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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

A New Conducting Polymer Based on the Complex of Cu(II) with *N,N'*-Bis(3-methoxysalicylidene)-1,3-propylenediamine

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Abstract—Conducting polymeric form of the complex of Cu(II) with *N,N'*-bis(3-methoxysalicylidene)-1,3-propylenediamine was obtained by the electrochemical method. X-ray photoelectron spectroscopy and electronic absorption spectroscopy were used to characterize the starting substances and their polymeric forms. The invariance of the charge state of copper in the oxidation-reduction of the polymer based on the complex of Cu(II) with a Schiff base was substantiated.

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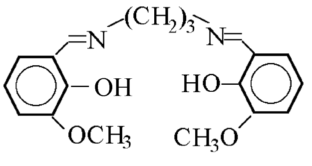
The appearance and rapid development of a promising field of modern chemistry, supramolecular chemistry concerned with organized associations of saturated-coordination species, is due to advances in modern basic research and high technologies [1–3]. A particular place in supramolecular chemistry belongs to electrically conducting supramolecular structures—polymers based on organometallic and complex compounds of transition metals. As a rule, these are intensely colored substances possessing a set of valuable properties. To these properties belong redox conductivity of polymeric complexes, photosensitivity, photo- and electrical activity, capacity for electrocatalysis, and electrochromic properties.

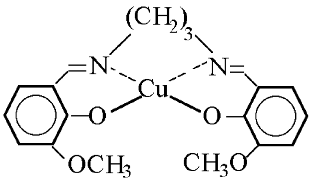
Of particular importance from the standpoint of the possible practical use are polymeric structures stable against chemical and physical action, characterized by a high rate of charge transport in the bulk of the solid phase. Polymeric compounds satisfying these requirements, including those based on complexes with Schiff bases, can be regarded as promising materials for sensor, chemotronic, photo- and electrocatalytic devices, and solid-phase converters of luminous energy [1].

Previously, the method of electrochemical oxidation has been employed to obtain polymers based on complexes of transition metals with tetra- and bidentate Schiff bases of the N_2O_2-, N_4-, and NO-types [4–9].

This communication reports on synthesis of a new complex of Cu(II) with a tetradentate Schiff base of the N_2O_2 type, *N,N'*-bis(3-methoxysalicylidene)-1,3-propylenediamine (H_2msalpn-1,3), and of a conducting polymer by electrochemical oxidation of [Cumsalpn-1,3]. The starting substances (Fig. 1) and the polymeric form of the complex [Cumsalpn-1,3] in the oxidized and reduced states were characterized by X-ray photoelectron spectroscopy (XPS) and electronic absorption spectroscopy.



H_2msalpn-1,3



[Cumsalpn-1,3]

EXPERIMENTAL

N,N'-Bis(3-methoxysalicylidene)-1,3-propylenediamine (H_2msalpn-1,3) was synthesized by condensation of 2-hydroxy-3-methoxybenzaldehyde with propylenediamine-1,3. For this purpose, equal volumes of ethanol solutions containing reagents in stoichiometric amounts were mixed. The resulting yellow precipitate was filtered off, recrystallized from ethanol, and dried at 70°C. The yield of the substance was 90%. The preparation obtained had a melting point of 75–77°C.

To obtain [Cumsalpn-1,3], an equal volume of an aqueous solution containing a stoichiometric amount of $Cu(CH_3COO)_2 \cdot H_2O$ was added under agitation to a solution of H_2msalpn-1,3 in ethanol (2.5 mmol, 10 ml of ethanol). A solution of copper(II) acetate was acidified with acetic acid to preclude hydrolysis. The resulting heterogeneous mixture was agitated for 1 h under moderate heating, after which dark green crystals were filtered off. The complex obtained was several times washed with distilled water, hot ethanol, and diethyl ether. The substance was dried at a temperature of 70°C and then in a vacuum over phosphorus pentoxide. The yield of the product was 86%.

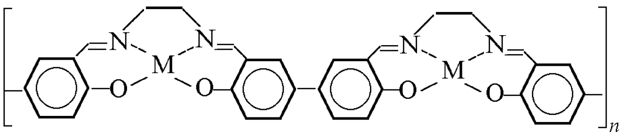
The Schiff base and the complex on its basis were identified using results of XPS, elemental analysis, and electronic absorption spectroscopy.

Voltammetric measurements with a linear potential sweep were performed on an IPC-Pro potentiostat with a hermetically sealed three-electrode Pyrex cell with separated spaces of the working, auxiliary, and reference electrode. A platinum wire sealed in a Pyrex sheath served as the indicator electrode, and a platinum grid, as the auxiliary electrode. A silver chloride electrode filled with a saturated sodium chloride solution was used as the reference. A 0.1 M solution of tetraethylammoniun perchlorite in acetonitrile, purified by the procedure reported in [10], served as a supporting electrolyte.

An oxidative electrochemical synthesis of polymers based on H_2msalpn-1,3 and [Cumsalpn-1,3] complex was carried out with the electrode polarized under potentiostatic and potentiodynamic conditions at potentials in the range 0.0–+1.2 V. Oxidized forms of the polymers were converted to the reduced state under a potentiostatic polarization of modified electrodes in a supporting solution at a potential of 0.0 V for 1 h.

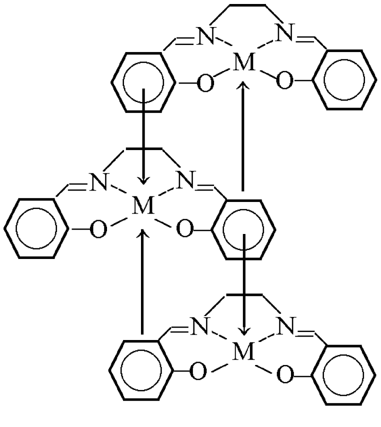
In the last decade, a considerable body of experimental data on properties of polymers based on complexes of transition metals with Schiff bases of various types has been accumulated. However, no common opinion about the formation mechanism, structure of poly-[MSchiff] polymeric complexes and charge-transfer processes in these complexes has been formed.

According to the ligand-centered model of the poly-[MSchiff] structure, [MSchiff] complexes polymerize by the cation-radical mechanism with formation of carbon–carbon bonds between the phenyl moieties of ligands:



As charge carriers serve species of polaronic nature; complex-forming agent does not change its charge state in the oxidation-reduction of the polymer [11, 12]. It should be noted that the commonly accepted concept is that about polarons and bipolarons (cation-radicals and dications, respectively, from the chemical standpoint) as forms in which charge is stored in organic electron-conducting polymers with a nondegenerate ground state [13].

The metal-centered structural model assumes that the polymer is formed via a donor-acceptor interaction between the metal ion of one moiety with ligands of neighboring moieties:



Polymers possess a redox conductivity, i.e., the charge transfer in the polymer phase is regarded as electronic exchange between metallic centers in different oxidation states via the π-system of ligands [6, 14].

It should be noted that none of the models of formation and structure of poly-[MSchiff], mentioned above, can be considered completely confirmed because of being unable to account for the whole body of experimental data.

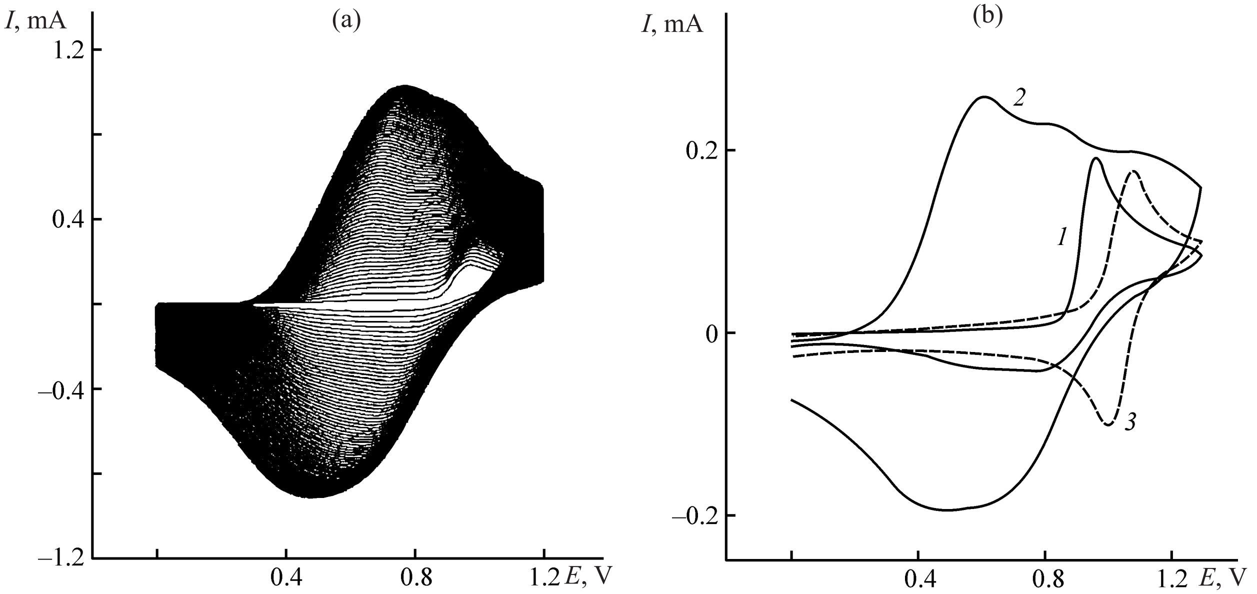


Fig. 1. (a) Formation of the polymeric form of the complex in a 2 × 10^{-3} M solution of [Cumsalpn-1,3] in CH_3CN/0.1 M Et_4NClO_4 and (b) voltammograms of redox processes involving (*1*) [Cumsalpn-1,3] complex, (*2*) poly-[Cumsalpn-1,3] obtained in 70-fold potential sweeping in the range 0.0–+1.2 V, and (*3*) $[Fe(phen)_3](ClO_4)_2$. Potential sweep rate 50 mV s^{-1}. (a) 70 cycles of scanning and (b) 0.1 M solution of Et_4NClO_4 in CH_3CN as supporting electrolyte. (*I*) Current and (*E*) potential.

In electrochemical oxidation of the [Cumsalpn-1,3] complex, a dark green electrically conducting polymeric film is formed on the surface of the platinum electrode. Under similar conditions occurs intense polymerization of *N,N*'-bis(3-methoxysalicylidene)-1,3-propylenediamine (H_2msalpn-1,3) and *N,N*'-bis(3-methoxysalicylidene)ethylenediamine (H_2msalen).

Figure 1a shows voltammograms that reflect the polymerization of the [Cumsalpn-1,3] complex in cyclic variation of the potential of the platinum electrode. The steady increase in the currents of the anodic and cathodic peaks in the voltammograms indicates that a conducting film of poly-[Cumsalpn-1,3] is formed on the electrode surface and is stabilized. Figure 1b shows voltammograms of [Cumsalpn-1,3] and <pilot> compounds: tris(1,10-phenanthroline)iron(II) perchlorate and ferrocene. Comparison of the voltammograms suggests that the oxidation of the starting complex is of single-electron nature. The anodic part of the voltammogram of the starting monomeric compound [Cumsalpn-1,3] in acetonitrile has a peak at +0.96 V. The voltammogram of poly-[Cumsalpn-1,3] shows anodic peaks at +0.61, +0.84, and +1.11 V and a broad poorly resolved cathodic wave. As the most probable reason for the existence of several oxidation peaks should be considered generation of various charge carriers of polaronic nature, cation-radicals and dications, in the polymeric phase [15–17].

The XPS technique was used to identify the compounds obtained and to substantiate the charge state of the metallic center in the oxidized and reduced forms of the polymer. XPS spectra were recorded on an AXIS Ultra electronic spectrometer (Kratos Analytical, Great Britain) under excitation with monochromatic X-ray radiation ($Al_{K\alpha}$, 1486.6 eV). Crystalline samples of the ligand and monomeric complex were manually compacted into a special-purpose powder holder. Polymers in the oxidized and reduced forms were synthesized on optically transparent electrodes with a conducting tin dioxide layer deposited by thermal evaporation in a vacuum. When the spectra were recorded, the samples were cooled with liquid nitrogen to diminish the risk of their possible decomposition. To compensate for the surface charging, a low-energy electron gun was used. The base residual pressure in the spectrometer in the course of the experiments was 5 × 10^{-7} Pa. The spectra were processed using the Vision 2 software package from Kratos Analytical Co. The error in determining the binding energy E_b of electrons from inner shells did not exceed ±0.1 eV, and that of quantitative analysis, 10 rel %. The scale of binding energies was calibrated against the C1s line of aliphatic carbon (E_b = 285.0 eV). The energies of binding of inner-shell electrons with nuclei of the corresponding atoms and the atomic concentrations of elements for H_2msalpn-1,3 and [Cumsalpn-1,3] are listed

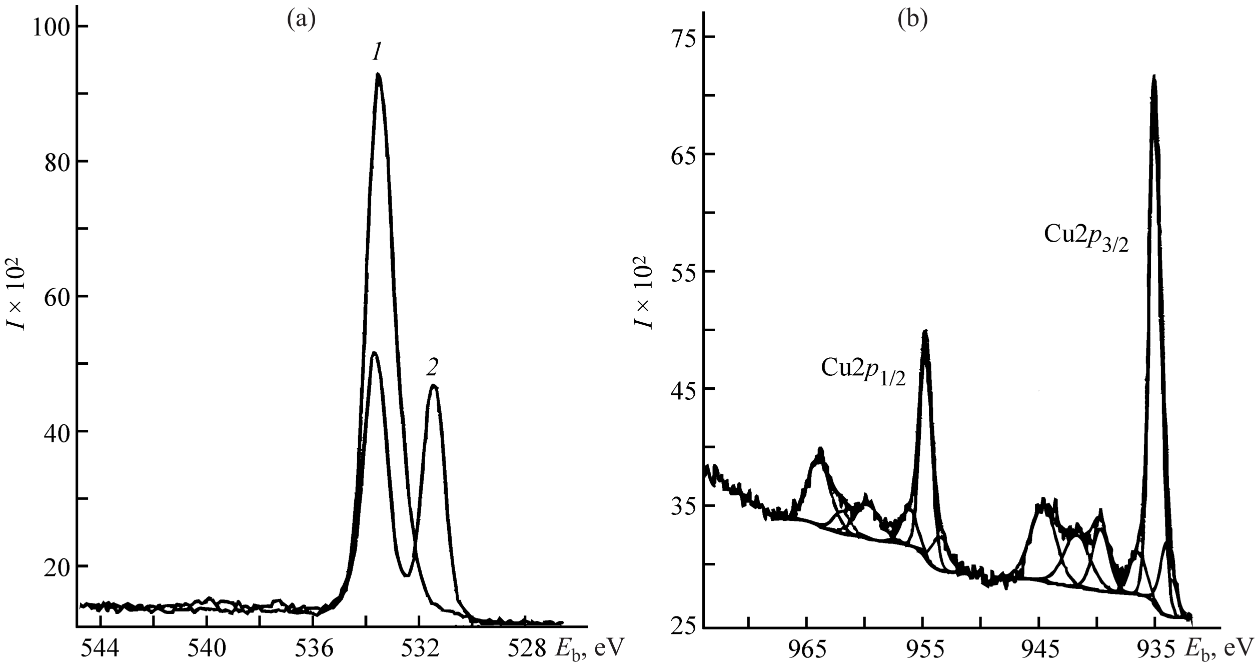


Fig. 2. (a) O1s XPS spectra of (*1*) H_2msalpn-1,3 and (*2*) [Cumsalpn-1,3]. (b) $Cu2p_{3/2}$ XPS spectrum of the [Cumsalpn-1,3] complex. (*I*) Signal intensity and (E_b) binding energy.

in Table 1. The ratios between the atomic concentrations of the main components confirm the composition of the Schiff base obtained and of the complex Cu(II) compound on its basis.

Comparison of the binding energies of donor centers in free and coordinated states can be used to judge about changes in the type of the electron density distribution upon complexation, as well as about donor and acceptor properties of the corresponding ligands [18, 19].

The XPS spectra can be used to analyze spectra of the functional atoms, N1s and O1s, and of the metallic center. The chemical shifts were found from experimental values of E_b for N1s and O1s of the monomeric complex of Cu(II) relative to H_2msalpn-1,3.

The highest intensity lines peaked at 399.3 and 399.5 eV for H_2msalpn-1,3 and [Cumsalpn-1,3], respectively, are attributed to the nitrogen atom in the azomethine group. The N1s spectrum of the ligand contains additional two low-intensity lines (400.1 and 402.8 eV). The appearance of the first line is due to protonation of the nitrogen of the azomethine group and its low intensity is associated with the lowered acidity of hydroxo groups of the ligands, in the *ortho* position to which are situated donor-type, as regards the mesomeric effect, methoxy groups. The N1s line in the spectrum of H_2msalpn-1,3 (402.8 eV) is attributed to the electronically excited state of the π–π* type of the nitrogen atom in the azomethine group [20].

Processing of the O1s XPS spectrum of H_2msalpn-1,3 (Fig. 2a, curve *1*) resolves two components, at 533.4 and 532.1 eV; the first is attributed to oxygen in hydroxo and methoxy groups, and the second with a substantially lower intensity, to deprotonated oxygen O^-.

Table 1. Binding energies of 1*s* and 2*p* electrons and atomic concentrations of elements, found from photoelectron spectra of H2msalpn-1,3 and [Cumsalpn-1,3]

Element, line	H_2msalpn-l,3		[Cumsalpn-1,3]	
	E_b, eV	*C*, %	E_b, eV	*C*, %
Cls	285.0	37.01	285.0	35.57
	286.5	40.43	286.5	41.14
O1s	532.1	0.95	531.5	6.16
	533.4	14.27	533.6	7.34
Nls	399.3	6.08	399.5	5.75
	400.1	0.42	401.4	0.27
	402.8	0.59	403.2	0.49
			404.1	0.16
$Cu2p_{3/2}$			933.9	
			935.1	3.12
			936.5	

Table 2. Binding energies of 1*s* and 2*p* electrons and atomic concentrations of elements, found from photoelectron spectra for poly-[Cumsalpn-1,3] in oxidized and reduced forms

Element, line	Poly[H_2msalpn-l,3]$_{red}$		Poly-[Cumsalpn-l ,3]$_{ox}$	
	E_b, eV	*C*, %	E_b, eV	*C*, %
Cls	285.0	28.82	285.0	29.3
	286.3	27.6	286.3	28.35
	287.0	9.52	287.4	7.76
	288.5	3.18	288.6	2.52
	289.7	2.04	289.6	2.23
Ols	531.5	5.45	531.4	4.23
	533.1	11.63	532.9	11.87
	534.0	2.23	533.7	3.44
	536.1	0.67	535.5	0.83
Nls	399.5	3.45	399.4	2.73
	400.6	1.5	400.5	2.01
			401.6	0.55
	403.0	0.7	402.9	0.65
Cu2$p_{3/2}$	933.4		933.0	
	935.1	1.84	935.0	1.73
	936.9		936.7	
Cl2$p_{3/2}$	198.2	0.3	198.1	0.39
	200.8	0.32	200.8	0.51
	207.9	0.74	207.9	1.02

Figure 2a (curve *2*) shows an XPS spectrum of H_2msalpn-1,3 in the coordinated state. The coordination with Cu(II) ions leads to a substantial negative shift of the O1s line of the ligand from 533.4 to 531.5 eV (–1.9 eV), whereas the spectral component attributed to oxygen in methoxy groups does not change its position. Simultaneously, the peak of the binding energy of N1s electrons is shifted to higher values, to 399.5 eV (+0.2 eV) for [Cumsalpn-1,3], compared with H_2msalpn-1,3.

Figure 2b shows an XPS spectrum of the Cu2$p_{3/2}$ core level for the monomeric complex [Cumsalpn-1,3]. The spectrum contains, in addition to the main line (935.1 eV) corresponding to the bivalent state of copper [21], two low-intensity peaks at 933.9 and 936.5 eV. The presence of these components in the Cu2$p_{3/2}$ spectrum and the negative chemical shift of the O1s lines are probably due to an intermolecular interaction of the stacking type, characteristic of the crystalline state of the [Cumsalpn-1,3] complex. The possibility of an interaction of this kind was confirmed for Cu(II) complexes with Schiff bases and can lead to formation of dimeric structures with Cu–O–Cu intermolecular bonds via acceptance of the electron density of the metallic center of one monomeric moiety by an oxygen atom of another moiety [22–24].

The Cu2$p_{3/2}$ XPS spectrum of the starting complex also shows a broadened satellite peak in the form of a poorly resolved triplet whose shape is determined by the multiplet splitting of 3*d* states of copper(II) [25], caused by tetragonal distortion of the structure of the complex.

The formation of covalent bonds between phenyl moieties of the complex (evidenced by the capacity of H_2msalpn-1,3 for polymerization) and the structuring of the polymer on the secondary level via stacking interaction of neighboring polymeric chains occur simultaneously. It can be assumed that a 2D conjugated system is formed in the process, in which Cu–O–Cu fragments are “electronic channels” determining the direction and improving the efficiency of charge transfer in the bulk of a polymer in its formation and oxidation-reduction.

Probably, the interaction of the stacking type between the monomeric moieties of neighboring chains predetermines the structuring of poly-[Cumsalpn-1,3] on the secondary level.

It should be noted that the inclusion of the metallic center into the conjugation chain and the charge transfer in the polymeric chain does not necessarily mean a change in its charge state [16, 26].

Table 2 lists XPS data for the oxidized and reduced forms of poly-[Cumsalpn-1,3]. Compared with the starting [Cumsalpn-1,3] complex, additional lines characterizing the chemical state of elements appear in the XPS spectra of the polymers. This may be due to existence in the polymeric phase of quinoid moieties associated with generation of charge carriers, ions of the supporting electrolyte ions interacting with these moieties, and solvent molecules [16]. Although additional data are necessary for a more detailed analysis of structural changes occurring in the formation and oxidation-reduction of poly-[Cumsalpn-1,3], it is, nevertheless, possible to make certain conclusions.

The charge state of the metallic center remains unchanged upon oxidation-reduction of a polymer based on [Cumsalpn-1,3]. For the oxidized and reduced forms of the polymer and of the starting monomeric complex, the binding energy for the Cu2$p_{3/2}$ line is within the range 935.0–935.1 eV. At the same time, a positive chemical shift of one of the C1s lines (+0.4 eV) and a decrease in the binding energy of O1s electrons by 0.2–0.6 eV are observed in oxidation of poly-[Cumsalpn-1,3]. Thus, the reversible transition of the polymer from the oxidized to

Table 3. Main parameters of electronic absorption spectra of H_2msalpn-1,3 and [Cumsalpn-1,3]

Compound	C_2H_5OH, Z^a = 79.6 kcal mol^{-1}		CH_3CN, Z = 71. kcal mol^{-1}		CH_2Cl_2, Z = 64.2 kcal mol^{-1}	
	λ_{max}, nm	log ε	λ_{max}, nm	log ε	λ_{max}, nm	log ε
H_2msalpn-l,3	222	4.44	221	4.02	221	4.17
	263	4.15	261	3.74	262	4.04
	295^b	3.74	328	3.10	330	3.37
	330	3.43				
	421	3.26				
[Cumsalpn-1,3]	236	4.57	238	4.08	239	4.20
	284	4.40	283	3.79	286	4.08
	374	4.04	376	2.08	384	3.57

[a] *Z* is the empirical spectroscopic parameter reflecting the solvent polarity [28].
[b] Shoulder.

the reduced form is formally a ligand-centered process.

The ratio between the atomic concentrations of chlorine and copper makes it possible to estimate to a first approximation the number of perchlorate ions per a monomeric moiety in the oxidized and reduced forms of poly-[Cumsalpn-1,3]. This ratio exceeds unity for the oxidized form of poly-[Cumsalpn-1,3] (1.1–1.3) and is smaller than unity for the reduced form (0.7–0.8).[1] These concentration ratios Cl : Cu suggest that the reduction of the oxidized form of poly-[Cumsalpn-1,3] under the potentiostatic conditions occurs only partly, which enables identification of its reduced state as “half-oxidized.”

The increased content of chlorine in the oxidized form of the polymer, compared with the reduced form, is an indirect evidence that, in oxidation, an additional amount of counter ions is incorporated into the polymer, for its electroneutrality to be maintained. Probably, the effect of X-ray radiation in recording of XPS spectra leads to partial disintegration of perchlorate ions, which is indicated by the presence of three components in the Cl2$p_{3/2}$ line.

The electronic absorption spectra of the starting substances and polymers in the oxidized and reduced forms were recorded on a Shimadzu UV-2550 spectrophotometer. The accumulation of oxidation products on the optically transparent electrodes with a conducting SnO_2 layer enables recording of electronic absorption spectra of the polymers in the both oxidized and reduced forms. Polymeric forms of [Cumsalpn-1,3] and H_2msalpn-1,3 on the Sn dioxide surface were obtained in the potentiostatic mode under optimal formation conditions.[2] The oxidized form directly formed in electrochemical synthesis of the polymer was converted to the reduced form by potentiostatic polarization of a chemically modified electrode at *E* = 0.0 V for 1 h in a supporting electrolyte solution.

Solutions of H_2msalpn-1,3 in ethanol, acetonitrile, and dichloromethane are characterized by the presence

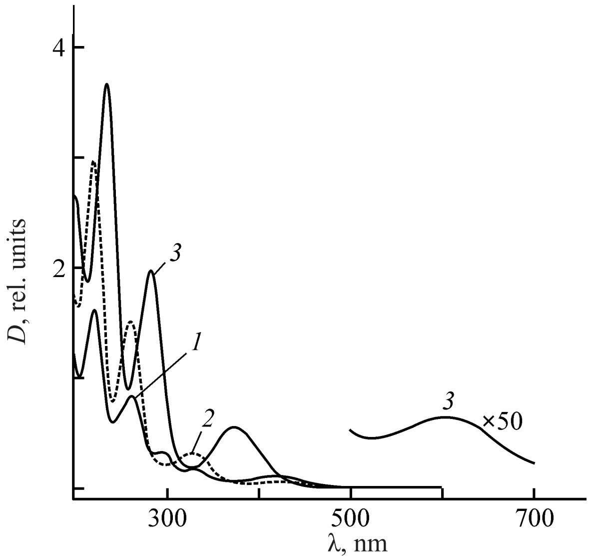


Fig. 3. Electronic absorption spectra: H_2msalpn-1,3 in (*1*) C_2H_5OH and (*2*) CH_3CN; (*3*) [Cumsalpn-1,3] in CH_3CN. T = 293 K, c = 0.1 mg ml^{-1}. (*D*) Optical density and (λ) wavelength; the same for Fig. 4.

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[1] According to XPS data and results of scanning electron microscopy with X-ray fluorescence microanalysis.

[2] Supporting electrolyte 0.1 M solution of Et_4NClO_4 in CH_3CN; $c(H_2$msalpn-1,3) = c(Cumsalpn-1,3) = 2 × 10^{-3} M; electrode polarization potential +1.1 V; time of polarization of the electrodes in solutions of monomeric compounds, 30 min.

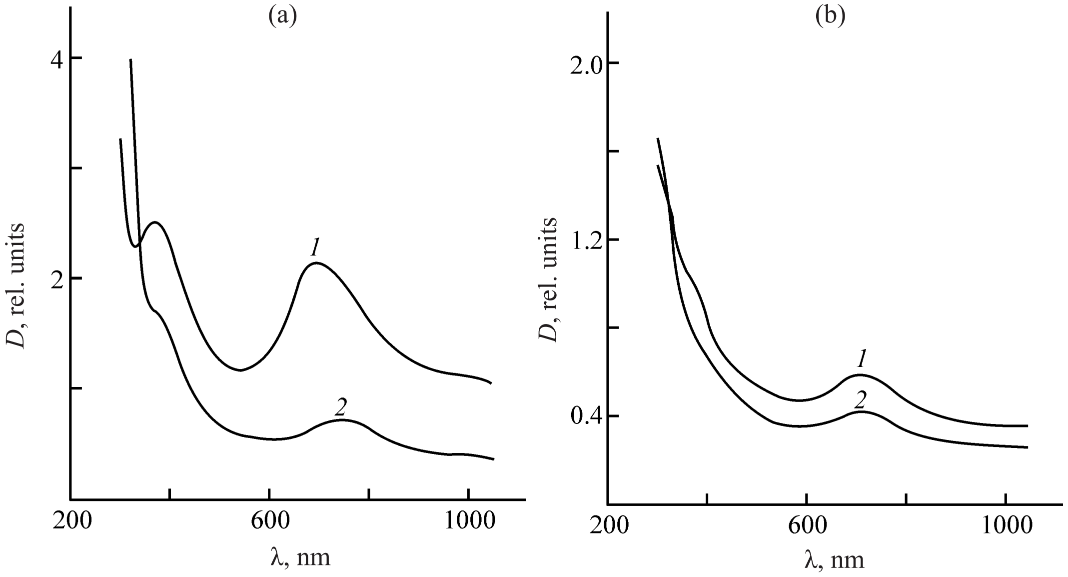

Fig. 4. Electronic absorption spectra of (a) poly-[Cumsalpn-1,3] and (b) poly-H_2msalpn-1,3 in (*1*) oxidized and (*2*) reduced forms.

of high-intensity absorption bands (π–π* transitions) peaked at λ = 221–222 and 261–263 nm, whose positions are hardly affected by changes in the solvent polarity (Table 3).

The absorption spectra of H_2msalpn-1,3 in all the solvents contain a band with λ_{max} = 328–330 nm, which corresponds to a low-energy π–π* transition (Fig. 3). It should be noted that the solution of a Schiff base in the most polar of the solvents used, C_2H_5OH, has an additional absorption feature of the π–π* type at λ = 295 nm (shoulder) and a band with λ_{max} = 421 nm. The nature of the latter is possibly associated with an intramolecular charge transfer [27] between the nitrogen atom of the azomethine group and the oxygen of a polarized hydroxo group.

The complexation leads to a regular bathochromic shift of the peaks of the high-intensity bands of the intraligand type to 238–239 and 281–286 nm. In this case, an additional high-intensity absorption band appears in the spectrum of the [Cumsalpn-1,3] complex at λ_{max} = 376–384 nm (depending on the solvent polarity). This band can be attributed to a charge-transfer electron transition of the d_M–π_L* type. The long-wavelength low-intensity band peaked at 606 nm (ε H” 220 l mol cm^{-1}) is identified as corresponding to the *d–d* transition [7].

The polymerization of H_2msalpn-1,3 and [Cumsalpn-1,3] is accompanied by significant changes in the absorption spectra, compared with the starting monomeric compounds; this is characteristic of processes accompanied by particle aggregation and, in particular, formation of conducting polymeric structures.

The transition of the polymers based on H_2msalpn-1,3 and [Cumsalpn-1,3] from the oxidized to the reduced form is not accompanied by any clearly pronounced electrochromic effect. Both the polymers are dark green in the oxidized state and become light green upon reduction.

Figures 4a and 4b show absorption spectra of poly-H_2msalpn-1,3 and poly-[Cumsalpn-1,3] in the oxidized and reduced forms. The absorption spectrum of the oxidized form of poly-[Cumsalpn-1,3] contains a high-intensity band peaked at 376 nm, which corresponds to charge transfer of the d_M–π_L* type in the starting complex. The intensity of charge-transfer processes decreases upon reduction of the polymer, which is indicated by the almost complete elimination of his absorption band.

The main spectral distinction of the oxidized and reduced forms of the polymers from the starting monomeric complex is that broad absorption bands at wavelengths in the range 600–900 nm appear upon oxidation and are noticeably eliminated upon reduction. The existence of isosbestic points in the absorption spectra of the corresponding polymers indicates that there exists an equilibrium between the oxidized and reduced moieties in the bulk of the solid phase. The incomplete elimination of the absorption band in the red part of the spectrum upon reduction of the polymers enables identification of their reduced state as “half-oxidized.”

As stated in [29], the absorption by the oxidized forms of polymers based on complexes of transition metals with Schiff bases in the range 600–900 nm is a consequence of intervalence transitions, i.e., electron transitions between metallic centers in different charge states. However, in the case of poly-[Cumsalpn-1,3], this conclusion is contradictory to the invariable charge state of copper in transition from the oxidized form of the polymer to its reduced form (Table 3), unambiguously confirmed by the XPS method. Moreover, the presence of broad absorption bands in this spectral range for poly-H_2msalpn-1,3 and poly-[Cumsalpn-1,3] is characteristic of oxidized forms of organic semiconductors [30] and is largely due to localized polaronic states [31].

CONCLUSIONS

(1) The compounds H_2msalpn-1,3 and [Cumsalpn-1,3], synthesized for the first ime, were characterized by XPS and electronic absorption spectroscopy.

(2) It was found that electrochemical oxidation of the complex of Cu(II) with *N,N'*-bis(3-methoxysalicylidene)-1,3-propylenediamine yields an electrically conducting polymeric film on the surface of an inert electrode. The ligand-centered nature of the electrochemical oxidation-reduction of the polymer was confirmed by XPS.

(3) It was demonstrated that the nature of absorption by the oxidized form of poly-[Cumsalpn-1,3] in the red spectral range predetermines its similarity to organic conducting polymers.

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