Formation of coordination polymeric structures on the basis of 4,4´-dipyridylethylene and Ag^+ in solutions

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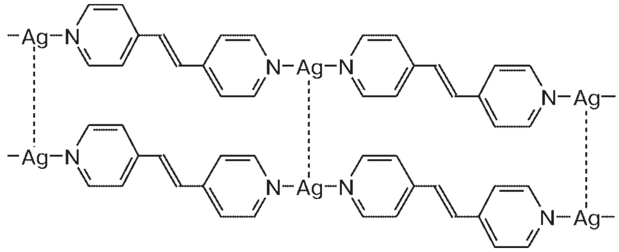
The formation of coordination polymeric chain structures in which silver ions alternate with dipyridylethylene (DPyEt) ligands was studied. In a homogeneous ethanol solution, complex formation of DPyEt with silver cations takes place. The outcome of this reaction depends on the ligand/cation molar ratio, the initial ligand concentration, and the counter-ion type. Conditions were identified under which the coordination polymer is formed as a microdispersed solid precipitating from the solution. The precipitates formed in the DPyEt—$AgNO_3$ and DPyEt—$AgClO_4$ systems were investigated by various experimental techniques. The counter-ion was found to be incorporated in the polymer and to influence the structure of the precipitate particles.

Key words: complex formation, coordination polymers, dipyridylethylene ligands, silver cations.

A large number of recent publications have been devoted to the study of complex coordination compounds that were classified as polymers on the basis of numerous formal criteria such as large molecular masses, structure regularity (*i.e.*, the presence of a elementary unit), diversity of the possible structures (linear, branched, cross-linked, interpenetrating), and the presence of cross-links of various natures (including so-called physical cross-links, *i.e.*, electrostatic, van der Waals, and hydrogen ones, which are very close in energy to coordination bonds) *etc.* Usually, these coordination polymers are crystalline solids formed by metal ion complexes with organic ligands (as a rule, bidentate or polydentate ligands).[1—5] The interest in these systems is due to their unusual crystal structures and to the possibility of using them for various purposes. One of the reasons for formal ascription of these substances to the class of polymers is the fact that their framework is a regular system of one-dimensional chains, or two- or three-dimensional networks of coordination bonds characterized by alternation of organic molecules of polydentate ligands and metal ions. Unlike traditional polymers, which are usually amorphous, coordination polymers are normally crystalline solids. In some cases, their crystal lattice contains extended regular nano-sized cavities resembling a honeycomb. The crystal structure of coordination polymers is determined by the fact that secondary intermolecular interactions play a substantial role in its formation.

For example, in solutions of *trans*-4,4´-dipyridylethylene (DPyEt) and $AgBF_4$, chains consisting of alternating DPyEt ligand molecules and Ag^+ ions are formed.[6] It is known that such linear chains tend to form "sandwich" structures due to Ag—Ag and π—π interactions.[7]



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An argument in favor of this structure is the fact that exposure of solutions of these complexes to UV radiation yields 1,2,3,4-tetrakis(4-pyridyl)cyclobutane (TPCB), which is always formed as a single isomer. Meanwhile, in concentrated solutions of DPyEt, two cyclobutane isomers are produced in approximately equal amounts, while in the crystalline state, DPyEt is not dimerized at all. Thus, the selectivity of the structure of the resulting dimers is due to the steric control of the photochemical reaction in the "sandwich" aggregates of linear chains. It is of interest that, when this reaction slowly proceeds in a two-phase system at a liquid—liquid interface (acetonitrile—dichloromethane) in the light, TPCB forms a solid crystalline three-dimensional coordination polymer in which each silver ion coordinates in a tetrahedral geometry four pyridine groups belonging to different TPCB ligands.[6]

At present, a lot of X-ray diffraction data on the structure of two- and three-dimensional coordination polymers can be found in the literature.[8—17] The occurrence of the Ag—Ag and π—π interactions mentioned above provides for the possibility of formation of a broad spectrum of intricate supramolecular complexes that form the basis of coordination polymers. However, no data on the intermediate steps of transition from the "ligand—ion" molecular complexes to a regular three-dimensional polymer structure, or on the stability and structures of intermediate supramolecular complexes are available. The spectral characteristics of neither molecular complexes nor larger aggregates, nor the coordination polymers based on them have been investigated.

The purpose of this work is to follow the process of complex formation between DPyEt and Ag^+ *en route* from the molecular complex to the coordination polymer under various experimental conditions.

Experimental

Commercial DPyEt and $AgClO_4$ (Fluka) and $AgNO_3$ (Reachim) were used as received. The complexation of DPyEt with the silver cation, introduced as $AgNO_3$ or $AgClO_4$, was studied in ethanol solutions. Rectificate grade 96% ethanol was used. Electronic absorption spectra of solutions were recorded on a Specord M-40 spectrophotometer in 10-mm thick standard quartz cells. Electron microscopy studies were carried out on a JEOL JEM-1200EX microscope.

Complexation was studied using the following procedure for mixing the components. A concentrated solution of $AgNO_3$ or $AgClO_4$ was added to a solution of DPyEt with a concentration of 10^{-4}—10^{-5} mol L^{-1}; the total increase in the volume was slight but controlled, and it was taken into account in the subsequent processing of the absorption spectra, for example, in analysis for the presence of isosbestic points. After addition of a solution of Ag^+ and stirring, an absorption spectrum was recorded. Then the next portion of the solution of Ag^+ was added and the absorption spectrum was recorded once again. This method of successive titration made it possible to study the dependence of the spectral pattern on the ion/ligand ratio.

In the second procedure, a concentrated solution of DPyEt was added to a solution containing Ag^+ in a specified concentration. This procedure was mainly used to obtain solid precipitates of complexes for subsequent analysis. For this purpose, after mixing the solutions in which Ag^+ ions were taken in a substantial excess and the DPyEt concentration was about 10^{-4} mol L^{-1}, the resulting suspension was centrifuged. The DPyEt concentration in the supernatant separated from the solid precipitate was 2—3 orders of magnitude lower than that before mixing, while the concentration of the Ag^+ ions remained virtually unchanged. The concentrations of DPyEt and $AgNO_3$ in solutions were monitored by spectrophotometry and by argentometric titration, respectively. The excess of silver salt was removed by washing the solid precipitate by several portions of water on a glass filter. Since the washing was fast, it did not result in any visible signs of dissolution of the precipitate, because it was much less soluble in water than $AgNO_3$. The process was monitored by spectrophotometric analysis or argentometric titration of washings. The precipitate was dried at 50 °C for 24 h. To check the solubility of the resulting dry precipitate, a portion was dispersed by long-term shaking in a known volume of ethanol or water.

Results and Discussion

When a moderate excess ($\leq 30 : 1$) of silver ions and solutions of DPyEt with concentrations of $6 \cdot 10^{-5}$ mol L^{-1} were used, a slight bathochromic shift of the absorption spectra and smoothing of their electronic-vibrational structure were observed (Fig. 1, spectrum *2*). This indicates apparently that only molecular complexes of DPyEt with silver ions are formed under these conditions, but not supramolecular complexes in which the chromophore fragments could interact. During successive titration of a solution of DPyEt with a solution of Ag^+, feebly marked

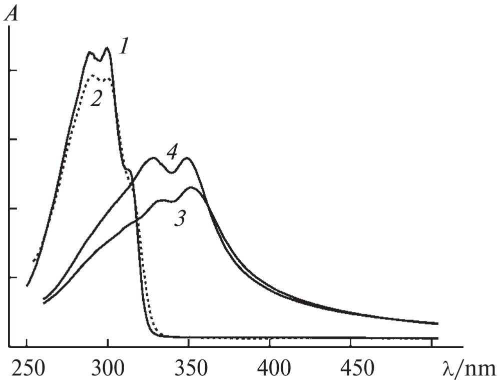

Fig. 1. Absorption spectra (*A*) of the ethanol solution of DPyEt (*1*) and mixtures prepared by mixing ethanolic solutions of $AgNO_3$ with DPyEt in 30 : 1 (*2*) and 100 : 1 (*3*) ratio; $AgClO_4$ with DPyEt in 55 : 1 ratio (*4*). The concentration of DPyEt is $6 \cdot 10^{-5}$ mol L^{-1}.

isosbestic points appear in the absorption spectra in the presence of a slight excess of Ag^+. Therefore, the observed spectra might represent superpositions of the spectra of the initial DPyEt and the molecular complexes with silver ions. On the basis of absorption spectra alone, it is difficult to draw conclusions concerning the composition and structure of these molecular complexes. However, study of Ag^+/DPyEt solutions with 10 : 1, 20 : 1, and 40 : 1 ratios carried out by high-resolution time-of-flight mass spectrometry (electrospray ionization, ESI[18]) showed the presence of DPyEt—Ag and $(DPyEt)_2Ag$ molecular complexes. The range of measurements in this experiment was restricted from above by the limiting mass numbers of about 600; therefore, we were unable to gain reliable data concerning the formation of higher complexes. Nevertheless, the possibility of existence of more extensive linear, ring, folded, and other structures in solutions is discussed in the literature (see, for example, a review[19]). The observed shift of the spectra clearly attests to perturbation of the electron density of the DPyEt molecule, apparently, due to electrostatic interaction of the Ag^+ ions with the electronic system of the ligand. This interaction cannot be selective; therefore, molecular complexes with different structures and compositions can account for closely similar absorption spectra and feebly defined isosbestic points in the spectra of Ag^+/DPyEt mixtures.

When the metal/ligand ratio in solution increases to ≥60 : 1 (the DPyEt concentration is $6 \cdot 10^{-5}$ mol L^{-1}), the spectral pattern sharply changes. The initial absorption spectrum of DPyEt completely disappears being replaced by a new spectrum with a long-wavelength absorption band at about 350 nm (Fig. 1, spectra *3*, *4*) and opalescence appears, which is indicated, in particular, by smearing of the long-wavelength edge of the absorption spectrum. Opalescence points to the formation of a microdispersed solid phase responsible for the new spectrum in the region of 350 nm. This phase is readily precipitated by centrifuging for 20 min at 3000 rpm; as a result, the absorption band at about 350 nm disappears. It is of interest that transition from the spectrum of the ligand to that of the microdispersed solid phase occurs jumpwise as some critical ion/ligand ratio has been reached.

It should be noted that the ion/ligand ratio corresponding to transition to the new absorption spectrum and to the appearance of opalescence depends on many factors including the procedure used to mix the solutions, the method of titration, and the DPyEt concentration. A stepwise consecutive increase in the ion/ligand ratio produces opalescence at a higher ratio than the at-once preparation of a solution with a specified "critical" ratio. For the appearance of the characteristic long-wavelength absorption spectrum and opalescence, not only reaching of a definite ion/ligand ratio is required but also a particular DPyE concentration. Indeed, when the DPyEt concentration is $< 1 \cdot 10^{-5}$ mol L^{-1}, the characteristic long-wavelength absorption and opalescence do not appear even when the ion/ligand ratio is about 300 : 1, while for a DPyEt concentration of 10^{-4} mol L^{-1}, they can be reliably observed at 20 : 1 ratio.

The formation of a similar finely dispersed solid in the DPyEt—$AgClO_4$ system (for DPyEt concentration of $6 \cdot 10^{-5}$ mol L^{-1}) takes place even when the metal : ligand ratio in the solution is 50 : 1. In addition, in the case of silver perchlorate, this ratio depends appreciably on the initial ligand concentration. After a fourfold decrease of this concentration (to $1.5 \cdot 10^{-5}$ mol L^{-1}) with an equal excess of Ag^+, the precipitate is not formed, *i.e.*, the boundary of formation of the finely dispersed solid shifts toward a greater excess of the metal. It should be noted, however, that, despite the very close similarity of the DPyEt—$AgNO_3$ and DPyEt—$AgClO_4$ systems, the spectrum of the finely dispersed solid obtained from silver perchlorate differs somewhat from the spectrum of the phase formed from silver nitrate (Fig. 1, *cf.* spectra *3* and *4*). This prompts the conclusion that the counter-ion present in the system with the silver cation plays an important role and influences the structure of the product formed.

When Ag^+ is added to the system in an amount that ensures exceeding of the threshold Ag^+/DPyEt ratio for the given DPyEt concentration, a solid precipitate is formed. Perhaps, an increase in the concentration of silver ions shifts the equilibrium toward the formation of supramolecular complexes; after a definite critical concentration has been reached, the complexes start to aggregate to give the coordination polymer, which is produced as a microdispersed solid phase. The substantial bathochromic shift of the absorption spectra of the phase formed might be due to interaction of the chromophore groups of neighboring chains.

The solid precipitate was isolated from a solution of DPyEt and $AgNO_3$ with a metal/ligand ratio of 400 : 1; the precipitate was freed from excess $AgNO_3$, dried, and studied by electron microscopy and elemental analysis.

The data of elemental analysis (C, 39.63%; H, 3.32%; N, 11.45%; Ag, 28.88%; O, 16.73%) correspond to the stoichiometric composition of the solid product $Ag(DPyEt)(H_2O)NO_3$; the calculation gives C, 38.92%; H, 3.24%; N, 11.35%, Ag, 29.2%; O, 17.3%, *i.e.*, the material contains one Ag^+ cation and one NO_3^- anion per DPyEt molecule. The water molecule appears to enter the solid phase from the solvent during complex formation.

The electron microscopy study showed that the substance has a needle structure with a typical needle length of 1 μm and a needle thickness of about 100 nm (Fig. 2).

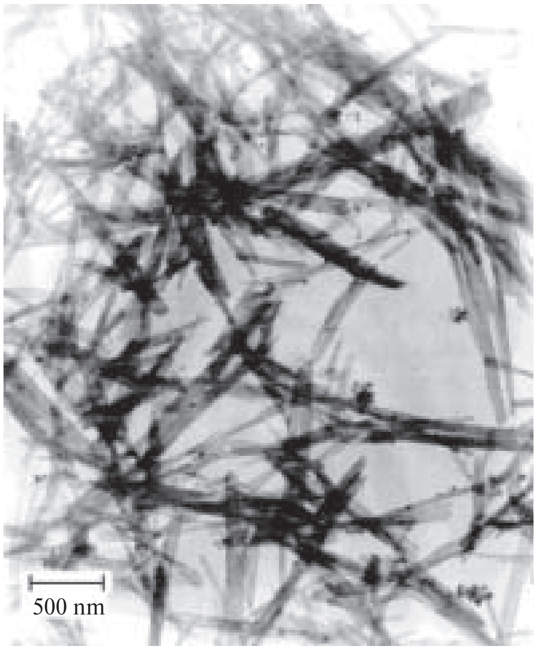

Fig. 2. Photomicrograph of the solid precipitate of the $AgNO_3$—DPyEt polymeric complex.

The data from electron microdiffraction (the presence of two diffraction rings) allow one to conclude that these aggregates have a crystal-like structure or have long-range order, at least, in one direction.

The precipitate has a limited solubility; it is soluble in water much better than in ethanol. When the precipitate freed from excess $AgNO_3$ by washing is dispersed in water for a long period (several hours), the material dissolves and the complex is destroyed; the resulting solution exhibits the absorption spectrum of the initial ligand, *i.e.*, in water, the solid precipitate gradually decomposes to give the initial components. Thus, without excess $AgNO_3$, the equilibrium shifts toward DPyEt and $AgNO_3$, readily soluble in water, which points to a small complexation constant. Since the coordination polymer is less soluble in ethanol than in water, a similar dispergation of the freshly prepared solid in ethanol gives rise to the spectrum of a suspension with a long-wavelength band in the region of 350 nm corresponding to the absorption spectrum of the microdispersed phase of the coordination polymer. When this dispersion is highly diluted with ethanol, the solid phase slowly and gradually dissolves and, after several days, the spectrum of a molecular solution of DPyEt is recorded. It is of interest that for moderate dilution of the initial dispersion, the spectrum of the supernatant is intermediate between the spectra of the molecular complex and the coordination polymer (Fig. 3).

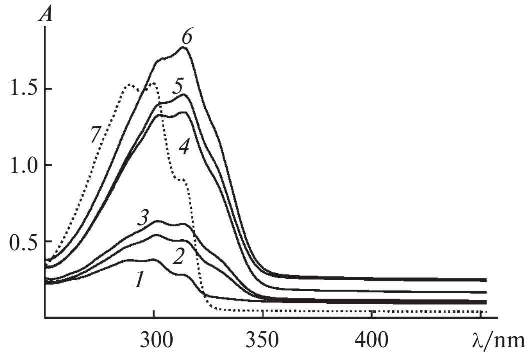

Fig. 3. Absorption spectra (*A*) of an ethanol solution equilibrated with the solid phase of the $AgNO_3$—DPyEt polymeric complex within the following periods of time after dispergation: 30 min (*1*), 60 min (*2*), 2 h (*3*), 15 h (*4*), 5 days (*5*), 15 days (*6*). For comparison, the spectrum of DPyEt in ethanol is given (*7*). The DPyEt concentration is $5 \cdot 10^{-5}$ mol L^{-1}.

Thus it was shown in this study that DPyEt molecules form loose molecular complexes with silver ions. When the metal/ligand ratio is relatively low, complexes of different compositions and structures whose absorption spectra differ only slightly from the spectrum of the ligand coexist in the solution. This shows itself as smoothing of the vibrational structure of the absorption spectrum and a slight bathochromic shift (up to 9 nm, or ~800 cm^{-1}) of the long-wavelength edge of the spectrum of the molecular complex.

High metal/ligand ratios result in the formation of a microdispersed phase of the coordination polymer, which gradually precipitates, the critical metal/ligand ratio being dependent on the initial ligand concentration.

Thus, as the concentration of silver ions increases, the system passes through a number of consecutive stages, namely, the formation of molecular complexes, supramolecular complexes and, finally, the avalanche-like formation of the solid microdispersed phase of the coordination polymer, which gradually precipitates.

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