Study of Complexation between Cu²⁺ Ions and *ortho*-Azidobenzoic Acid

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Abstract—An aqua complex of copper(II) *o*-azidobenzoate, $[Cu(OH)ABA \cdot 2H_2O]_2$ (ABA is *o*-azidobenzoic acid), was synthesized in an aqueous solution and identified by IR and electronic absorption spectroscopy. In the complex, the azido group is not coordinated by Cu²⁺. When dissolved in dry organic solvents (DMF, DMSO, dioxane, and methanol), the complex undergoes dehydration to give a chelate complex (CC) containing the Cu²⁺-coordinated azido group as a result of the electron density redistribution at its N atoms. The IR spectrum of the chelate complex contains no absorption band at 2135 cm⁻¹ corresponding to the stretching vibrations of the azido group. The resulting CC is unstable in solutions and spontaneously decomposes with a release of molecular nitrogen. The interaction of a Cu²⁺ ion with *o*-azidobenzoic acid in dry organic solvents affords a CC similar to the complex obtained on the dissolution of $[Cu(OH)ABA \cdot 2H_2O]_2$ in dry solvents.

Complexation between various N-containing organic compounds and transition metal ions is determined by the possibility of the nitrogen atom to donate its lone electron pair for the formation of a bond to metal ions. There are a great number of complexes of nitriles, Schiff bases, aromatic azo compounds, and amines that form chelate complexes with metal ions [1–4].

Like other N-containing groups, the azido group can form complexes [5–7] involving the lone electron pairs at its first and third N atoms [8]. The specific character of the interaction of the azido group with metal ions can explain the mechanism of the catalyzed decomposition of organic azides [8] and can be used to obtain various heterocyclic compounds. That is the reason why the synthesis of transition metal complexes with organic azides and the study of the properties of the azido group in them are of topical interest.

This study was devoted to the complexation between Cu^{2+} ions and *o*-azidobenzoic acid (ABA) in water and organic solvents.

EXPERIMENTAL

Synthesis of ABA. A cooled solution of NaNO₂ (1.08 g) in 10 ml of water was added dropwise at 5°C to a vigorously stirred mixture of anthranilic acid (2.1 g, 0.15 mol), water (15 ml), and concentrated HCl (17 ml). The solution was stirred for another 15 min and a solution of NaN₃ (1.08 g) in 10 ml of water was added dropwise. The resulting mixture was warmed to

room temperature and kept for about 2 h. White crystals were filtered off and recrystallized from boiling light petroleum–benzene (5 : 2 v/v). The yield of ABA was 1.57 g (65%), $T_{\rm m} = 144$ °C.

For C ₇ H ₅ N ₃ O ₂		
anal. calcd. (%):	C, 51.54;	H, 3.09.
Found (%):	C, 51.53;	Н, 3.07.

Synthesis of potassium *o*-azidobenzoate $C_6H_4(N_3)COOK$ (I). A solution of KOH (0.336 g) in 20 ml of ethanol was added to a solution of ABA (1 g) in 30 ml of ethanol. The ethanol was removed in a water bath *in vacuo* (30 mmHg) until crystallization started. The resulting white crystals of salt I were filtered off.

Synthesis of $[Cu(OH)ABA \cdot 2H_2O]_2$ (II). A hot solution of compound I (1.2 g) in 100 ml of water was added at 75°C to a solution of $CuSO_4 \cdot 5H_2O$ (1.5 g) in 50 ml of water. The resulting light green crystals of complex II were filtered off and recrystallized from THF.

Synthesis of the chelate complex (CC). A solution of compound I (0.6 g) in 20 ml of an organic solvent (DMF, DMSO, dioxane, or methanol) was added to a solution of $Cu(CH_3COO)_2 \cdot H_2O(0.3 g)$ in 30 ml of the same solvent. The reaction mixture was left in the dark



Fig. 1. IR spectra of (1) ABA, (2) salt I, (3) complex II, and (4) CC.

for a day and then chloroform (120 ml) was added. The resulting violet crystals of a CC were filtered off.

For $C_{14}H_{10}N_6O_6Cu$	1 ₂		
anal. calcd. (%):	C, 34.57;	Н, 2.06;	Cu, 26.34.
Found (%):	C, 34.73;	Н, 2.52;	Cu, 25.32.

Electronic absorption spectra were recorded on an SF-46 spectrophotometer (quartz cells, l = 1 cm) in the 220–800 nm range. IR spectra were recorded on a Specord IR75 spectrophotometer in the 400–4000 cm⁻¹ range (Nujol). The EPR spectrum was recorded on a Bruker ER-200D-SRC spectrometer. The gas evolved upon the dissolution of complex **II** in dry DMF was analyzed by gas chromatography with a Tsvet 102 instrument. Photodecomposition of complex **II** was carried out in a quartz tube exposed to the radiation from a DRK-120 quartz mercury lamp. The number of azido groups in the molecule of complex **II** was determined from the volume of the evolved nitrogen.

RESULTS AND DISCUSSION

Since complex II is insoluble in water, its composition was determined by isomolar series method from the weight of the precipitate formed in the reaction of $CuSO_4 \cdot 5H_2O$ with salt I. It was found that complex II contains one mole of salt I per mole of copper sulfate; i.e., the product is basic copper(II) *o*-azidobenzoate $Cu(OH)ABA \cdot nH_2O$. According to [9], the composition of copper(II) complexes with organic acids is determined by the concentration of OH⁻ ions in aqueous solution and can vary from normal to basic salts.

The number of molecules of crystallization water in complex II was calculated from the volume of nitrogen evolved upon its complete photochemical decomposition. Because the photolysis of aromatic azides is accompanied by a release of molecular nitrogen to give primary amines and azo compounds (a mole of nitrogen per mole of basic copper(II) *o*-azidobenzoate), the molecular mass of the complex calculated from the volume of the evolved nitrogen suggests its dihydrate formula Cu(OH)ABA \cdot 2H₂O.

The absence of a signal in the EPR spectrum of complex **II** indicates, as shown in [10], an exchange interaction between two copper centers resulting in a binuclear associate. Therefore, the molecular formula of complex **II** can be written as $[Cu(OH)ABA \cdot 2H_2O]_2$.

The formation of a copper(II) complex with ABA is also evident from IR spectroscopic data. For instance, the v_{as} (COOH) bands in the 1500–1700 cm⁻¹ range are shifted from 1680 and 1650 cm⁻¹ in ABA to 1575 and 1550 cm⁻¹ in salt I and to 1590 and 1550 cm⁻¹ in complex II (Fig. 1). This indicates the presence of a carboxylate ion, thus confirming the formation of complex II.

In the IR spectra of salt I and complex II, the $v_s(N_3)$ and $v_{as}(N_3)$ bands retain the same positions (at 2135 and 1290 cm⁻¹, respectively) as in the spectrum of free ABA; this indicates that the azido group is not coordinated by the Cu²⁺ ion. The presence of water of crystallization in complex II was confirmed by a δ (OH) band appearing at 1625 cm⁻¹, which is absent from the IR spectra of ABA and salt I. The broad v(OH) band at



Fig. 2. Electronic absorption spectra of (1) ABA, (2) salt I, and (3) complex II in methanol and (4) CC in DMF; $c = 5 \times 10^{-5}$ mol l⁻¹.

3250 to 3500 cm⁻¹ is due to the presence of both water of crystallization and hydroxy ions in complex **II**.

The electronic absorption spectra of ABA, salt I, and complex II in aqueous methanol were also examined. The spectrum of complex II contains a band at 700 nm (Fig. 2, curve 3) characteristic of the $d-d^*$ transition in organic copper(II) salts [11]. In the range of intraligand transitions (< 350 nm), ABA, salt I, and complex II absorb at 254 nm (Fig. 2, curves 1-3). This suggests that the electronic structure of the organic anion remains unchanged and that the azido group is not coordinated by the Cu²⁺ ion. Thus, although the azido group is spatially close to Cu^{2+} in complex II, it remains uncoordinated because the vacant coordination sites of Cu²⁺ are occupied by molecules of crystallization water. According to the literature data and the results of our study, complex II and other binuclear copper(II) carboxylates [9, 10] can be represented by the following structural formula:



When dissolved in dry organic solvents, complex II turns from green to dark violet as for a complex obtained in the reaction of $Cu(CH_3COO)_2 \cdot 2H_2O$ with salt I in dry DMF, DMSO, dioxane, or methanol



Fig. 3. Kinetics of the formation of the CC in DMF with the water content $c_w = (1) 0, (2) 1, and (3) 10\%$.

(Fig. 2, curve 4). The electronic absorption spectra of the CC obtained in dry solvents are insensitive to the nature of an organic solvent and identical with the electronic absorption spectrum of the CC obtained from complex II.

A comparison of the electronic absorption spectra of complex **II** and the CC (Fig. 2, curves 2, 3, and 4) showed that the absorption band in the range of the $d-d^*$ transition of copper is shifted from 700 to 570 nm. Two new absorption bands at 320 and 365 nm can be assigned to intraligand $\pi-\pi^*$ and $n-\pi^*$ transitions in the CC.

To elucidate the role of water in the conversion of complex **II** into the CC, complex **II** was dissolved in DMF containing different amounts of water (from 0 to 10 vol %). The curves of changing optical density of solutions of complex **II** in DMF at 365 nm with time indicate that an increase in the water content of DMF inhibits the formation of the CC (Fig. 3).

Since the rate of formation of the CC depends on the water content in the solvent, one can assume that the dissolution of complex \mathbf{II} in dry solvents is accompanied by its dehydration. This is the case with those solvents that can themselves form complexes with water molecules. A similar dehydration of copper salt hydrates was described in [12].

The IR spectrum of the CC (Fig. 1, curve 4) shows neither an absorption band at 1625 cm⁻¹ for the OH group of crystallization water, which confirms the dehydration of complex **II**, nor a $v_{as}(N_3)$ band at 2100 cm⁻¹. In dry DMF, the formation of the CC from complex **II** is completed in ~20 min without nitrogen evolution, which suggests the retention of three N atoms in the ligand. Apparently, the dehydration of complex **II** makes it possible for the Cu²⁺ ion to coordinate the azido group with the CC formation and to change the azido group electronic configuration in such a manner that it no longer absorbs at 2100 cm⁻¹.

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Fig. 4. Kinetics of the nitrogen evolution during decomposition of the CC in dry DMF in the dark.

In the solid state, the CC is stable at room temperature. However, when left in solution for several days, it decomposes through a release of nitrogen. The kinetics of nitrogen evolution during the spontaneous decomposition of the CC is shown in Fig. 4. The volume of the evolved nitrogen also confirms the presence of three N atoms in the ligand.

Hence, the water of crystallization in complex II prevents the azido group from being coordinated by the Cu^{2+} ion. In dry organic solvents, complex II undergoes dehydration and the azido group is coordinated by the Cu^{2+} ion but decomposes with time.

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