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Quantum-Chemical Justification of Possibility of Electrochemical Polymerization of N_2O_2 Azomethines and Their Complexes with Cu(II)

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Abstract—Electronic structures of a series of aromatic N_2O_2-azomethines and their complexes with Cu(II) have been simulated by quantum chemistry methods. By analyzing the spin density and the highest occupied molecular orbital structure of the single-electron oxidation products (cation-radicals) of the monomers, we have concluded about possibility of the monomers polymerization to give the electroconductive polymers.

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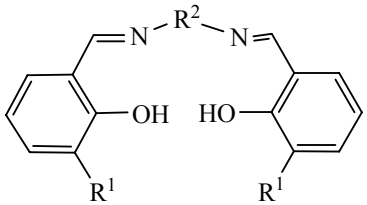
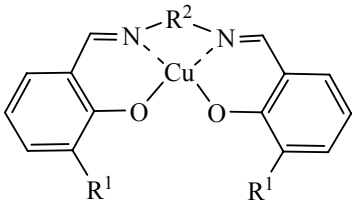
Electroconductive polymers based on transition metal complexes often combine peculiar electrocatalytic, electrochromic, and sensor properties [1–3]. Detailed reports are available on the mechanism of electrochemical synthesis, structure, and properties of polymeric forms of *d*-elements complexes with aromatic N_2O_2-, NO-, and N_4-azomethines (the Schiff's bases) [4–7]. According to the referenced literature [8, 9], anodic polymerization of the complexes proceeds via the cation-radical mechanism and is somewhat similar to phenols oxidative polymerization. The conductive polymer phase is formed due the cation-radicals interaction to covalently bind the aryl fragments of monomers. The secondary structure of the polymer can result from the π–π and *d*–π interactions. The ligand-centered model of poly-[M(Schiff)] formation has been supported by data on electrochemical polymerization of some free aromatic azomethines [10, 11].

The compounds ability to undergo electrochemical polymerization has been usually justified experimentally. It has been an open question so far, whether quantum-chemical modeling may clarify the polymerization mechanism and allow choice of monomers leading to the polymer with desired properties. In this work we examined that possibility in the case of a series of aromatic N_2O_2-azomethines (**Ia**–**IVa**) and their Cu(II) complexes (**Ib**–**IVb**); those model compounds differed in the nature of azomethine bridge and the presence of methoxy substituents in the aryl fragments.

The initial compounds were previously studied by X-ray photoelectron, electron absorption, and infrared



Ia–**IVa**



Ib–**IVb**

R^1 = H, R^2 = $(CH_2)_3$ (**Ia, Ib**), **Ib** – H_2(salpn-1,3)/[Cu(salpn-1,3)]; R^1 = OCH_3, R^2 = $(CH_2)_3$ (**IIa, IIb**), **IIb** – H_2(msalpn-1,3)/[Cu(msalpn-1,3)]; R^1 = H, R^2 = *o*-C_6H_4 (**IIIa, IIIb**), **IIIb** – H_2(salphen)/[Cu(salphen)]; R^1 = OCH_3, R^2 = *o*-C_6H_4 (**IVa, IVb**), **IVb** – H_2(msalphen)/[Cu(msalphen)].

HOMO structure of the initial monomers and of their single-electron oxidation products

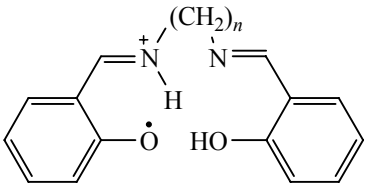
Compound	AOs contribution to HOMO				Capable of polymerization
	O(2*p*)	C(2*p*)	N(2*p*)	Cu(3*d*)	
H_2(salpn-1,3)]	0.397	0.369	0.128	–	No
	0.228	0.313	0.081	–	
	0.184	0.309		–	
H_2(salpn-1,3)$^{+\cdot}$	0.698	–	–	–	
	0.594	–	–	–	
H_2(msalpn-1,3)	0.401	0.350[a]	0.133	–	Yes
	0.269	0.334	0.095	–	
	0.238	0.316	–	–	
H_2(msalpn-1,3)$^{+\cdot}$	0.814	0.149[a]	–	–	
	0.494	0.125	–	–	
	0.175	0.099	–	–	
H_2(salphen)	–	0.322	0.297	–	No
	–	0.306	0.185	–	
	–	0.287	0.100	–	
H_2(salphen)$^{+\cdot}$	–	0.163	0.783	–	
	–	0.132[b]	0.396	–	
	–	0.112	0.316	–	
H_2(msalphen)	–	0.311	0.303	–	No
	–	0.298	0.181	–	
	–	0.280	–	–	
H_2(msalphen)$^{+\cdot}$	–	–	0.864	–	
	–	–	0.324	–	
	–	–	–	–	
[Cu(msalpn-1,3)]	–	–	–	0.751	Yes
	–	–	–	0.395	
	–	–	–	–	
[Cu(msalpn-1,3)]$^{+\cdot}$	0.249	0.261[a]	0.093	–	
	0.248	0.238	0.093	–	
	0.120	0.238[a]	–	–	

[a] Carbon atom in *para*-position with respect to OH. [b] Carbon atom of diamine bridge bound to azomethine groups.

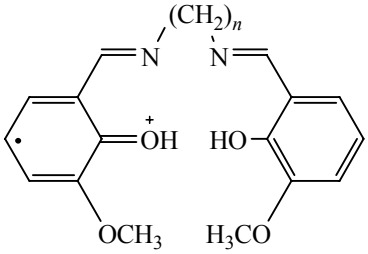
spectroscopy [6, 10–14]. Experimental data on ability of the compounds to polymerize electrochemically is given in the Table.

The computer simulation was performed in the GAMESS 9.0 software package [15] via the Hartree-Fock method in the 6-31G full basis set of atomic wave functions [16]. Geometry parameters of the species, energy and structure of the molecular orbitals, the bonds population, and the effective charges at atoms were determined in the cases of the studied azomethines, their complexes with Cu(II), and the corresponding cation-radicals. The most important coefficients of atomic orbitals (reflecting their contributions to the HOMO of the monomers and the cation-radicals) are given in the Table. Analysis of the tabulated data allowed prediction of the compounds ability to polymerize electrochemically.

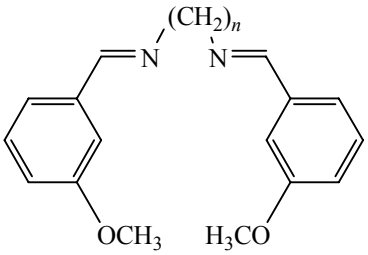
Azomethines of the H_2(salen) group (products of salicylic aldehyde condensation with aliphatic diamines) did not yield conductive polymers upon electrochemical oxidation [3]. Let us check if that conclusion could be made from the HOMO (redox orbital) structure taking the single-electron oxidation of *N,N*-bis(salicylidene)-1,3-propylenediamine H_2(salpn-1,3) as a representative example. The azomethine redox orbital was combined of 2*p* orbitals of oxygen, aromatic carbon, and (to a much lesser extent) nitrogen atoms (see Table). According to the simulation, the single ionization of H_2(salpn-1,3) molecule led to decrease of the effective charge at phenolic oxygen from −0.308 to −0.015, pointing at that atom as the source of electrons in the oxidation process. The results obtained showed that the unpaired electron of the cation-radical was almost completely localized at the 2*p* orbital of oxygen atoms; as they were not conjugated with the aryl ring, the electron density could not be spread over the aryl fragments, and, therefore, the carbon–carbon bonds could not be formed between the monomeric units (structure **A**). Furthermore, formation of the H_2(salpn-1,3)$^+$ cation-radical was accompanied with noticeable (by 0.076 Å) elongation of the O–H bond and simultaneous decrease of the N–H distance from 1.770 to 1.419 Å. Thus, the charge separation was accompanied by transfer of the hydroxyl proton to the imine group nitrogen atom of the cation-radical, the latter process being facilitated by formation of the intramolecular hydrogen bonds.



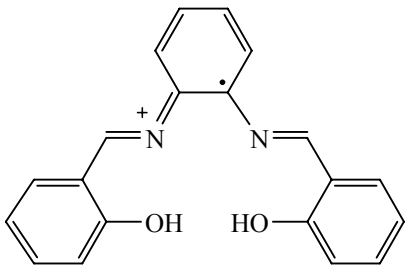
A



B

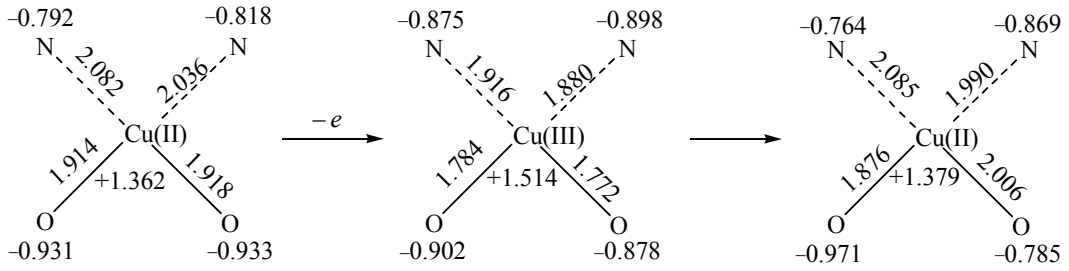


C



D

In contrast to the H_2(salen) azomethines, the derivatives of *o*-vanillin and aliphatic diamines [H_2(msalen), H_2(msalpn-1,3), etc] formed the colored conductive films at the electrode surface in the course of electrochemical polymerization [10, 11]. The above-mentioned compounds revealed the close character of the redox orbitals, almost irrespectively of the aliphatic diamine bridge nature; therefore, their common HOMO features could be examined taking H_2(msalpn-1,3) as a representative example. From the tabulated data it followed that in the initial state of the molecule, the HOMO electron density was noticeably delocalized along the aryl ring and was significantly determined by the contribution of the nonbonding orbitals of phenolic



Change of the interatomic distances (Å) and the effective charges at atoms of the $[CuN_2O_2]$ coordination node upon oxidation of the [Cu(msalpn-1,3)] complex.

oxygen. The oxidation site, similarly to the case of H_2(salpn-1,3), was phenolic oxygen, as evidenced by the increase of its effective charge from −0.302 to −0.086 upon single ionization. The structure of H_2(msalpn-1,3)$^+$ cation-radical HOMO pointed at noticeable localization of spin density at 2*p* orbital of phenolic oxygen; however, it was conjugated with aryl fragment. Thus, we suggested that the reactivity of the cation-radicals towards recombination (leading to polymer formation) was due to migration of the unpaired electron to the aryl ring (structure **B**). Possibility of electrochemical polymerization of H_2(msalpn-1,3) and its close homologs as well as of some NO-azomethines [17] served as one of the arguments supporting the ligand-centered model of the [M(Schiff)] complexes polymerization. Furthermore, the decisive role of phenolic oxygen in cation-radicals formation upon oxidation of diamine was proved by the fact that H_2(msalpn-1,3) analogs without phenolic hydroxyl groups (structure **C**) did not polymerize [11].

The H_2(salphen) and H_2(msalphen), differing from the above-discussed compounds in the aromatic nature of the diamine bridge, did not form polymeric conductive films upon electrochemical oxidation. According to the simulation results (see Table), the nitrogen and carbon atomic orbitals gave the major contribution to the HOMO. The electrons source upon oxidation of H_2(salphen) and H_2(msalphen) were 2*p* orbitals of imine nitrogen atoms. For instance, the single-electron oxidation of H_2(msalphen) decreased the effective charge of that nitrogen atom from –0.252 to –0.077. The structure of HOMO of the H_2(msalphen)$^+$ cation-radical corresponded to localization of the unpaired electron at nitrogen atom; in the case of H_2(salphen)$^+$, the unpaired electron was delocalized between nitrogen atom and the adjacent carbon atoms of diamine bridge (structure **D**). Such distribution of the spin density suppressed the cation-radicals recombination and prevented polymerization.

Thus, the ability of azomethines to undergo the oxidative polymerization was determined by their structural features; in particular, it was favored by aliphatic nature of the diamine bridge and by the presence of donor substituents in the aryl fragments.

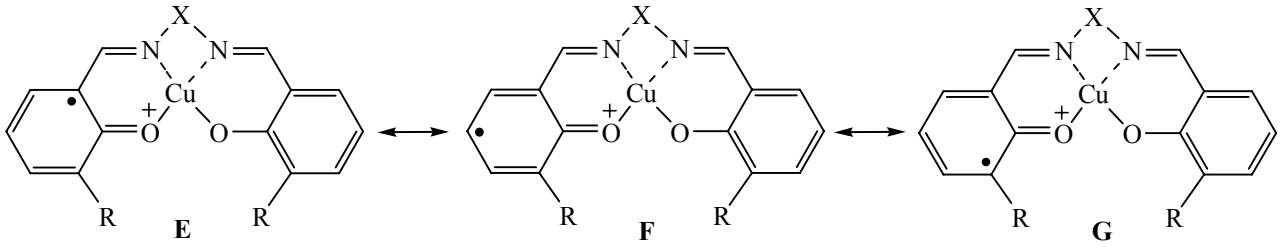
Hereafter we will consider the [Cu(Schiff)] complexes yielding conductive polymers upon electrochemical oxidation [6, 12]. According to results of their simulation, in all the cases the singly populated $d(x^2 - y^2)$ orbital of Cu(II) acted as redox orbital; that is indicated in the Table using the [Cu(msalpn-1,3)] complex HOMO as an example. The stated peculiarity was in agreement with the electron absorption spectroscopy data: the excited *d*–*d* state lower in energy was typical of the [Cu(Schiff)] complexes [18]. Single-electron oxidation of the [Cu(Schiff)] complexes was accompanied with copper transition to the unusual +3 oxidation state. The restoration of the stable Cu(II) state could occur via the intramolecular electron transfer from the nonbonding orbital of the coordinated oxygen atom, conjugated with the aryl part of the ligand. The [Cu(Schiff))] oxidation mechanism deduced from the quantum-chemical data was in agreement with the data reported in [9]. In particular, simulation revealed that with increasing of copper charge the $[Cu^{III}N_2O_2]$ coordination node was contracted: the Cu−N and Cu−O bonds length were decreased (see figure).

That favored the intramolecular electron transfer from oxygen atom to Cu(III), leading to restoration of copper usual charge accompanied with formation of organic (ligand) cation-radical.

Thus, we proposed that the electronic state of oxygen (potential electron source) determined the

possibility of oxidative polymerization of *d*-elements complexes with aromatic N_2O_2- and NO-azomethines. The above-described mechanism was confirmed by X-ray photoelectron spectroscopy data: the transition from free azomethines to the [M(Schiff)] complexes was accompanied by appearance of excessive electron density at the coordinated oxygen atom. Simultaneously, significant (up to 2.0 eV) negative shift of the O1*s* binding energy of the coordinated oxygen was observed, as compared to the free azomethine base. Moreover, copper charge was not changed upon redox reactions of poly-[Cu(Schiff)]: the binding energy of the prevailing component of the Cu2$p_{3/2}$ spectrum on the redox polymeric forms was close to that in the monomers spectra [6, 12, 19].

According to the final state analysis, oxidation of the [Cu(Schiff)] complexes was of ligand-centered type and yielded conductive polymers at the electrode. The formed cation-radicals were stabilized by the resonance forms **E–G**. In the cases of complexes without donor methoxy groups in the *ortho* position with respect to hydroxyl groups (R = H), structures **F** and **G** were favorable. With *o*-OMe groups in the ligand structure, **F** was the only structure not subjected to steric hindrance effects.



E **F** **G**

R = H or OCH_3; X = $(CH_2)_3$ or *o*-C_6H_4.

To conclude, quantum-chemical simulation and analysis of the derived HOMO structure accounting for the spin density distribution in the N_2O_2-azomethines, the corresponding Cu(II) complexes, and the primary oxidation products have refined the electropolymerization mechanism. Moreover, the possibility of such reaction could be predicted from the simulation data; the theoretical results coincided with the experimental data (spectroscopy and cyclic voltammetry).

EXPERIMENTAL

Azomethine bases and their Cu(II) complexes were prepared as described in [6, 12–14]. The products were identified by elemental analysis, X-ray photoelectron, electron absorption, and infrared spectroscopy.

Electrochemical polymerization of the monomers was performed with IPC-Pro voltammetry device with computer control. Platinum wire (S = 0.2 cm^2) was used as working electrode, platinum plate (S = 2.2 cm^2) served as auxiliary electrode, and the reference electrode was the silver-chloride one, filled with saturated NaCl solution. Bu_4NClO_4 in CH_3CN (0.1 mol/L) was used as background electrolyte. Polymerization process was monitored by recording voltamperograms (in the electrode potential range of 0.0 to +1.2 V). The coherent increase of the anodic and cathodic maxima currents pointed at formation of conductive polymeric films at the electrode surface and at their stabilization.

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