SYNTHESIS AND SPECTROSCOPIC AND CATALYTIC PROPERTIES OF A COMPLEX OF PALLADIUM(II) WITH ALIZARIN COMPLEXONE

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A 1:1 complex of Pd(II) with alizarin complexone was synthesized and characterized. This complex displays high catalytic activity in the hydrogenation of nitrobenzene and 1-hexene.

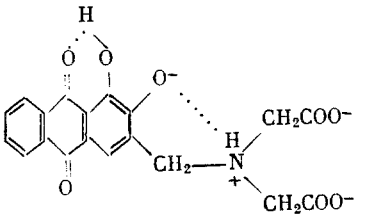
Alizarin and its derivatives have a highly pronounced capacity to form colored complexes with a number of transition metal ions [1-3]. Some of these complexes have catalytic properties in hydrogenation [4-7]. One of the most interesting alizarin derivatives is alizarin complexone (AC),* which contains several chelate groups. According to Leonard and West [3], AC forms more stable chelates than alizarin or alizarin red S.

In the present work, the complex of AC with Pd(II) was synthesized and its spectroscopic and catalytic properties were studied.

RESULTS AND DISCUSSION

The stoichiometric composition of the complex was studied by the isomolar series method in aqueous solution at pH 4.01 and 6.86 and in DMF and dioxane solution. K_2PdCl_4 was used in the aqueous solutions, while palladium acetate was used in the organic solutions. In all four cases, the formation of a 1:1 complex was determined. As an illustration, the dependence of D on $(C_R/(C_M + C_R))$ for pH 6.86 is given in Fig. 1.

A sharp change in the color of the solution is noted upon the addition of palladium salts to the AC solutions in all cases and a new UV band is found at 520 nm (Fig. 2), whose position is independent of the solution pH and the nature of the solvent used. These changes are identical to those observed upon studying the reaction of AC with Co(II), Cu(II), and Fe(II) ions [3]. The data of Leonard and West [3] and our results indicate that the spectra of the complex formed coincides in the position of its maximum with the spectrum of the doubly ionized form of AC.



After determining the stoichiometric composition in solution, we carried out the synthesis of the complex and its isolation in the solid state. The complex is a dark red powder soluble in water, DMF, and DMSO. The IR spectra of this complex show a new band at 1543 cm^{-1} and disappearance of the band at 1734 cm^{-1} (these bands belong the uncoordinated carbonyl group of the carboxyl fragments). Electron-spectroscopic chemical analysis gave the palladium bond energy (338.2 eV), which corresponds to the Pd(II) oxidation state. These result in conjugation with finding that the UV absorption bands of the doubly ionized form of AC and the palladium complex of AC are identical indicate that the structure of this complex is as follows:

*3-Di(carboxymethyl)aminomethyl-1,2-dihydroxyanthraquinone (AC).

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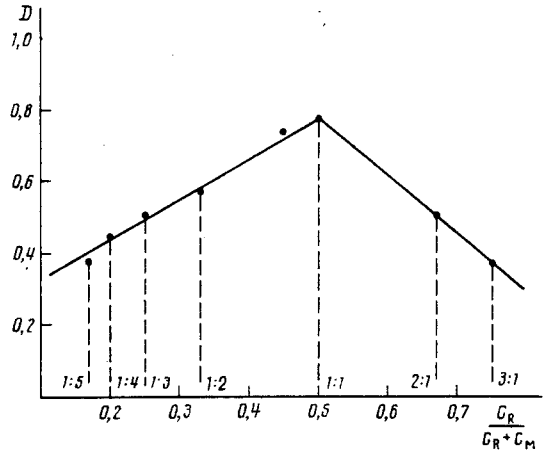


Fig. 1. Dependence of the optical density on the composition of the isomolar solution (C_R and C_M are the concentrations of AC and K_2PdCl_4, respectively.

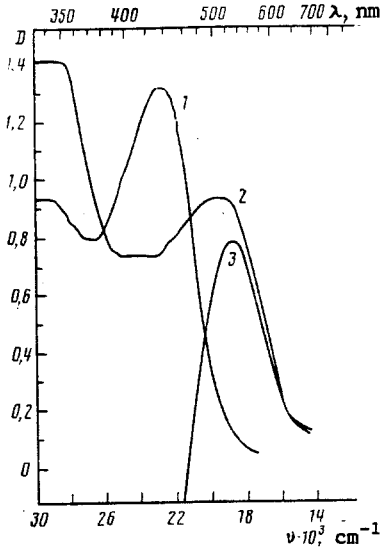
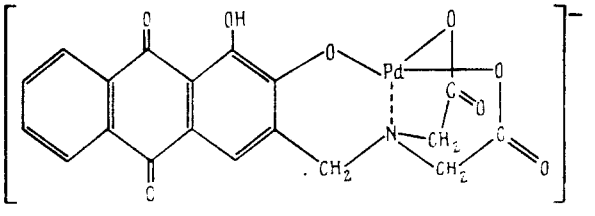


Fig. 2. Absorption spectra for alizarin complexone and its complex: 1,2) solution of AC in H_2O at pH 4.01 (1) and 6.68 (2); 3) solution of palladium complex of AC.



The complex displayed catalytic activity in the hydrogenation of nitrobenzene (NB) and 1-hexene (Table 1).

EXPERIMENTAL

Analytical grade alizarin complexone (AC) was used without further purification, while a sample of K_2PdCl_4 was prepared according to a standard procedure [8]. The samples of water, DMF, and dioxane used as solvents were freshly distilled. The buffer solutions were prepared by dissolving 0.025 mole KH_2PO_4 and 0.025 mole Na_2HPO_4 (pH 6.86) and 0.05 M potassium

TABLE 1. Catalytic Activity of the Palladium Complex with AC

Substrate	Solvent	pH	T, °C	W_{av}, mole H_2 / mole Pd·min
NB*	H_2O	4.01	50	80.8
1-Hexene**	»	»	»	43.9
NB	»	6.86	25	55.8
NB	»	Without added buffer	35	57.8
NB	»	»	45	71.8
NB	DMF	»	80	50.4
NB	DMF***	»	80	111.3

*Aniline is the product.
**Hexane is the product.
***As a salt with Bu_4N^+.

phthalate (pH 4.01). The concentration of the starting solutions of AC and the palladium salts was $6 \cdot 10^{-5}$ mole/liter. The stoichiometric composition of the complexes was studied by the isomolar series method [9]. The electronic spectra were taken on a Specord spectrophotometer, while the IR spectra for KBr pellets were taken on a Specord IR-75 spectrometer. The x-ray photoelectron spectra were taken on a Varian IEE-15 spectrometer with a high-intensity magnesium cathode. The samples were deposited as a powder onto an adhesive strip. The calibration was carried out relative to the carbon 1s line, E_b = 285 eV.

The catalytic activity of the complex was studied in an agitated glass reactor placed in a rapid rocker at atmospheric pressure. The reaction rate was determined relative to the hydrogen absorption rate using a burette. The products were analyzed by thin-layer chromatography and gas-liquid chromatography.

Synthesis of the Complex of Pd(II) with AC. A sample of 0.385 g (0.001 mole) AC was dissolved in 100 ml water containing 2 M KOH and the solution temperature was brought to about 90°C. Then, a solution of 0.326 g K_2PdCl_4 in 25 ml water at 60°C was added with rapid stirring. The formation of a precipitate was noted upon mixing, which was filtered off after cooling of the solution. The yield of the complex was 0.44 g (84%). Found: C, 42.5; H, 2.6; N, 2.4; Pd, 19.8; K, 7.6%. Calculated for $PdC_{19}H_{12}O_8KN$: C, 43.22; H, 2.27; N, 2.65; Pd, 20.17; K. 7.41%.

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