can be accompanied by difficulties in interpretation of data of physical methods, which was observed for the incorrect interpretation of the structures of the palladium(II) and platinum(II) derivatives rightly mentioned earlier [8, 9]. The development of this trend is seriously retained by the problems of understanding the electronic structures of the complexes (or metal moieties), which requires additional studies. One of such efficient methods is X-ray photoelectron spectroscopy (XPS) determining a direct dependence of the binding energy on the effective charge of the atom forming the "map" of the electron density distribution in the molecule, distribution of electrons between the orbitals, and changes in the number of uncompensated *d* electrons.

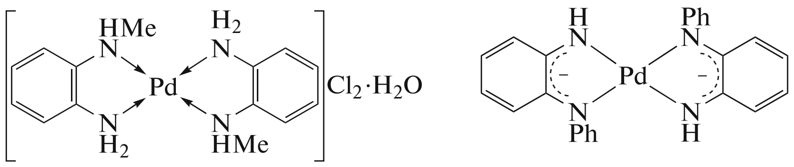
The purpose of this work is to perform the XPS study of the electronic structures of the palladium complexes with the redox-active ligands in the oxidized and nonoxidized forms, i.e., in the forms with ambiguous interpretation, and to determine the role of the nature of the substituent at the imine nitrogen atom.

EXPERIMENTAL

The XPS spectra were recorded on an Axis Ultra DLD spectrometer (Kratos Analytical, Great Britain). The samples were studied as thin layers of the powder pressed into a two-sided adhesion ribbon. The spectra were recorded at the constant transmission energy of the analyzer equal to 160 eV for the survey spectrum and 40 eV for the high-resolution spectra. The size of the analyzed range was ~300 × 700 μm^2. The preliminary calibration of the energy scale of the spectrometer corresponded to the following values of peaks of the standards (purified by ion sputtering of the metal surfaces): Au $4f_{7/2}$ 83.96 eV, Cu $2p_{3/2}$ 932.62 eV, and Ag $3d_{5/2}$ 368.21 eV. The spectra were recorded using a neutralizer in order to eliminate the effect of sample charging. The measurements were carried out at least two times under a pressure of ~10^{-9} Torr. The determination accuracy for binding energies was 0.1 eV. The spectra were recorded at 298 and 153 K. The obtained spectra were calibrated by the binding energy of the C1*s* line of electrons of carbon adsorbed on the sample surface corresponding to the C–C/C–H bonds and accepted equal to 285.0 eV. The spectra were separated into components using the Casa XPS software (version 2.3.23, www.casaxps.com).

RESULTS AND DISCUSSION

The electronic structure and character of the electron density redistribution in the palladium complexes with the redox-active ligands (*o*-phenylenediamine derivatives) and the dependence of the structure of the Pd3*d* spectra on the ligand nature were studied by the XPS method for the first time. The following palladium(II) complexes were studied: with coordinated diamines in the bis(chelate) cationic complex with *N*-methyl-*o*-phenylenediamine $\mathrm{Pd(L_{Me})_2]\cdot 2Cl\cdot H_2O}$ (**I**) and with the oxidized form of the *o*-phenylenediamine derivative (*N*-phenyl-*o*-phenylenediamine) in the complex with the $\mathrm{L_{Ph}}$–$[\mathrm{Pd}(\mathrm{L_{Ph}^{ISQ}})_2]$ ligand (**II**) with two chelate-bonded radical anions of *N*-phenyl-*o*-benzosemiquinonediimine. The structures of complexes **I** and **II** are shown in Scheme 1. The reference compound was $\mathrm{[Pd(NH_3)_4]\cdot 2Cl}$ (**III**) [10]. The elemental analysis data for complexes **I** and **II** correspond to their empirical formulas within the sensitivity of the XPS method.



(I) **(II)**

Scheme 1.

The structure of complex **I** was determined earlier at room temperature [11]. Compound **I** is the bis(chelate) dicationic complex. Complex **II** is the oxidation product of the cationic complex similar to complex **I** but containing the *N*-phenyl-*o*-phenylenediamine ligands due to which coordinated diamine transforms into the semiquinonediimine form. The electronic structures and character of the electron density redistribution in the Pd(II) complexes can be compared using oxidized form $\mathrm{L_{Ph}^{ISQ}}$ as an example. Two polymorphs, **II-A** and **II-B**, were detected for complex **II** [12, 13]. It was experimentally found that complexes **I** and **II** were resistant to X-ray radiation in high vacuum. The balance of atoms in the complexes retained at both 298 and 153 K. The binding energies (E_b) for the lines of the C1*s*, Pd3*d*, and N1*s* levels and atomic concentrations (AC%) were determined. The change in the temperature of spectra recording from room (298 K) to 153 K (on cooling with liquid nitrogen) made it possible to study the influence of structural transformations of the complex on the formation of the photoelectron spectra and, as a result, on the properties of the newly synthesized complexes. These data assume the determination of a relationship between the properties of the donor-acceptor redox-active complexes and characteristics of the photoelectron spectra. All obtained results are given in Table 1. The XPS spectra of complexes **I** and **II** recorded at two temperatures (298 and 153 K) are presented in Fig. 1.

Table 1. XPS characteristics of the palladium complexes

Complex (*T*, K)	E_b, eV	FWHM	E_b, eV	
	Pd3$d_{5/2}$ (AC%)*		N1*s* (AC%)	C1*s* (AC%)
I (153)	338.8(2.3)	1.16	400.5(16.0)	C–H 285.0 (37.9) C–N 285.9 (26.2) $(C–C)^-$ 284.4 (1.5)
II (153)	338.6 (1.4)	0.72	399.9 (4.7) 398.7 (4.6)	C–H 285.0 (51.2) C–N 285.9 (19.1) $(C–C)^-$ 284.4 (9.5)** C–OH 286.9 (4.7)
I (298)	338.8 (1.0)	1.16	400.5 (15.0)	C–H 285.0 (39.4) C–N 286.0 (25.5)
II (298)	338.2 (1.6)	0.86	398.2 (5.0) 399.3 (1.3) 400.4 (1.5)	C–H 285.0 (52.4) C–N 286.3 (9.8) $(C–C)^-$ 284.2 (23.6)
III (298)	339.1		400.5	$[Pd(NH_3)_4]Cl_2$ [10]

* Atomic concentration.
** $(C–C)^-$ is the "negatively charged" group.

The Pd3*d* lines of palladium in the spectra of complexes **I** and **II** are doublet (Fig. 1a). The values of E_b of the main Pd3$d_{5/2}$ line for these complexes range from 338.2 to 339.2 eV, and the spin-orbital splittings (Δ) of Pd3$d_{5/2}$–Pd3$d_{3/2}$ are 5.18–5.22 eV. The full width at half maximum (FWHM) for the Pd3$d_{5/2}$ line lies in a range of 0.72–1.16 (Table 1). The additional lines in the Pd3*d* spectra are shaking satellites of the main lines. It follows from the energy characteristics obtained for the Pd3*d* spectra of palladium that in complexes **I** and **II** the palladium ions exist in the Pd(II) oxidation state, which is consistent with the data for reference sample **III** and with the literature data [10, 14–16].

One energetically uniform symmetric line of Pd(II) with E_b = 338.8 eV and FWHM = 1.16 was revealed for complex **I** at 298 and 153 K, indicating that the palladium atoms in this complex are energetically uniform (Fig. 1a). A distinctive feature of this complex at both temperatures is the singlet line of nitrogen with E_b = 400.5 eV in the spectra at both temperatures. This line refers to both the $(CH_3)NH$ and H_2N groups (Fig. 1c) [15]. The C1*s* spectrum of carbon exhibits two lines assigned to the C–H and C–N groups (Fig. 1b). The

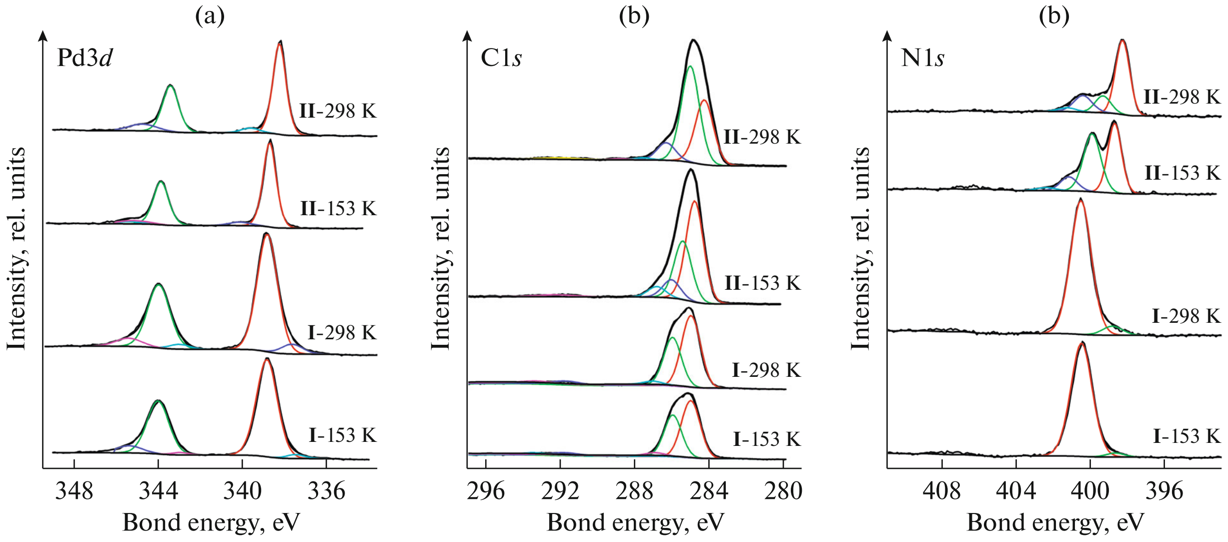


Fig. 1. XPS spectra for (a) palladium Pd3*d*, (b) carbon C1*s*, and (c) nitrogen N1*s* and complexes **I** and **II**.

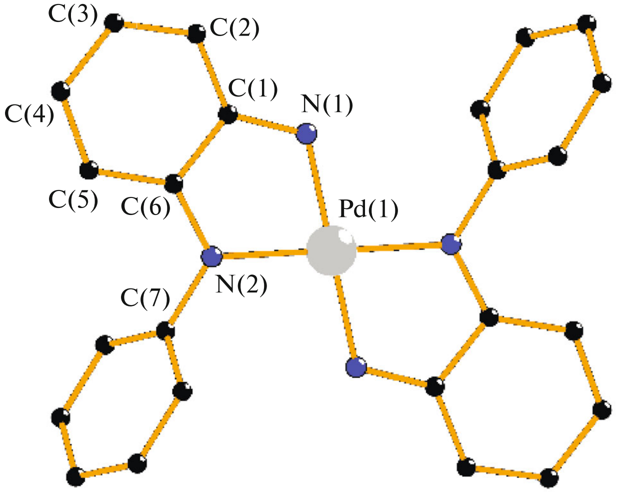


Fig. 2. Molecular structure of complex **II** (hydrogen atoms are omitted) [12].

weakly intense broad peak in the C1*s* spectra at the binding energy about 292 eV is caused by the π–π* satellite of the line of the sp^2-hybridized atoms of the aromatic ring.

In complex **II**, the intramolecular charge transfer is caused by the rearrangement of the π-conjugated system of the macrocyclic ring and quinoid structure formation. The main singlet N1*s* line in the nitrogen spectrum at 298 K (Fig. 1c) corresponds to E_b = 398.2 eV and is 64% of the total nitrogen content. This possibly indicates in favor of the π-electron density delocalization over the organic molecule and involvement of the nitrogen atoms with two intramolecular "antiferromagnetically paired" iminosemiquinonate ligands in the one-electron oxidation of complex **II** [17, 18]. A substantial change in the state of the nitrogen atoms (Table 1) upon oxidation (increasing electron density) should result in a high reactivity of the complex. Two weaker lines in the N1*s* spectrum with E_b equal to 399.3 and 400.4 eV are assigned to the nitrogen atoms in the NH and NPh groups, respectively [10, 15]. These lines can be attributed to the oxidized form (36%) of the complex with the π-electron density delocalization in the NCCN moiety. The N1*s* spectra at a binding energy of 407–408 eV exhibit weak lines caused by the strongly oxidized forms of nitrogen of presumably cocrystallized *N*-phenyl-*o*-phenylenediamine.

Considerable changes appeared as two main N1*s* lines of nitrogen with E_b = 398.7 and 399.9 eV (Fig. 1c), and equal ratios of atomic concentrations (Table 1) are observed in the spectrum of complex **II** at 153 K. This possibly indicates in favor of one form of complex **II**. The value of E_b of these lines indicates a higher electron density on the nitrogen atoms at 298 K than that at 153 K. A decrease in the electron density was simultaneously detected on the palladium atoms (E_b of Pd3$d_{5/2}$ is higher by 0.4 eV than that at room temperature). A decrease in the electron density on the palladium atoms was observed [19] at low temperature with the retention of the oxidation state. Since the unsaturated macrocycle has a smaller size of the cavity at low temperature, the Pd–N bond shortens resulting in a more efficient overlapping of the orbitals of nitrogen and palladium. The orbitals of the transition metals and frontier orbitals of the ligands are close in energy, and their mixing leads to the transition of a portion of the electron density from the palladium orbitals to the orbitals of nitrogen.

An analysis of the atomic concentrations of the functional carbon atoms of the macrocyclic ligands revealed significant differences at low and high temperatures. The fact worth of notion is that the atomic concentration of carbon at 298 K for the "negatively charged" C–C$^-$ group is 23.6 at %, which is more than two times higher than the value at 153 K (totally 9.5 at %). A significant difference in the atomic concentrations of the carbon atoms in the C–C$^-$ group can be explained by substantial structural transformations of complex **II** (atoms are enumerated according to Fig. 2). The average bond lengths are taken for comparison: the C(1)–N(1) distance shortens (from 1.345 to 1.340 Å), the C(6)–N(2) distance remains unchanged, and the C(1)–C(6) distance (from 1.437 to 1.442 Å) and other C–C bonds in the C(1)–C(6) ring elongate. The shortening of the Pd–N bonds (Pd(1)–N 1.970 and 1.997 Å at 298 K and 1.961 and 1.985 Å at 100 K) should be mentioned. These structural changes indicate the negative charge localization in the chelate node of the ligand with decreasing temperature. This confirms the electron density delocalization over the whole molecule. In total, the atomic concentration of carbon in complex **II** is 85.9% at 153 K and 85.8% at 298 K, indicating that the complex is stable during spectra recording.

Compound **II** is formed by two radical anions of the corresponding *o*-benzosemiquinonediimine bound to the Pd(II) atom via the chelate mode. Diamagnetism of this compound indicates a strong antiferromagnetic exchange between these radical anions. In fact, we can speak about a single π system of the whole bis(chelate) moiety of the complex. This appears structurally as follows: the lengths of the C–C bonds of the six-membered carbon ring and the C–N bonds are intermediate between the values observed in the quinoid and benzoid forms, whereas the Pd–N bonds are shortened compared to the ordinary bonds in amino complex **I**. All these facts indicate an increase in their multiplicity. The delocalization of the electron density of the π system over this fragment is also observed as an equivalence of the nitrogen atoms at room temperature (64%). In addition, the state in which the nitrogen atoms are not equivalent also contributes (36%) at room temperature. A temperature decrease results, most likely, in a decrease in the uniformity of the delocalization of the π-system electron density. This is manifested in the fact that the state with the nonequivalent nitrogen atoms is observed in the XPS spectra.

Thus, the transition from the neutral to oxidized semiquinone form (from $[Pd(L_{Ph})_2]\cdot 2Cl\cdot H_2O$ to $[Pd(L^{ISQ}_{Ph})_2]$) occurs, most likely, in the ligand and involves no palladium ions, and the oxidation state of palladium remains unchanged: Pd(II). The redox orbitals of the metal are weakly involved in these processes. The XPS data show that the ligands exist in different states (redox-active ligands) due to the redox processes proceeding "at ligand." The considerable difference in the XPS characteristics obtained for oxidized *trans*-complex **II** at 298 and 153 K indicates its specific electronic lability. This makes it possible to consider complex **II** as a promising catalyst for chemical and redox-active biochemical systems.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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