

Synthesis of the dioxygen complex of oil cobalt (II) porphyrin complex and study of its oxygenating properties

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Based on the porphyrin concentrate extracted from oil, a cobalt (II) porphyrin complex and its dioxygen adduct have been synthesized. The structure of resulting complexes has been established by studying their electronic and IR spectra. The molecular weight of the oil cobalt (II) porphyrin complex, determined by the mass spectroscopic method, was 456. The molar ratio of cobalt (II) porphyrin complex and molecular oxygen is 2 : 1. It has been established that the dioxygen adduct of cobalt (II) porphyrin complex possesses the ability to epoxidize alkenes. A possible mechanism for epoxidation of alkenes has been considered.

Key words: dioxygen complex, cobalt, porphyrin complex

Introduction

Over the past 25 years, various properties of synthetic metalloporphyrins have been established and studied. It has been shown that synthetic metalloporphyrins in their catalytic properties are not inferior to natural metalloporphyrins. However, synthetic metal porphyrins are practically insoluble in hydrocarbons. In this regard, there are serious technical difficulties in using them as a homogeneous catalyst or for other purposes.

Unlike synthetic metal porphyrin complexes, metal porphyrins isolated from heavy oils are quite soluble in hydrocarbons and hydrocarbon fractions of oil. The resulting porphyrin complexes of transition metals are of great interest as carriers of molecular oxygen.

In all metal porphyrin complexes, a regularity was established in the formation of the peroxide structure of dioxygen adducts, which was confirmed by the presence in the IR spectra of specific absorption bands of 1135–1140 cm⁻¹ characteristic of the fragment.

The study of the catalytic activity of transition metal complexes with porphyrins revealed their ability to oxidize unsaturated organic compounds and alkenes, and their dioxygen adducts had proved effective in epoxidation of alkenes to oxiranes.

The object of this paper was to synthesize dioxygen adducts of metalloporphyrin complexes and to investigate their structure by spectral methods.

Experimental part

The oil cobalt (II) porphyrin complex was obtained from the oil porphyrin concentrate [3] according to our method [4]. The obtained cobalt (II) porphyrin complex is a solid material of cinnamon-violet color, which dissolves in

toluene and xylene. A sample of the obtained cobalt (II) porphyrin complex was analyzed for cobalt content by the spectrophotometric method [7–10]. The content of cobalt in the sample was 12.65 %.

Preparation of the dioxygen adduct

2.28 g of petroleum cobalt (II) of the porphyrin complex and 40 ml of carbon tetrachloride were placed in the metal ampoule with a capacity of 100 ml, the ampoule was connected to the oxygen cylinder under a pressure of 5.0 mPa and the rocking chair was turned on. The reaction was carried out at room temperature for 3 hours. The end of the reaction was established based on completion of oxygen absorption. At the end of the reaction, the contents in a metal ampoule were cooled at normal pressure, and the precipitated sediment was filtered through the glass filter. 1.52 g (62.3 %) of a solid precipitate of cinnamon color was obtained, a solid precipitate, which, after washing from petroleum ether and drying at room temperature, was analyzed for cobalt content by a spectrophotometric method [7]. The cobalt content in the sample of the dioxygen adduct was 6.25 %.

Epoxidation of alkenes with a dioxygen adduct

0.45 g of the dioxygen adduct (5) and 35 g (0.5 mol) of 1-pentene were placed in the metal ampoule and heated at 600 °C for 3 hours; then the reaction mixture was filtered through the glass filter; yield of 1,2-oxidopentane determined in the filtrate by GC/LC was 65 % (based on the olefin reacted).

IR spectroscopic studies were carried out on the SPECORD-M80 spectrometer in the 4000–400 cm⁻¹ region in KBr tablets.

Electronic spectra were recorded on the SF-4A instrument.

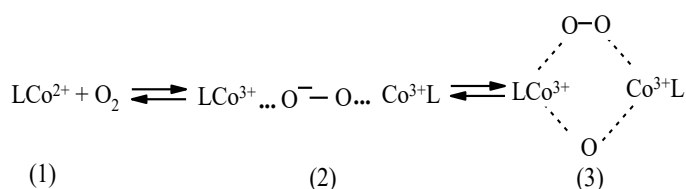
Some characteristics of cobalt porphyrine complex

Complex	Electron spectrum, nm	IR spectrum, cm ⁻¹	Absorption of molecular oxygen at 25 °C, g/cm ³
Co ^{II} P	521, 533, 572	1508, 1525, 1605 (pyrrole ring), 857 (CH ₂), 634 (=NH), 1030, 1046, 1076 (CH-pyrrole), 1380 (-C-N), 1451 (-C=N)	18,7

Gas-liquid chromatographic analyzes were performed on the LXM-8MD chromatograph, column dimensions: 5×2.5 m, carrier gas – helium, absorbent PEG-1000.

Results and discussion

The possibility of electroreduction of the dioxygen-containing anion to water [1] or peroxide has been shown before [2]. These studies are important for the creation of combustible elements and air batteries [3–5]. The essence of this method lies in the fact that the organometallic chelate complexes LCo²⁺ (1) possess extremely high molecular oxygen restoring abilities due to electron transfer, which leads to the formation of a dioxygen adduct (2).



L – is an organic ligand.

The latter, oxidizing the hydrogen ion to H₂O, turns into a complex of LCo³⁺ (3). At the cathode, it is again reconstituted to LCo²⁺ (1), which then easily recovers molecular oxygen. As a result of this combination of chemical and electrochemical processes, a large amount of energy is produced. Considering the great scientific and practical significance of the dioxides complexes, we have developed a method for obtaining such complexes based on petroleum cobalt (2) porphyrin.

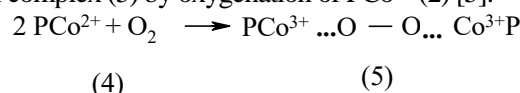
We synthesized oil cobalt (II) porphyrin complex PCo²⁺ on the basis of the oil porphyrin concentrate [3] according to the method developed earlier [4] and characterized by the study of its electronic and IR spectra (table).

The characteristic bands with maxima in the electron spectrum at 521, 572, and 533 nm confirm the existence of a coordination bond between the cobalt ions and the nitrogen atoms in the porphyrin ring. Spectrum area of the synthesized oil cobalt (II) porphyrin complex has been observed in the IR absorption bands confirming the presence of a macrocyclic porphyrin ring. The pyrrole cycles are characterized by absorption bands at vibrational frequencies ν 1508, 1525 and 1605 cm⁻¹. The absorption bands at ν 857 cm⁻¹ correspond to non-flat deformation vibrations of the methine bridges (= CH). Plane deformation vibrations at ν 1030, 1046 and 1076 cm⁻¹ characterize the presence of CH bonds of the pyrrole ring. The absorption band at ν 634 cm⁻¹

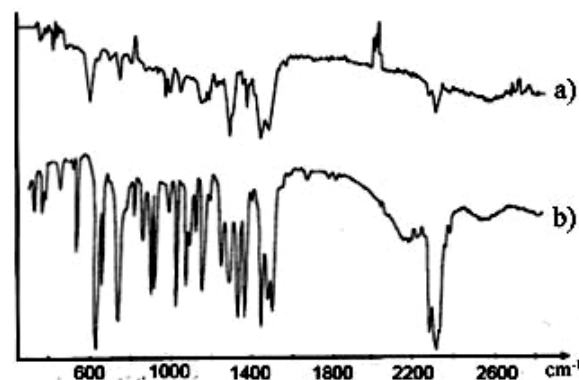
is a characteristic signal of the nonplanar deformation vibration of the groups = NH in the complex PCo³⁺. The absorption bands at ν 1380 and 1451 cm⁻¹ correspond to -C-N and -C = N groups in the petroleum cobalt (II) complex. Absorption bands, characterizing the presence of the functional groups: >C = O, -OH, -NH₂, -COOR, etc. in the lateral branches of the porphyrin molecule, appear in the areas, respectively, at 1705–1712, 3360–3475, 3214–3247 and 1736–1740 cm⁻¹. It should be noted that the PCo²⁺ petroleum metalloporphyrin complex synthesized by us dissolves rather well in aromatic and aliphatic hydrocarbons. The infrared spectrum (figure) of the sample of the complex obtained by us completely coincides with the data of the spectrum given in [3].

The molecular weight of the oil cobalt-porphyrin complex PCo²⁺ (4), determined by the mass spectroscopic method, is 466 carbon units.

For the first time, we obtained a dioxygen adduct of an oil complex (5) by oxygenation of PCo²⁺ (2) [5].



The purity of the obtained sample (5) was confirmed by repeated elemental analyses, the study of IR spectra and measurement of magnetic susceptibility. The IR spectrum of the dioxygen complex (5) exhibits a characteristic absorption band at ν = 1127 cm⁻¹, confirming the presence of dioxygen in the complex (5). The presence of O₂²⁻ in the dioxygen adduct is also established by the determination of its magnetic moment of 1.5 mV (23 °C). The IR spectral data and the magnetic characteristics of the dioxygen anion (O₂²⁻) in the complex (5) also agree well with the reference data [6]. When comparing the contents of cobalt in the



Infrared spectrum of complex compounds a) PCo²⁺ complex; b) the dioxygen adduct PCo²⁺

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Синтез дикислородного комплекса нефтяного кобальт(II) порфиринового комплекса и изучение его оксигенирующих свойств

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На основе порфиринового концентрата, выделенного из нефти, синтезированы кобальт (II) порфириновый комплекс и его дикислородный аддукт. Строение полученных комплексов установлено с помощью их электронных и ИК-спектров. Молекулярная масса нефтяного кобальт (II) порфиринового комплекса, определенная масспектропическим методом, составила 456. Мольное соотношение кобальт (II) порфиринового комплекса и молекулярного кислорода составляет 2 : 1. Установлено, что дикислородный аддукт кобальт (II) порфиринового комплекса обладает способностью эпоксидировать алкены. Рассмотрен возможный механизм эпоксидирования алкенов.

Ключевые слова: диоксидный комплекс, кобальт, порфириновый комплекс

Синтез дикисневого комплексу нафтового кобальт(II) порфиринового комплексу і вивчення його оксигенуючих властивостей

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На основі порфіринового концентрату, виділеного з нафти, синтезовані кобальт (II) порфіриновий комплекс і його дикисневий аддукт. Будову отриманих комплексів встановлено за допомогою їх електронних і ІЧ-спектрів. Молекулярна маса нафтового кобальт (II) порфіринового комплексу, визначена масспектропическим методом, склала 456. Мольне співвідношення кобальт (II) порфіринового комплексу і молекулярного кисню складає 2 : 1. Встановлено, що дикисневий аддукт кобальт (II) порфіринового комплексу має здатність эпоксидувати алкени. Розглянуто можливий механізм эпоксидування алкенов.

Ключові слова: діоксидний комплекс, кобальт, порфіриновий комплекс