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> INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Synthesis and Properties of Polymeric Copper Complexes with Schiff Bases

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Abstract—The electrochemical synthesis and properties of polymeric copper complexes with tetradentate (N_2O_2) Schiff bases were studied. The effects of the metal center and ligand surrounding of the starting compounds on the mechanism and kinetics of the charge transport in the polymers are discussed.

Polymeric complexes of transition metals (M) with tetradentate (N_2O_2) Schiff bases {poly-[M(Schiff)]} have a number of unique properties, such as directed redox conductivity, electrochromism, and the capability of selective catalysis of important chemical processes involving organic compounds [1–3]. This set of properties of poly-[M(Schiff)] polymers makes them promising for development of new optoelectronic and sensory devices and energy-storing and catalytic systems.

Nickel(II) and copper(II) compounds are the most practically significant among poly-[M(Schiff)] polymers owing to a relatively low cost. Papers devoted to nickel-containing polymers are numerous, but only a few studies [4–6] concerned poly-[Cu(SalEn)] polymers



where M is Cu; R, R' = H, [Cu(SalEn)]; R = OCH₃, R' = H, [Cu(CH₃O–SalEn)]; R = H, R' = CH₃, [Cu(SaltmEn)]; R = OCH₃, R' = CH₃ [Cu(CH₃O–SaltmEn)].

Here we made a first systematic study of the formation and properties of [Cu(Schiff)] polymeric complexes. These results make it possible to carry out a purposeful synthesis of materials with preset properties for various applications.

EXPERIMENTAL

The complexes $[Cu(CH_3O-SalEn)]$ and [Cu(SalEn)] were synthesized by the procedures from [5, 7], and

[Cu(SaltmEn)] and [Cu(CH₃O–SaltmEn)], by the following procedure.

The ligands H_2 SaltmEn and H_2CH_3O -SaltmEn were prepared by mixing hot saturated alcoholic solutions containing stoichiometric amounts of the corresponding aldehydes and diamino derivatives: salicyl-aldehyde (Aldrich) and 2,3-diamino-2,3-dimethylbutane (H₂SaltmEn) or *o*-vanillin (Aldrich, 97%) and 2,3-diamino-2,3-dimethylbutane (H₂CH₃O-SaltmEn). 2,3-Diamino-2,3-dimethylbutane was obtained by the reduction of 2,3-dimethyl-2,3-dinitrobutane (Aldrich) with hydrogen [8]. The resulting ligands were filtered under vacuum, washed with cold distilled water and ethanol, and dried in air.

To prepare the complexes, a saturated acetonitrile solution of appropriate ligand was added to a saturated aqueous solution of $Cu(CH_3COO)_2$ (Vekton, chemically pure grade); the solutions contained stoichiometric amounts of the reactants. Then the mixture of the reactants was refluxed for 20–30 min; the precipitates were washed with water and acetonitrile, filtered off, and recrystallized from acetonitrile. The yield of [Cu(CH_3O-SaltmEn)] and [Cu(SaltmEn)] was 44 and 49%, respectively.

All the complexes were identified by X-ray diffraction analysis using a Bruker D-5000 diffractometer. The composition and structure of the synthesized complexes [Cu(SaltmEn)] (a) and [Cu(CH₃O–SaltmEn)] (b) are shown below.

To prepare supporting electrolyte solutions, we used the following salts: tetraethylammonium tetrafluoroborate (Et_4N) BF_4 , tetraethylammonium perchlorate (Et_4N) CIO_4 , and tetraethylammonium hexafluorophosphate (Et_4N) PF_6 (all purchased from Merck, 97%). Before preparing the solutions, the salts



were dried at 125°C for 12 h in an inert atmosphere. Solvents were acetonitrile (AN, Kriokhrome, 0 grade) and dimethylformamide (DMF, Merck, 98%).

To determine the number of electrons participating in electrochemical processes, we used ferrocene $Fe(C_5H_5)_2$ (Merck, 98%) as a reference.

We used a computerized complex based on an Epsilon 2 (BAS) potentiostat for electrochemical experiments, which were carried out in a hermetically sealed three-electrode cell with separated electrode compartments. A working electrode was a BAS MF 2012 glassy graphite disk 3 mm in diameter (surface area 0.07 cm²). The surface of the working electrode was polished prior to the experiments using diamond powders with particle sizes of 3 and 1 μ m (BASi PK-4 polishing kit), washed with acetonitrile, and dried in air. The reference electrode was AgCl/Ag filled with a saturated NaCl solution (RE-5B BAS). All poten-

tials are given relative to this reference electrode. An auxiliary electrode was a platinum grid (surface area about 5 cm^2). The voltammograms of the processes involving some of the complexes under study in acetonitrile solutions are given as an example in Fig. 1. The voltammograms were recorded by single scanning of the potential from 0 to the anode region up to 1.2–1.4 V and back. The anode part of the voltammograms is the most informative for studying electrolytic oxidation of the compounds under consideration, as the reverse potential scanning is accompanied by reduction of the forming polymeric complexes immobilized on the electrode surface, which is described by the relationships characteristic of thinlayer voltammetry. The voltammograms of all the complexes under study are characterized by the presence of two anode maxima; the overall shape of the anode branches of the voltammograms corresponds to the EEC [9] mechanism of the electrolytic oxidation



Fig. 1. Voltammograms of redox processes involving (1) complexes and (2) ferrocene, recorded with a glassy graphite electrode $(S = 0.07 \text{ cm}^2)$ in an AN solution. Potential scanning rate $V_s = 0.05 \text{ V s}^{-1}$; the same for Fig. 2. Concentration (M): complexes and ferrocene 1×10^{-3} , (Et₄N)BF₄ 0.1. (*I*) current strength and (*E*) potential; the same for Fig. 2. (a) [Cu(SaltmEn)] and (b) [Cu(CH₃O–SaltmEn)]; the same for Fig. 2.

(E is an electrochemical stage, and C, a chemical reaction conjugated with it). Comparison of the oxidation voltammograms of the copper complexes and ferrocene used as a reference shows that both electrochemical steps are one-electron. The potentials of the anode maxima in the voltammograms of the complexes and individual ligands in AN and DMF solutions are given in Table 1.

An electrochemical study of the oxidation of [Cu(Schiff)] complexes revealed the following facts.

The formation of polymeric compounds on the electrode surface was observed only when the complexes were oxidized in a solvent with a low coordinating power (AN). As shown previously [10, 11] for the related nickel and palladium complexes, passing from AN to DMF having a higher donor number [10] favors stabilization of the electrochemical oxidation products in the form of inert octahedral complexes containing axially coordinated solvent molecules.

Using the reference compound, we found that the electrolytic oxidation of all the complexes under study is a two-electron process in both acetonitrile and DMF. When the complexes [Cu(SalEn)] and [Cu(SaltmEn)] are oxidized in DMF solutions, the potentials of the maxima of both oxidation waves are close to each other, and, as a result, only one anodic current maximum is observed in the voltammograms. At the same time, it was found by *in situ* microgravimetry [12] that the electrochemical oxidation of the copper complexes under consideration in acetonitrile solutions involves one electron per fragment of a [Cu(Schiff)] polymer. The whole set of these facts indicates that,

when a polymer is formed, the two-electron oxidation of the starting complex is accompanied by a chemical reaction of the coordination of a [Cu(Schiff)] molecule to the product of the electrolytic oxidation.

The potentials E_{pa1} for [Cu(SalEn)] and [Cu(Saltm-En)] and E_{pa2} for [Cu(CH₃O–SalEn)] and [Cu(CH₃O– SaltmEn)] in the voltammograms of the complexes in acetonitrile solutions are close to each other (1.00– 1.12 V), irrespective of the presence of electron-donor methoxy groups in the phenyl moiety. A similar fact is observed also in the voltammograms recorded in DMF (1.05–1.08 V).

Table 1. Potentials of anode maxima E_{pa1} and E_{pa2} of voltammograms of the complexes [Cu(Schiff)] and ligands H₂(Schiff). $V_s = 0.05 \text{ V s}^{-1}$

	AN		DMF		
Complex, ligand	E _{pa1}	E _{pa2}	E _{pa1}	E _{pa2}	
	V				
[Cu(SalEn)]	1.00	1.22	1.08	_	
$H_2(SalEn)$	1.10*	1.24	1.34	_	
$[Cu(CH_3)O-SalEn)]$	0.83	1.10	0.99	1.07	
H ₂ (CH ₃ O–SalEn)	0.86	0.96	1.01	_	
[Cu(SaltmEn)]	1.01	1.27	1.05	-	
$H_2(SaltmEn)$	1.13	1.44	1.31	_	
[Cu(CH ₃ O–SaltmEn)]	0.86	1.12	0.99	1.07	
H ₂ (CH ₃ O–SaltmEn)	0.83	1.09	0.99	1.05	

* Shoulder.



Fig. 2. Voltammograms of redox processes involving complexes, recorded with a glassy graphite electrode ($S = 0.07 \text{ cm}^2$) in acetonitrile solutions. Concentration (M): complexes 1×10^{-3} , (Et₄N)BF₄ 0.1. (a) [Cu(SaltmEn)] and (b) [Cu(CH₃O–SaltmEn)]. Numbers at curves correspond to successive cycles. Dashed lines: voltammograms of polymers recorded after polymerization termination (20 cycles) and transfer of the modified electrode into a supporting electrolyte [0.1 M (Et₄N)BF₄, AN, $V_s = 0.05 \text{ V s}^{-1}$].

Presumably, these oxidation waves correspond to the electron transfer from predominantly metalcentered orbitals of the complexes. Apparently, the second oxidation waves of the complexes [Cu(SalEn)] and [Cu(SaltmEn)] and the first oxidation waves of [Cu(CH₃O–SalEn)] and [Cu(CH₃O–SaltmEn)] are determined by the electron transfer from predominantly metal-centered orbitals. This is proved by the fact that the maxima of potentials of these waves are considerably shifted toward the negative region when electron-donor methoxy groups are introduced into the phenyl moieties.

The introduction of four methyl groups into the diamine bridge connecting the phenyl moieties does not result in a noticeable change in the electron density on the ligands, as methyl groups are weak donors. Therefore, the potentials of the current maxima in the oxidation voltammograms of the complexes [Cu(SalEn)] and [Cu(SaltmEn)] are close to each other. The same is also true for [Cu(CH₃O–SalEn)] and [Cu(CH₃O–SaltmEn)].

The limiting step of the polymerization of the complexes under study is the diffusion of the starting compounds to the electrode surface, which is confirmed by the fact that the currents of the anode maxima in the voltammograms increase linearly as the concentration of the starting substances in solution increases (in the range 1×10^{-4} – 3×10^{-3} M).

On the whole, the experimental data for the complexes [Cu(Schiff)] agree with the general mechanism of the electrochemical oxidation of complexes [M(Schiff)] suggested previously [10, 11].

The formation of the polymeric complexes poly-[Cu(SaltmEn)] and poly-[Cu(CH₃O–SaltmEn)] on the surface of a glassy graphite electrode in the case of potential cycling is shown in Fig. 2. The voltammograms of the polymers recorded after the polymerization was complete and the modified electrode was transferred into the supporting electrolyte are also shown in Fig. 2 for comparison.

The regular increase in the currents of the anode and cathode maxima in the voltammograms correspond to the growth of polymeric compounds on the electrode. In the course of the formation of polymers, starting from the second cycle, a new broad anodic wave of the oxidation of polymers on the electrode surface is observed in the voltammograms at potentials more negative than E_{pal} . At the same time, the anode wave corresponding to the transfer of the second electron, after which the formation of the polymer was observed according to [13], is absent from the voltammograms recorded in the supporting electrolyte solution with electrodes modified with the polymers (Fig. 2, dashed curves). The common trend for all the polymers studied is a shift of the region of redox processes to the side of less positive potentials when donor methoxy groups are introduced into the ligand. The introduction of methyl groups into the diamine bridges between phenyl moieties does not noticeably affect the shape and position of the voltammograms of the polymers. Thus, the voltammograms of the polymeric complexes poly-[Cu(SalEn)] and [Cu(SaltmEn)] only slightly differ from each other in the specified parameters.

Two pairs of anode and cathode waves are observed in the voltammograms of all the polymeric complexes studied. At the same time, it was found previously for nickel [14] and copper [12] polymeric complexes that the reduction–oxidation of polymers in the range of potentials 0-1.3 V is characterized by the transfer of one electron per fragment. At present, the nature of processes giving rise to two pairs of waves in the voltammograms of the polymeric complexes under discussion is not determined unambiguously. A possible reason for the observed shape of the voltammograms can be the presence of two polymeric forms on the electrode surface, which are bound to the surface owing to the interaction between predominantly metal- or ligand-centered orbitals of the surface fragments of stacks and are correspondingly oxidized (or reduced) at different potentials. The other probable reason for the appearance of the broadened oxidation waves corresponding to the redox processes in the polymers can be the presence of polymeric stacks of different length on the surface, having different resistance to charge transfer.

Polymeric complexes can be formed also in a static mode when an electrode is polarized in a solution of the starting compound at a constant potential. In this case, the most important parameter is the polymer formation potential providing, on the one hand, a sufficient rate of the electrochemical process and, on the other hand, the absence of side reactions resulting in the degradation of the polymer or in the loss of its electrochemical activity. The criterion for choosing the optimal potential of the formation of polymers can be the charge diffusion coefficient D_{ct} reflecting the redox conductivity of the polymeric compounds.

To choose an optimal formation potential, we have prepared polymer films at various potentials in the range 0.9-1.2 V. The coefficients of charge diffusion in polymers were calculated by the Randles-Sevcik equation [15] on the basis of voltammograms recorded at potential scanning rates that provided the occurrence of redox processes in the polymer in the mode corresponding to the conditions of semiinfinite diffusion of current carriers. The calculation of the charge diffusion coefficients implies the exact knowledge of concentration of redox centers in the polymer, i.e., of the density of the polymeric film [16]. The density of the polymeric films based on the complexes with the ligand SalEn, about 1 g cm⁻³, was determined previously by in situ ellipsometry [13]. Certainly, the density of the polymers depends on the presence of various substituents in the ligand surrounding, altering the geometry of the starting monomeric fragments. The exact values of the density of the polymers containing SaltmEn and CH₃O-SaltmEn ligands are unknown; therefore, the density of the polymers in these calculations was taken equal to 1 $g \text{ cm}^{-3}$. This assumption does not allow us to compare the charge

transfer rates in various polymers. Nevertheless, the resulting $D_{\rm ct}$ values can be used for comparison of charge transfer rates in the same polymer formed under different conditions.

The resulting D_{ct} values for all the complexes under study are close to each other and fall into the range $(1\pm0.5)\times10^{-10}$ cm² s⁻¹ for the range of the formation potential 1.00-1.10 V. This range of the polymer formation potentials is more positive than the potential of the first anodic maximum in the oxidation voltammograms of the starting complexes and, at the same time, overlaps with the range of potentials of the second oxidation process (Table 1). The formation of polymers at potentials lower than 0.95 V apparently results in the fact that the primary product of the electrolytic oxidation of the starting compound is partially stabilized owing to side processes involving a solvent, instead of the transfer of the second conduction electron. Monomeric and oligomeric fragments forming by the side processes can be captured by the growing polymeric film, which disturbs its structure and results in a decrease in the efficiency of the motion of charge carriers (in this case, the resulting $D_{\rm ct}$ values are close to 10^{-11} cm² s⁻¹).

The formation of polymers at potentials higher than 1.2 V is accompanied by the irreversible oxidation of the ligand surrounding of the complexes and results in the loss of the polymer electrochemical activity.

The nature of the limiting step of charge transfer processes in the films of the polymers under study was determined by studying the effect of the size of charge-compensating ions (BF_4^- , ClO_4^- , and PF_6^-) [17] and concentration of supporting electrolytes (0.05–0.5 M) on D_{ct} . The experiments showed that the charge transfer rate in all the polymers studied is independent of the size of charge-compensating anions and of their concentration in solution. The results obtained show that the charge transfer in these films is limited not by the stage of diffusion of counterions in them, but by the rate of electron motion along polymeric stacks; therefore, the resulting D_{ct} values characterize the rate of specifically this process.

To compare characteristics of the charge transport in the polymeric complexes with various ligands and metallic centers, we can use the products of the concentrations of redox centers in a polymer c (mol cm⁻³) by $D_{ct}^{1/2}$ values dependent on changes in the structure of polymers with variation of their composition and on the efficiency of the motion of charge carriers. The $cD_{ct}^{1/2}$ values for the poly-[Cu(Schiff)] polymers calculated by the Randles–Sevcik equation are given in Table 2; the related characteristics of nickel- and

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Complex	$cD_{\rm ct}^{1/2} \times 10^8$, mol cm ⁻² s ^{-1/2}	Complex	$cD_{\rm ct}^{1/2} \times 10^8$, mol cm ⁻² s ^{-1/2}
poly-[Ni(SalEn)] poly-[Pd(SalEn)] poly-[Cu(SalEn)] poly-[Ni(CH ₃ O–SalEn)] poly-[Pd(CH ₃ O–SalEn)] poly-[Cu(CH ₃ O–SalEn)]	$\begin{array}{c} 4.0 \pm 0.5 \\ 2.5 \pm 0.5 \\ 1.5 \pm 0.5 \\ 5.0 \pm 0.5 \\ 3.0 \pm 0.5 \\ 1.5 \pm 0.5 \end{array}$	poly-[Ni(SaltmEn)] poly-[Pd(SaltmEn)] poly-[Cu(SaltmEn)] poly-[Ni(CH ₃ O–SaltmEn)] poly-[Pd(CH ₃ O–SaltmEn)] poly-[Cu(CH ₃ O–SaltmEn)]	$12.0 \pm 0.5 \\ 5.6 \pm 0.5 \\ 2.0 \pm 0.5 \\ 5.5 \pm 0.5 \\ 4.6 \pm 0.5 \\ 2.0 \pm 0.5 \\ \end{array}$

Table 2. Values of $cD_{ct}^{1/2}$ for poly-[Cu(Schiff)] polymers

palladiuim-containing polymeric complexes obtained previously [18] are given for comparison.

Our results allow the following conclusions: (i) $cD_{ct}^{1/2}$ parameters for the copper complexes studied are lower than those for the polymeric nickel and palladium complexes; (ii) poly-[Cu(Schiff)] polymers are characterized by slow electron transport in stacks in contrast to nickel- and palladium-containing polymers, in which the limiting step of the charge transport is the motion of charge-compensating ions [18]; (iii) the effect of substituents in ligand surroundings on the behavior of compounds in polymeric complexes poly-[Cu(Schiff)] essentially differs from that in the nickeland palladium-containing polymers owing to a change in the nature of the limiting step of the charge transport. In particular, for poly-[Ni, Pd(Schiff)] complexes, $cD_{ct}^{1/2}$ substantially increases on passing from the polymers with the SalEn ligand to those with the SaltmEn ligand. As shown in [19], the introduction of four methyl groups into the structure of the diamine bridge between the phenyl moieties results in a noticeable increase in the repulsive interactions between the polymer stacks and in the formation of a less compact polymeric film. For [Cu(Schiff)] polymers, such a change in the ligand surrounding results in increasing efficiency of the motion of charge-compensating ions, but does not noticeably affect the charge-transfer rate.

It is known that [Cu(Schiff)] complexes, unlike the related nickel and palladium compounds, form intermolecular associates in the solid phase, in which copper atoms are bound to each other through the oxygen atom of a Schiff base. In the associates, the length of the bond between the copper atom of one molecule and the oxygen atom of another molecule is 2.41 Å [20]. Presumably, in [Cu(Schiff)] the bonds between separate fragments in a stack are similar in nature [21]. At the same time, it was found that in the nickel and palladium polymeric complexes with Schiff bases, the bonds between separate fragments of stacks are formed by interaction of the metallic centers with the phenyl moieties of the ligands [22,

23]. The difference in the nature of bonds between fragments of stacks in the copper polymeric complexes compared to nickel- and palladium-containing polymers offers an explanation for the data obtained in this study, in particular, for a lower electronic conductivity of poly-[Cu(Schiff)] complexes.

CONCLUSIONS

(1) Previously unknown polymeric copper complexes with the ligands N,N'-2,3-dimethylbutane-2,3-diylbis(salicylidenimine) and N,N'-2,3-dimethylbutane-2,3-diylbis(3-methoxysalicylidenimine) were prepared. The conditions for the electrochemical synthesis of the polymers with the highest redox conductivity [optimal potentials of the formation of copper(II) polymeric complexes with Schiff bases, nature and concentration of the supporting electrolyte] were determined.

(2) The oxidation of the poly-[Cu(Schiff)] complexes occurs by the two-electron mechanism with the subsequent chemical step of the coordination of a starting complex molecule to the product of the electrochemical oxidation; the limiting step of the polymerization is the diffusion of the starting compounds to the electrode surface.

(3) A study of the mechanism and kinetics of charge transport showed that the electron transfer in a stack occurs through an oxygen atom. Therefore, these polymeric compounds are characterized by a slow electron transport along stacks, and the parameter $cD_{ct}^{1/2}$ for the copper(II) complexes studied is lower than for the related nickel and palladium polymeric complexes.

(4) Variation of the ligand surrounding does not affect the charge-transfer rate.

(5) The trends revealed in this study allow purposeful synthesis of electroactive polymeric materials with a preset range of potentials of the electrochemical activity and with the required rate of charge transport.

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