SYNTHESIS OF POLYMERS CONTAINING o-PHENANTHROLINE GROUPS AND STUDY OF THEIR COMPLEXING WITH COPPER(II) IONS

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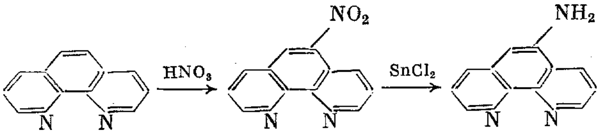
Complexes of metals of variable valence with macromolecular ligands are active in the catalysis of liquid-phase reactions [1, 2] and are also interesting for modeling of processes of natural photosynthesis [3]. These complexes are usually assigned to one of two types. The first type consists of the so-called anchor-type complexes in which the metal atom is monodentately bound with only one functional group in the carrier [2, 4]. In complexes of the second type, the metal atom is coordinated with several ligand atoms in the macromolecule, which increases their thermodynamic stability [5, 6]. Complexes of a third type, where the metal ion is chelated with one bidentate ligand group in the polymer and the remaining coordination sites are occupied by low-molecular-weight ligands and solvent molecules have been much less studied. This type of complexing makes it possible to form structures of different composition and structure.

The purpose of the present study was to synthesize a polymer containing a small number of o-phenanthroline groups and to study the composition and structure of the coordination sphere of complexes of Cu(II) with the polymer obtained. The small number of bidentate o-phenanthroline groups in the polymer decreases the probability of coordination of more than one such ligand on the Cu atom and the formation of cross-links in the polymer.

EXPERIMENTAL

The polymer containing o-phenanthroline groups was prepared by the reaction of polyacrylic acid ($\overline{M}_\eta$ = 200,000) with 5-amino-o-phenanthroline in the presence of a condensing agent, N,N'-dicyclohexylcarbodiimide (DCC). 5-Amino-o-phenanthroline was synthesized from o-phenanthroline according to the scheme



Thin-layer chromatography was conducted on Silufol plates (Czechoslovakia). The mobile phase was acetic acid:ethyl acetate:water = 3:2:1 (by volume). The absorption spectra in the ultraviolet region were recorded on a Specord M-40 spectrophotometer (GDR). The EPR spectra were recorded on EPR-V (Institute of Chemical Physics Academy of Sciences of the USSR) and Varian E-4 radiospectrometers at 77°K. A well-vitrified mixture of D_2O and MeOH (1:1 by volume) was used as the solvent. The principal values of the g factor $g_\parallel$, $g_\perp$, and the hyperfine interaction constants of the unpaired electron with the copper nucleus $A_\parallel$ and $A_\perp$, as well as with the ^{14}N nuclei of the ligand molecules $a_\perp^N$ in the first coordination sphere of the complexes were determined from the EPR spectra. The calculation was performed according to [7]. The value of the unpaired electron density α^2 on the Cu(II) coordinating ion was estimated with the relation in [8]

$$\alpha^2 = A_\parallel/0{,}036 + (g_\parallel - 2) + 3/7\,(g_\perp - 2) + 0{,}04$$

where $A_\parallel$ is measured in cm^{-1}.

5-Nitro-o-phenanthroline (NP) was prepared with the improved method in [9]. While stirring, 30 ml of conc. HNO_3 (d 1.40) was added to 10 g (0.055 mole) of o-phenanthroline dissolved in 70 ml of 18% oleum (d 1.84) so that the temperature of the reaction mixture

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TABLE 1. Parameters of the EPR Spectra of Complexes of Cu(II) with PAAP and Low-Molecular-Weight Analogs at 77°K

Complex	$A_{\parallel}$ ±2 Oe	$g_{\parallel}$ ±0.004	$g_{\perp}$ ±0.004	$a_{\perp}^{N}$ ±0.2 Oe	α^2
Cu(PAAP), A	163	2.280	2,068	14	0.83
Cu(PAAP), B	140	2.354	–	–	0.84
"	155	2.326	2,062	18,6 *	0.85
$Cu(COO)_1$ [10]	141	2.349	–	–	0.83
$Cu(COO)_2$ [10]	157	2.320	2,059	18,3 *	0.85
$Cu(phen)_1$	150,5	2.321	2.069	13.8	0.84
$Cu(phen)_2$	155,5	2.267	2.070	13.4	0.79
$Cu(AP)_1$	149,5	2.318	2,070	13,7	0,83
$Cu(AP)_2$	154	2,264	2.066	13.5	0,78
$Cu(phen)(PA)_1$	162	2.286	2.071	14	0.83
$Cu(PAAP)(phen)_1$	155	2.267	2.067	–	0.79

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*Value of $A_{\perp}$.

did not exceed 100°C. After addition of all of the nitric acid, the mixture was heated for 2 h at 100-110°C. It was then poured on 250 g of crushed ice and neutralized with 30% NaOH. The sediment was filtered off and recrystallized from isopropyl alcohol. Yield of 63%. The purity of the product was confirmed by the TLC data. Found: C 60.17; H 3.67; N 17.94%. $C_{12}H_7N_3O_2$. Calculated: C 59.26; H 3.70; N 17.28%.

5-Amino-o-phenanthroline (AP). While stirring, 3.6 g (0.016 mole) of NP was added to 15.2 g (0.08 mole) of $SnCl_2$ dissolved in 46 ml of hydrochloric acid (d 1.19). The suspension was stirred for 1 h at 80-90°C, cooled, treated with a 40% solution of NaOH, and 250 g of crushed ice was added. The sediment was filtered off, washed with water to a neutral reaction, and recrystallized from ethanol. Yield of 58%. The purity of the product was confirmed by the TLC data. Found: C 66.80; H 4.48; N 18.35%. $C_{12}H_9N_3$. Calculated: C 67.60; H 5.16; N 19.12%.

Polyacrylic Acid, Partially Amidated with 5-Amino-o-phenanthroline (PAAP). A solution of 0.47 g (0.002 mole) of DCA in 4 ml of DMF was added to a solution of 0.165 g (0.0023 mole) of polyacrylic acid (M_η = 200,000) in 14 ml of DMF and held at 20°C for 2 h. The precipitated sediment was filtered off, 0.045 g (0.00023 mole) of AP in 4 ml of DMF was added to the mother solution and held for 12 h at 20°C, then 0.5 ml of H_2O was added. After 2 h, the sediment was filtered off and diethyl ether was added to the solution. The precipitated polymer was dissolved, dialyzed, and dried lyophilically.

Cu(II) perchlorate was used for preparation of the complexes with the polymeric and low-molecular ligands.

DISCUSSION OF THE RESULTS

o-Phenanthroline and its derivatives have a characteristic absorption band in the region of λ_{max} = 282 nm, and the Lambert–Beer law is obeyed in a wide range of concentrations (Fig. 1). Using the extinction coefficient found for AP $\varepsilon_{282} = 1.83 \cdot 10^4$ liter/mole·cm, it was found that the fraction of units in PAAP containing an o-phenanthroline group was $\beta \leq 2\%$.

Complexing with PAAP was studied in a wide range of concentrations of Cu(II). With small concentrations of Cu(II), only type A complexes were present in the sample (Fig. 2). As the concentration of Cu(II) increased with a constant concentration of PAAP, lines assigned to the type B complex appeared in the EPR spectrum, and their intensity increased with an increase in [Cu(II)]. The intensity of lines A remained unchanged. With large concentrations of Cu(II), lines characterizing $Cu(H_2O)_6{}^{2+}$ ions appear in the spectrum (Table 1).

The EPR spectra of complexes containing phen and AP were studied to determine the composition and structure of the coordination sphere of the Cu(II) ions (Fig. 3, Table 1).

High values of the stability constants are characteristic of complexes of o-phenanthroline and its derivatives [11]. For this reason, Cu(II) is almost totally bound in a complex with L (L: o-phen or its derivative). Addition of L results in the appearance of CuL_2 complexes, and when [L]:[Cu] ≥ 5 in a solution vitrified at 77°K, only CuL_2 complexes are present. The $Cu(phen)_3{}^{2+}$ complexes described in [12] are apparently not formed in a water–methanol medium.

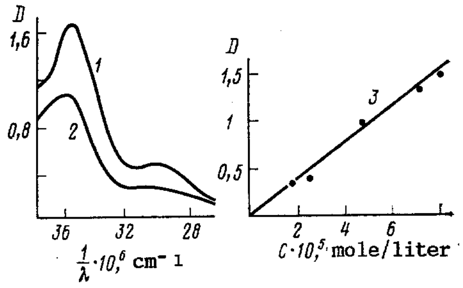

Fig. 1. Absorption spectra of AP (1) and PAAP (2) and concentration dependence of the optical density for AP (3).

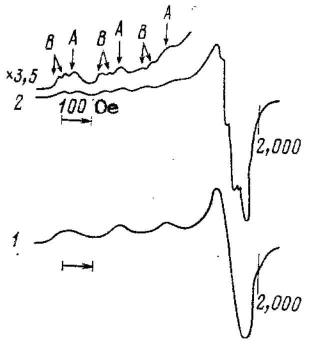

Fig. 2

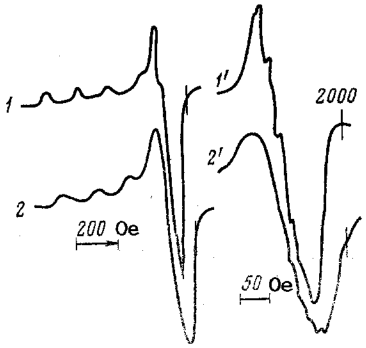

Fig. 3

Fig. 2. EPR spectra of complexes of Cu(II) with PAAP with [L]:[Cu] = 1:1 (type A complexes) (1) and 1:2 (type B complexes) (2) in a 50% mixture of D_2O + CH_3OH at 77°K; L = phenanthroline groups contained in the polymer.

Fig. 3. EPR spectra of complexes of $Cu(AP)_1$ (1) and $Cu(AP)_2$ (2) at 77°K in a 50% mixture of D_2O + CH_3OH. 1' and 2') components of the perpendicular orientation of the corresponding complexes.

The analysis of the hyperfine splitting in the EPR spectrum caused by interaction of the ligands with the ^{14}N nuclei, observed in the components of the perpendicular orientation of the complexes, also indicate the successive formation of complexes with two (CuL) and four (CuL_2) N atoms in the coordination sphere of Cu(II).

The insignificant increase in $A_{\|}$ (see Table 1) in going from CuL to CuL_2 and marked decrease in the density of the unpaired electron in the coordinating copper ion α^2 (by $\sim$0.05) indicate small tetrahedral distortions of the structure of the Cu(II) coordinating sphere [13] due to steric hindrances, and as a result, the four N atoms of the ligands are not in the same plane with the central Cu(II) atom. This conclusion is in agreement with the data from the x-ray structural analysis of $Cu(phen)_2Cl_2$ and $Cu(bipy)_2I_2$ [14, 15] (bipy = 2,2'-dipyridyl).

Table 1 shows that the parameters of the EPR spectrum of type B complexes are very close to the corresponding parameters of Cu(II) complexes with polyacrylic and propionic acids [10].

The parameters of the EPR spectrum of complex A differ from the parameters of the spectrum of Cu(AP) and $Cu(AP)_2$ complexes. Since the number of o-phenanthroline groups contained in PAAP is no greater than 2% of the total number of units in the chain, the formation of CuL_2 structures in the polymer is not very probable. The difference in the parameters of complex A and complex CuL in which two molecules of solvent are positioned in the equatorial plane suggests that in addition to one ligand, complex A also contains one or two COO^- groups of the polymer. The local concentration of COO^- groups in the PAAP coil is apparently very high, and their effective complexing constant significantly exceeds the constants for molecules of H_2O and CH_3OH. This hypothesis is confirmed by the fact that the parameters of the EPR spectrum for the $Cu(phen)_1(PA)_1$ complex obtained in the interaction of stoichiometric quantities of $Cu(ClO_4)_2$, phen, and PA, coincide with the parameters for the polymer complex (see Table 1).

It is possible to vary the composition and structure of the metal-complex sites by adding low-molecular ligands to a solution of Cu(PAAP). When phen is added to a solution of complex A, the COO groups are displaced from the coordination sphere and Cu(PAAP)(phen) (see Table 1), and some amount of mixed Cu(COO)(phen) complexes added to the PAAP macromolecule due to the COO group are formed. A comparison of the concentration of PAAP in a solution with the limit concentration of Cu(II) at which formation of complex A still takes place permits independently determining the concentration of phen groups in the polymer. The value of $\beta = 1.4 \pm 0.3\%$ measured in this way is in agreement with the UV spectroscopic data.

The process of complexing of Cu(II) with PAAP containing a small amount of phen groups thus takes place as follows: as Cu(II) is added to a solution of the polymer, complexes with the highest stability constant, $Cu(phen)(COO)_1$, type A, are initially formed. After all of the phen groups in the polymer have complexes, further addition of Cu(II) results in $Cu(COO^-)_1$ and $Cu(COO^-)_2$ complexes similar to those observed in [10] for the $Cu(NO_3)_2$—PAA system. If the amount of Cu(II) exceeds the sorption capacity of the polymer, then $Cu(H_2O)_6{}^{2+}$ aqua ions appear in the solution. The addition of low-molecular-weight ligands to the solution of the polymer permits forming coordination-saturated structures with respect to phenanthroline in the macromolecule.

CONCLUSIONS

1. Derviatives of polyacrylic acid containing o-phenanthroline groups (PAAP) were prepared for the first time.

2. The composition and structure of the coordination sphere of complexes of copper(II) with PAAP and the corresponding low-molecular analogs were studied by EPR.

3. By varying the ratio of the concentrations of copper(II), PAAP, and the low-molecular ligands in the solution, it is possible to obtain metal complexes of varying structure in the PAAP macromolecule.

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