ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 3, pp. 423–429. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © A.M. Golyakov, A.V. Shchukarev, L.P. Ardasheva, A.N. Borisov, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 3, pp. 368–374.

Electrochemical and Spectral Properties of the Polymer Form of Cu(II) Complex with *N*,*N*'-Bis(salicylidene)-1,3-propylenediamine

A. M. Golyakov[a], **A. V. Shchukarev**[b], **L. P. Ardasheva**[a], **and A. N. Borisov**[a]

[a] *Herzen Russian State Pedagogical University, nab. r. Moiki 48, St. Petersburg, 191186 Russia*
e-mail: alexey-borisov@mail.ru
[b] *Umeå University, Sweden*

Received April 26, 2012

Abstract—A conductive polymer based on the Cu(II) complex with *N*,*N*'-bis(salicylidene)-1,3-propylenediamine was obtained electrochemically. The optimal mode of the synthesis of the polymer under potentiostatic conditions was found. We determined the charge diffusion coefficient and activation barrier and elucidated the nature of the limiting step of the charge transfer in the polymer bulk in the electrolyte medium. The azomethine base, Cu(II) complex, and its polymer form in the oxidized and reduced states were characterized by X-ray photoelectron spectroscopy and electron absorption spectroscopy.

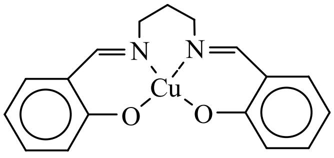
DOI: 10.1134/S1070363213030031

Relevance of the study of thin-film conducting polymers based on organic and coordination compounds of transition metals is due to the prospects of using them for sensors, electro- and photocatalytic devices, and solid-phase cells for the conversion of light energy [1, 2].

During the last quarter of 20th century the polymer films of the complex compounds of metals with aromatic azomethines of different composition and structure [2–5], porphyrins [6], phthalocyanines [7], etc. have been obtained and widely studied. The complexes with these ligands are the most interesting to researchers because they are model analogs of important natural organometallic compounds.

However, despite the accumulation of significant experimental material, the study the conditions of synthesis and the structure of conducting polymers based on transition metal complexes with macrocyclic ligands still remains topical. In particular, to date a consensus on the mechanism of the formation, structure, and the charge transfer processes in the polymer forms of the *d*-element complexes with aromatic azomethine bases was not reached.

This paper presents the data describing the optimal conditions of oxidative electrochemical synthesis, as well as electrochemical and spectroscopic properties of a polymer based on the Cu(II) complex with a tetradentate aromatic azomethine base of N_2O_2 type, *N*,*N*'-bis(salicylidene)-1,3-propylenediamine, denoted as H_2(salpn-1,3):



[Cu(salpn-1,3)]

Electrochemical oxidation of the complex [Cu (salpn-1,3)] results in the formation of a conductive polymer film on the surface of platinum electrode. The anodic polymerization of the *d*-element complexes with aromatic azomethines proceeds along the cation-radical mechanism [8, 9] and resembles the process of the oxidative polymerization of phenols [10]. The growth of the polymer film on the electrode surface occurs as a result of interaction of the cation-radicals and the formation of covalent bonds between the phenyl fragments of the monomeric units. The structuring of poly-[Cu(salpn-1,3)] at the secondary level can proceed through the ππ- and dπ-interactions and by the formation of Cu–O–Cu bonds [11, 12] between fragments of neighboring polymer chains.

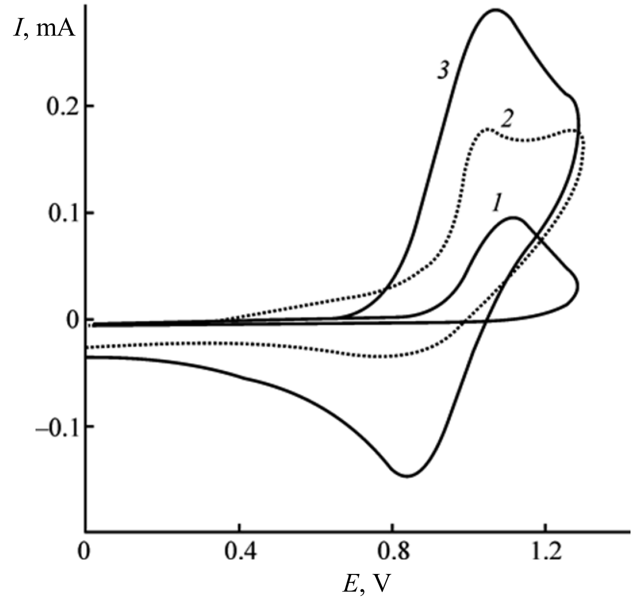


Fig. 1. Voltammograms of redox processes involving the complex H_2(salpn-1,3) (*1*), [Cu(salpn-1,3)] (*2*) and poly-[Cu(salpn-1,3)] (*3*). Supporting solution is CH_3CN–0.1 M Bu_4NClO_4, V_P 0.05 V s^{-1}.

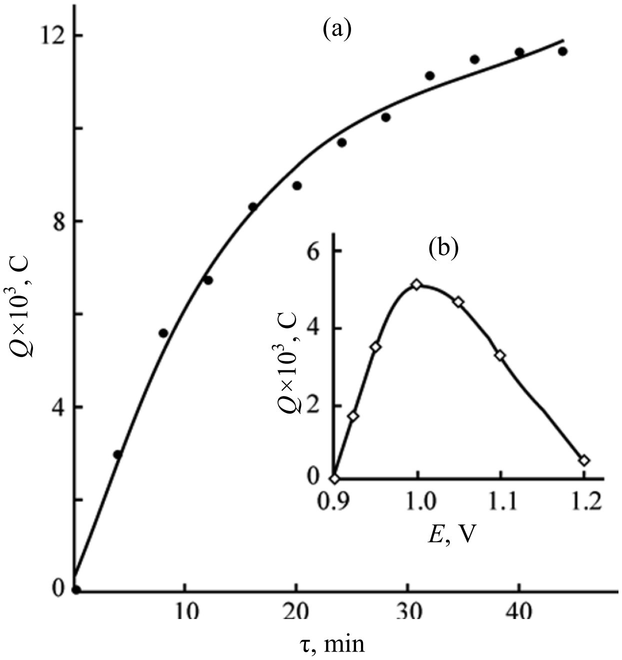


Fig. 2. The dependence of the amount of electricity consumed for complete reduction of poly-[Cu(salpn-1,3)] on the time of the electrode polarization in a solution of monomer at E_p = +1.0 V (a) and the polarization potential (b) for τ_p = 7 min.

Figure 1 shows the voltammograms of redox processes involving H_2(salpn-1,3), the complex [Cu(salpn-1,3)], and its polymeric form that has been obtained under potentiostatic conditions. Anodic part of the azomethine voltammograms is characterized by the presence of a maximum at +1.1 V, and its appearance points to the irreversible nature of the oxidation (curve *1*). The oxidation peak of [Cu(salpn-1,3)] (+1.03 V) is in the near potential region (curve *2*), which may indicate the ligand-centered character of the complex oxidation.

The voltammogram of poly-[Cu(salpn-1,3)] is characterized by broad anodic and cathodic peaks with potentials +1.06 and +0.84 V, respectively (curve *3*). The redox processes of such complexes are connected with the generation in the polymer phase a variety of the charge carriers of polaron nature, the delocalized radical cations and dications [13–15], and their subsequent disappearance.

The resulting polymer can stably exist both in the oxidized and reduced forms, which are of dark green and light green color, respectively. The transition between the redox forms of poly-[Cu(salpn-1,3)] is reversible and can occur in potentiostatic or potentiodynamic conditions.

In order to determine the optimum conditions of the electrochemical synthesis of poly-[Cu(salpn-1,3)] in potentiostatic conditions, we investigated the dependence of amount of the polymer formed on the potential (E_p) and the polarization time (τ_p) of the electrode in a solution of monomer complex . The amount of the poly-[Cu(salpn-1,3)] is proportional to the quantity of electricity *Q* consumed at its complete oxidation or reduction. The value of *Q* was determined by the integration of anode (cathode) parts of voltammograms recorded at complete oxidation (reduction) of the polymer at the potential sweep rate V_P = 0.01 V s^{-1}. The plot $Q = F(E_p)$ (Fig. 2b) is of extreme nature with a maximum at E_p = +1.0 V. The upward nature of the curve at the potentials E_p < +1.0 V is due to the increase in the rate of the electrochemical oxidation of the monomeric complex. A decrease in the amount of poly-[Cu(salpn-1,3)] at further increase in the potential of the electrode polarization is probably due to “peroxidation” of the polymer formed, namely, to irreversible violations in the system of π-conjugation. Thus, the value of E_p = +1.0 V, at which the rate of the formation of poly-[Cu(salpn-1,3)] is maximum, is optimal for the synthesis of the polymer in the potentsiostatich conditions.

The dependence of the amount of poly-[Cu(salpn-1,3)] obtained at the optimal E_p is linear at $\tau_p < 15$ min (Fig. 2). The gradual reaching saturation by the curve is likely to reflect the changes in the morphology of poly-[Cu(salpn-1,3)] resulting in hindering the charge transfer in the polymer bulk and associated with it voltage drop at the polymer-solution boundary.

The rate of charge transport in the polymer phase can be quantitatively characterized by the value of the charge diffusion coefficient D_{ct}. Depending on the nature of the limiting stage the D_{ct} value characterizes either the processes of transfer of charge carriers or the diffusion of ions of the supporting electrolyte in the polymer phase. At the sweep rates $V_P > 0.1$ V s^{-1} the oxidation/reduction of the polymer during one cycle is incomplete, that is, the conductive layer works under the conditions that are equivalent to the semi-infinite diffusion of electroactive material to the electrode surface. The diffusion current values recorded in these conditions were used to determine the value of D_{ct}. The D_{ct} in the poly-[Cu(salpn-1,3)] calculated by the Randles–Szewczyk equation [16] was 1.2×10^{-10} cm^2 s^{-1}.

The voltammogram parameters of poly-[Cu(salpn-1,3)] in the diffusion regime are largely depending on the nature of the supporting electrolyte anions and their concentrations. Our measurements showed that increase in the size of the counterions[1] is accompanied by a decrease in the value of the anode and cathode current peaks (Fig. 3a). Using as a background electrolyte the 0.1 M solution of $CF_3COONBu_4$ in CH_3CN leads to irreversible oxidation of the polymer and the complete loss of its electrical conductivity, which may be due to the impossibility of the trifluoroacetate ion to penetrate into the bulk of the polymer and to compensate its new charge state. Thus, the process of charge transport in the poly-[Cu(salpn-1,3)] films is limited by diffusion of the charge compensating ions in the polymer, the rate of which is characterized by the found D_{ct} values.

The latter was found to be about the charge transfer (E_a) we carried out the voltammetric measurements in the temperature range 250–293 K. Figure 3b shows the dependence of ln $D_{ct} = F(T^{-1})$, from which the value of E_a was determined. The latter was found to equal about 25 kJ mol^{-1}, which was observed when the process was limited by the ion diffusion. The dependence of the poly-[Cu(salpn-1,3)] voltammo-gram parameters on the nature and concentration of the ions of supporting electrolyte suggests that the resulting value of E_a characterizes the energy con-sumption at the displacement of polymer fragments for the formation of free volume where the counter-ions may move.

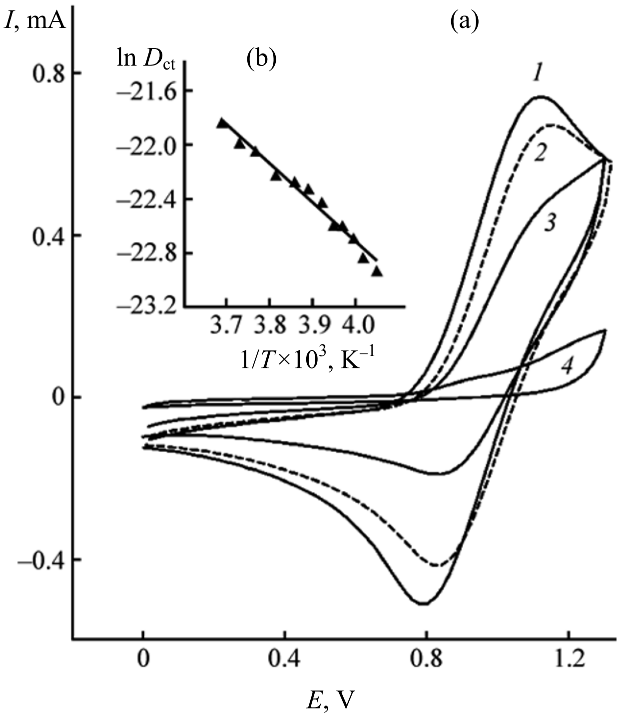


Fig. 3. (a) Voltammograms involving the complex poly-[Cu(salpn-1,3)] in difference background solutions: 0.1 M Bu_4NClO_4–CH_3CN (*1*), 0.1 M Bu_4NBF_4–CH_3CN (*2*), 0.1 M Bu_4NPF_6–CH_3CN (*3*), 0.1 M CF_3COOBu_4N–CH_3CN (*4*). V_P 0.2 V s^{-1}. (b) Determination of the activation barrier of charge transfer in poly-[Cu(salpn-1,3)]. Background solution 0.1 M Bu_4NClO_4–CH_3CN, V_P 0.2 V s^{-1}.

It should be noted that the D_{ct} values obtained depend on the time of accumulation (thickness) of the polymer film. For example, increasing the accumulation time of poly-[Cu (salpn-1,3)] from 4 to 16 min leads to an increase in the D_{ct} from 0.7×10^{-10} to 1.8×10^{-10} cm^2 s^{-1}. This fact apparently reflects the changes in the polymer morphology at its increasing thickness: the increase in the “porosity” or free volume of the polymer phase.

The investigated polymer complex is characterized by decreasing value of the diffusion current with increasing concentration of the supporting electrolyte. For example, in the sample of poly-[Cu(salpn-1,3)] obtained in a potentiostatic conditions, there is a two-

---

[1] The diameters of the ions ClO_4^-, BF_4^-, PF_6^-, and CF_3COO^- are, respectively, 3.37, 3.70, 4.35, and 7.20 Å.

The binding energies of 1*s*- and 2*p*-electrons and atomic concentrations of elements determined from the XPS spectra of H_2(salpn-1,3) and [Cu(salpn-1,3)]

Element, band	H_2(salpn-1,3)		[Cu(salpn-1,3)]	
	E_b, eV	C_{at}, %	E_b, eV	C_{at}, %
C1*s*	284.7	51.7	284.7	51.9
	286.1	28.5	286.1	28.6
O1*s*			529.3	0.1
	530.8	1.8	530.9	7.0
	532.7	7.9	531.8	0.5
N1*s*	398.8	7.1	399.2	7.2
	399.6	1.8		
	401.0	0.6	401.5	0.3
	402.6	0.6	403.2	0.6
$Cu2p_{3/2}$			934.4	3.7
			936.4	<0.1

fold reduction in peak currents with increasing concentration of the supporting electrolyte from 0.1 to 0.5 M. Probably, in concentrated solutions of the supporting electrolyte the degree of screening with counterions of the similarly charged sites in the polymer increases, and therefore the polymer takes a more compact configuration. Thus, at the decrease in the free volume in the poly-[Cu(salpn-1,3)] the ion diffusion decelerates which leads to a decrease in the rate of charge transport in the polymer phase.

To identify the azomethine base H_2(salpn-1,3) and the complex [Cu(salpn-1,3)], and to determine the charge state of copper in the oxidized and reduced forms of polymer we implemented the method of X-ray photoelectron spectroscopy (XPS). Of the XPS spectroscopic data we analyze the spectra of N1*s* and O1*s* of the functional atoms and of the metal center. The chemical shift values are determined from the experimental values of E_b of N1*s* and O1*s* of the Cu(II) complex with respect to the protonated azomethine H_2(salpn-1,3) (see the table).

In the H_2(salpn-1,3) molecule the nitrogen atom and the proton of hydroxy group are bound by a intramolecular hydrogen bond. This favors the transfer of the proton from the oxygen atom to the nitrogen atom with reaching the tautomeric equilibrium. Spectral lines of N1*s* with peaks at 398.8 and 399.6 eV are attributed to the nitrogen in the benzoid and quinoid forms of the azomethine base.

In the N1*s* spectrum of H_2(salpn-1,3) there are also two weak bands (401.0 and 402.6 eV), originating apparently from the redistribution of positive charge in the imino group at the formation of quinoid form. These additional components of the spectrum probably correspond to the nitrogen with localized (402.6 eV) and delocalized (401.0 eV) positive charges, and their low intensity is due to the low acidity of the hydroxy groups.

Processing the O1*s* XPS spectrum of H_2(salpn-1,3) allowed us to fit it by two components, at 530.8 and 532.7 eV, the first band corresponding to the phenolic oxygen, and the second, less intense, to the deprotonated (quinoid) oxygen.

The formation of the [Cu(salpn-1,3)] complex leads to the change in the binding energy of the strongest components in the O1*s* and N1*s* spectra compared with azomethine base. Thus, in the spectra a positive chemical shift in the binding energy of N1*s* electrons (+0.4 eV) is found and a decrease in the binding energy of the O1*s* band from 532.7 to 530.9 eV. Such negative chemical shift of O1*s* band of phenolic oxygen (–1.8 eV) indicates the total increase in the electron density in the ligand system upon complexation. Moreover, these changes in the binding energy of the spectral bands N1*s* and O1*s* confirm the formation of coordination node [CuN_2O_2].

The Cu2*p* spectrum of [Cu(salpn-1,3)] complex shows that in the initial compound copper is present in two different charge states, with E_b of $Cu2p_{3/2}$ 934.4 and 936.4 eV. The main band, with the E_b = 934.4 eV, corresponds to the ions Cu(II) [6]. The presence in the Cu2*p* spectrum of a low-intensity component, $Cu2p_{3/2}$, with E_b = 936.4 eV, and the negative chemical shift of the O1*s* band probably result from the intermolecular interaction of stacking type characteristic of the crystalline state of the [Cu(salpn-1,3)] complex. Such interactions lead to the formation of dimeric structures with the intermolecular Cu–O–Cu bonds due to the withdrawing of the electron density from the metal site of one monomeric fragment to the oxygen atom of another [7, 11].

The ratios of the atomic concentrations of the major components obtained by the analysis of the XPS spectra confirm the structure of the synthesized azomethine and its complex compounds with Cu(II).

Compared to the original [Cu(salpn-1,3)] complex, in the XPS spectra of the polymer there are additional bands belonging to other chemical elements. This is due to the presence in the polymer phase of the components of supporting electrolyte and the new structural fragments participating in the charge transfer [14].

The charge state of the metal site does not change at the oxidation/reduction of the polymer based on [Cu(salpn-1,3)]. In the oxidized and reduced forms of the polymer, as well as in the initial monomeric complex, the binding energy of the Cu2$p_{3/2}$ band is in the range 934.3–934.5 eV. The data obtained suggest the ligand-centered nature of the oxidation–reduction process of poly-[Cu(salpn-1,3)]. It should be noted that although the metal site formally does not change its oxidation state, it may act as a "bridging element" connecting the areas of the local conjugation of the polymer and participating in the processes of the charge transfer in the polymer phase [5, 14].

The oxidized form is characterized by a higher intensity of the Cl2*p* band of the XPS spectrum compared with reduced one. This demonstrates the insertion into the polymer of additional perchlorate ions at the oxidation required for maintaining its electroneutrality.

Figure 4 (curves *1* and *2*) shows the electron absorption spectra of azomethine H_2(salpn -1,3) and its complex [Cu(salpn-1,3)], as well as of the polymer form of latter in oxidized and reduced states (curves *3*–*5*). For the absorption spectrum of H_2(salpn-1,3) in acetonitrile the presence of strong absorption bands ($\pi\pi^*$-tranfer in phenyl moiety) is typical with maxima at λ 215 and 257 nm, whose positions are not affected by the solvent polarity. The low-energy band with λ_{max} 315 nm is identified as corresponding to $n\pi^*$- and $\pi\pi^*$-transitions in the azomethine group [18]. In the absorption spectrum of H_2(salpn-1,3) in the solvents of substantial polarity (alcohols) in the region of 400 nm the absorption band appears of medium intensity (log ε = 3.4) corresponding to $n\pi^*$ transition in the quinoid form of the azomethine base [19].

The complexation leads to a regular red shift of the peaks of high-intensity bands of intraligand type. In the absorption spectrum of the complex [Cu(salpn-1,3)] there is a new strong band with a maximum located in the range 358–365 nm depending on the solvent polarity. The red shift of the maximum with decreasing polarity of solvent allows us the assignment of this absorption band to the electronic transition with the charge transfer of d_M–π_L^* type [20].

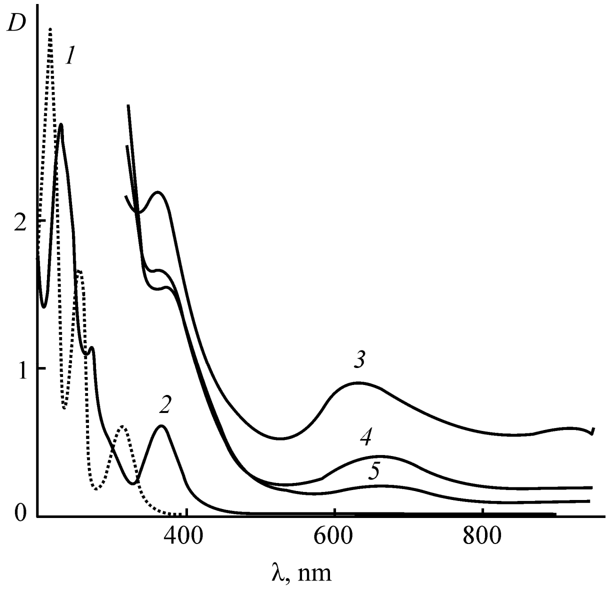


Fig. 4. Electron absorption spectra of H_2(salpn-1,3) (*1*) and [Cu(salpn-1,3)] (*2*) in CH_3CN (293 K, *c* 0.1 mg ml^{-1}). Electron absorption spectra of poly-[Cu(salpn-1,3)] in oxidized (*3*), rediced (*5*), and intermediate (*4*) forms, obtained by the optically transparent electrode polarization at +1.0, 0.0, and +0.5 V potentials,

The electrochemical polymerization of [Cu(salpn-1,3)] leads to significant changes in the absorption spectrum of the polymer compared to the parent monomeric complex. Figure 4 (curves *3*–*5*) shows the absorption spectra of poly-[Cu(salpn-1,3)] registered at gradual reduction of the oxidized form of the polymer. The reduction of the polymer is accompanied by a change of its dark-green color to light-green, that is, by an electrochromic effect. The strong absorption of the polymer at $\lambda \leq 300$ nm is due to $\pi\pi^*$-transitions in the phenyl moiety of the polymer [21].

In the absorption spectrum of the oxidized form of poly-[Cu(salpn-1,3)] a broad absorption band appears in the region of 600–800 nm, which is largely eliminated in going to the reduced form of the polymer. The absorption in this spectral region is characteristic of the polymer forms of the *d*-element complexes with aromatic azomethine bases [2, 22] and the doped forms of organic conducting polymers. To a large extent it is caused by the localized polaron states [23, 24]. The incomplete elimination of this absorption band in the red region of the spectrum in going to the reduced form of poly-[Cu(salpn-1,3)] demonstrates a partial retention in it of the oxidized fragments.

Thus, in this paper we considered the results characterizing optical and electrochemical properties of the polymer on the basis of the [Cu(salpn-1,3)] complex.

We determined the optimal mode of the electrochemical synthesis of the polymer under potentiostatic conditions. The rate of the oxidation/reduction of poly-[Cu(salpn-1,3)] in the electrolyte medium is limited by the mobility of the counter-ions in the polymer phase. The activation barrier of the charge transfer in the bulk of the polymer is about 25 kJ mol^{-1}.

Using XPS the constancy of the charge state of copper in the reversible transition between the oxidized and reduced forms of poly-[Cu(salpn-1,3)] is substantiated. The nature of the absorption spectra of poly-[Cu(salpn-1,3)] in the red region shows its similarity to the organic conducting polymers.

EXPERIMENTAL

Synthesis of the azomethine base H_2(salpn-1,3) and the complex [Cu(salpn-1,3)] was performed according to the procedures described in [22].

Identification of the starting materials was carried out by elemental analysis, XPS, ESR, and IR spectroscopy.

The electrochemical polymerization of the complex and the study of the properties of the polymer were carried out on a voltammetrc device controlled by IPC-Pro computer software. As the working electrode a platinum wire (S = 0.26 cm^2) was used. Auxiliary electrode was a platinum plate (S = 2.2 cm^2), the reference electrode was a silver chloride electrode filled with a saturated solution of NaCl.

As a supporting electrolyte at the preparation of the samples 0.1 M solution of Bu_4NClO_4 in acetonitrile was used. The concentration of the Cu(salpn-1,3)] complex in the supporting solution was 1×10^{-3} M. The polymer for the electrochemical measurement was prepared in potentiostatic conditions: $E_\text{p} = +1.0$ V; τ_p = 7 min. The D_ct values in the polymer were determined within the error $\pm0.5\times10^{-10}$ $\text{cm}^2\ \text{s}^{-1}$.

The low-temperature electrochemical experiments were performed with the use of a special cylindrical three-electrode cell, placed in a compact thermostat to maintain the temperature of the supporting solution in the range 243–293 K.

The XPS spectra were recorded on an AXIS Ultra DLD electron spectrometer (Kratos Analytical Ltd, UK) with the excitation by AlK_α monochromatic X-ray radiation (1486.6 eV).

Electron absorption spectra of the starting materials and the polymer in the oxidized and reduced forms were recorded on a Shimadzu UV-2550 spectrophotometer.

REFERENCES

1. Abruna, H.D., *Coord. Chem. Rev*., 1988, vol. 86, no. 1, pp. 135–189.
2. Shagisultanova, G.A., Orlova, I.A., and Borisov, A.N., *Photochem. Photobiol. A: Chemistry*, 1997, vol. 103, no. 3, pp. 249–255.
3. Shagisultanova, G.A., *Teor. Prikl. Khim*., 1991, vol. 27, pp. 330–338.
4. Dahm, C.E. and Peters, D.G., *Anal. Chem*., 1994, vol. 66, no. 19, pp. 3117–3123.
5. Vilas-Boas, M., Freire, C., de Castro, B., Christensen, P.A., and Hillman, A.R., *Inorg. Chem*., 1997, vol. 36, pp. 4919–4924.
6. *Handbook of X-ray Photoelectron Spectroscopy*, Chastein, J., Ed., USA: Perkin Elmer Corp., 1992.
7. Shen, H.Y., Liao, D.Z., Jiang, Z.H., Yan, S.P., and Wang, G.L., *Chem. J. of Chinese Universities*, 1999, no. 7, pp. 1017–1020.
8. Hoferkamp, L.A. and Goldsby, K.A., *Chemistry of Materials*, 1989, vol. 1, pp. 348–352.
9. Blaho, J.K. and Hoferkamp, L.A., *Polyhedron*., 1989, vol. 8, pp. 113–117.
10. Reutov, O.A., Kurts, A.L., and Butin, K.P., *Organicheskaya khimiya* (Organic Chemistry), Part III, Moscow: Binom, 2004.
11. Boca, R., Elias, H., Haase, W., Hüber, M., Klement, R., Müller, L., Paulus, H., Svoboda, I., and Valko, M., *Inorg. Chim. Acta*., 1998, vol. 278, no. 2, pp. 127–135.
12. Green, M. and Tasker, P.A., *Inorg. Chim. Acta*., 1971, vol. 5, no. 1, pp. 65–69.
13. Vilas-Boas, M., Freire, C., de Castro, B., and Hillman, A.R., *J. Phys. Chem. B*., 1998, vol. 102, no. 43, pp. 8533–8538.
14. Vilas-Boas, M., Freire, C., de Castro, B., Christensen, P.A., and Hillman, A.R., *Chem. Eur. J*., 2001, vol. 7, no. 1, pp. 139–144.
15. Vilas-Boas, M., Santos, I.C., Henderson, M.J., Freire, C., Hillman, A.R., and Vieil, E., *Langmuir*,. 2003, vol. 19, no. 18, pp. 7460–7465.
16. Plambeck, D., *Elektrokhimicheskie metody analiza. Osnovy teorii i primenenie* (Electrochemical Methods of Analysis. Basis and Application), Moscow: Mir, 1985.
17. Leidner, C.R. and Murray, R.W., *J. Am. Chem. Soc*., 1985, vol. 107, nos. 1–3, pp. 551–556.

18. Alexander, P.V. and Sleet, R.J., *Aust. J. Chem.*, 1970, vol. 23, no. 6, pp. 1183–1190.
19. Estiu, G.L., Jubert, A.H., Costamagna, J., and Vargas, J., *Mol. Struct. (Theochem).*, 1996, vol. 367, pp. 97–110.
20. Demas, J.N. and DeGraff, B.A., *Anal. Chem.*, 1991, vol. 63, p. 829.
21. Chen, H. and Archer, R.D., *Inorg. Chem.*, 1994, vol. 33, no. 23, pp. 5195–5202.
22. Borisov, A.N., Shchukarev, A.V., and Shagisultanova, G.A, *Zh. Prikl. Khim.,* 2009, vol. 82, no. 7, pp. 1147–1154.
23. Patil, A.O., Heeger, A.J., and Wudl, F., *Chem. Rev.,* 1988, vol. 88, no. 1, pp. 183–203.
24. Ivanov, V.F., *Doctorate (Chem.) Dissertation*, Moscow, 2006.