

## Synthesis of Crown-Substituted Phthalocyanic Ruthenium Complexes of the Same Composition

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**Abstract:** The method for the synthesis of crown substituted phthalocyanic ruthenium complexes has developed. IR spectroscopic study of synthesized complexes revealed differences in IR spectra of ruthenium complexes of the same composition, but obtained from different initial components.

**Key words:** ruthenium, phthalocyanin, synthesis, complex compounds, ligands

### I. Introduction

Currently, more than 100,000 tons of phthalocyanin are produced worldwide to be used as photosensitive materials in photocopy technics, devices for storing and reading information, conductors and electro catalysis. The variety of properties of materials created on their basis is due to the specificity of the electronic structure of the phthalocyanic ligand [1-3].

The present work is devoted to the study of the features of coordination and supramolecular chemistry of ruthenium complexes with crown-substituted phthalocyanic ligands. The urgency of the work is determined on the one hand, by fundamental properties of crown substituted phthalocyanic complexes of ruthenium specifically transition metals, on the other hand, in the hope of finding useful properties suitable for the practical use of such substances in certain fields of material science.

As a precursor, pre-synthesized dicyano-benzo-15-crown-5 was used.  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ru}_3(\text{CO})_2$ ,  $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$ , and  $[\text{Ru}_2(\text{OAc})_4\text{Cl}]_n$  were chosen as ruthenium compounds. Experiments showed that irrespective of the choice of source in all cases tetra-15-crown-5-ruthenium phthalocyanine containing CO and methanol molecules as axial ligands -  $(\text{R}_4\text{Pc}) \text{Ru}(\text{CO})(\text{CH}_3\text{OH})$  have been formed.

Due to the disposition of dicyano-benzo-15-crown-5 to oxidation, the synthesis of tetra-crowned phthalocyanic ruthenium was carried out in a corked up ampoule.

As a result of the conducted experiments, it was established that only  $(\text{R}_4\text{Pc}) \text{Ru}(\text{CO})(\text{CH}_3\text{OH})$  can be obtained by varying various parameters as a result of template synthesis in the melt of dicyano-benzo-15-crown-5 and the investigated ruthenium compounds. Maximum yield (80%) is achieved using ruthenium carbonyl in the reaction. In this case, the source of CO is the initial compound, but not the decomposition product of dinitrile.

In the case of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  use, the decrease of the yield of the complex  $(\text{R}_4\text{Pc}) \text{Ru}(\text{CO})(\text{CH}_3\text{OH})$  was provoked by the reduction of Ru (III) Ru (II) with simultaneous oxidation of initial dicyano-benzo-15-crown-5.

In the coordination chemistry, the stability of Ru (II) complexes is usually low due to the high probability of their oxidation to Ru (III).

It should be noted that in our situation, the anomalous stability of low-spin Ru (II) complexes is associated with the peculiarities of the nature of the aromatic planar, tetra dentate phthalocyanic ligand system that stabilizes the lowest oxidation states of transition metals [4-6].

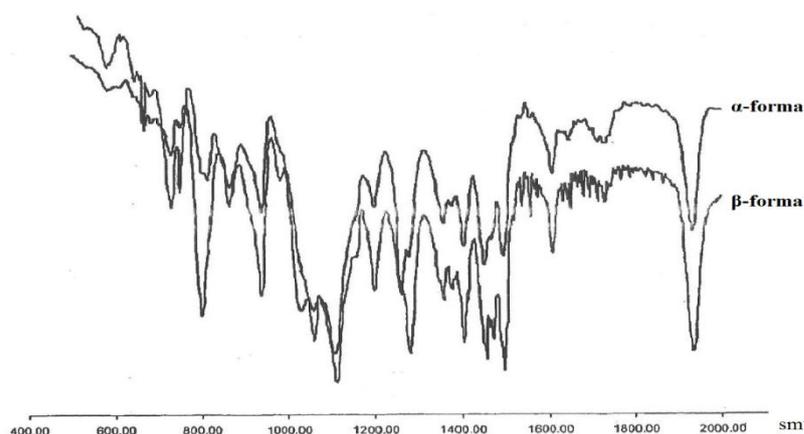
It should also be noted that, as a by-product of the reaction. The formation of the free ligand  $\text{H}_2(\text{R}_4\text{Pc})$  was observed when all the salts, except  $\text{Ru}_3(\text{CO})_2$  ruthenium carbonyl, were used to obtain ruthenium complexes with tetra-15-crown-5-phthalocyanine and N-donor ligands from DCB15K5 and ruthenium compounds in N-donor solvent.

Thus, in the high-temperature template synthesis of tetra-15-crown-5-phthalocyaninates of ruthenium both in the melt of DCB15K5 and in the solution of the N-donor ligand, the main product of the reaction is the complex  $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$ .

**Table 1.** Results of the synthesis of ruthenium tetra-15-crown-5-phthalocyaninate.

Reagents	Ratio	Time	T, °C	Exit, %
DSB15C5:RuCl <sub>3</sub> *nH <sub>2</sub> O (I)	1:1	4	200	12%
DSB15C5: Ru <sub>3</sub> (CO) <sub>12</sub> (II)	24:1	4	200	85%
DSB15C5:[Ru <sub>2</sub> (OAc) <sub>4</sub> Cl] <sub>n</sub> (III)	16:1	4	200	18%
DSB15C5:[Ru(DMSO) <sub>4</sub> Cl <sub>2</sub> ] (IV)	8:1	4	200	10%

We also found out that boiling of (R<sub>4</sub>Pc) Ru (CO) (CH<sub>3</sub>OH) in pyridine within hours does not lead to decarbonylation of the complex. In the IR spectrum of the resulting complex, there is an intensive band of stretching vibrations of  $\nu$  (CO) at 1945  $\text{cm}^{-1}$ . A similar reaction with pyrazine within 5 hours also does not lead to decarbonylation. Based on IR spectroscopy data, it was also found out unlike CO, the methanol molecule in the (R<sub>4</sub>Pc) Ru (CO) (CH<sub>3</sub>OH) complex is easily replaced by the N-donor ligand molecule upon dissolution in an appropriate solvent.



**Figure 3.** IR spectra of the complex (R<sub>4</sub>Pc) Ru (CO)(CH<sub>3</sub>OH) obtained from RuCl<sub>3</sub> \* 3H<sub>2</sub>O ( $\alpha$ -form) and Ru<sub>3</sub>(CO)<sub>12</sub> ( $\beta$ -form)

Some differences are found in IR spectra of ruthenium complexes of the same composition, but obtained from different initial components. Thus, the IR spectrum of the ruthenium complex obtained by using ruthenium chloride differs significantly from the IR spectrum of the complex obtained from ruthenium carbonyl.

In the IR spectrum of the  $\alpha$ -shape, along with the most intense band of about 1100  $\text{cm}^{-1}$ , there is a rather intense doublet of about 1030 and 1060  $\text{cm}^{-1}$  as for the  $\beta$ -form, only the high-frequency component. It indicates the conformational differences between crown-etheral fragments of  $\alpha$ - and  $\beta$ -forms. Another notable difference is observed in 800  $\text{cm}^{-1}$  area. In the IR spectrum of  $\alpha$ -form, a band of about 800  $\text{cm}^{-1}$  was released; its intensity is comparable with the band about 1100  $\text{cm}^{-1}$ . In the IR-spectrum of  $\beta$ -form, the band in this region is characterized by low intensity. There are also differences in the region 1250-1300  $\text{cm}^{-1}$ . In the IR spectrum of  $\alpha$ -form, a clear intense doublet is observed near 1260 and 1278  $\text{cm}^{-1}$ . In this case, the low-frequency component is much more intense than high frequency one and due to its relative intensity is comparable with band of about 1100  $\text{cm}^{-1}$ . In the IR spectrum of the  $\beta$ -form, an intense band of about 1280  $\text{cm}^{-1}$  with bending (or shoulder) of about 1260  $\text{cm}^{-1}$  is observed.

In this region, the IR spectrum of  $\beta$ -form shows analogy with IR spectra sandwich crown phthalocyanines and monocrown phthalocyanines, while, for example, for t-butyl-substituted metal phthalocyanines, such intensive bands in this area are not characteristic. In the IR spectra of  $\alpha$  and  $\beta$  forms of complexes, rather strong bands about 1934  $\text{cm}^{-1}$ , were revealed. These bands can be attributed to the stretching vibrations of the carbonyl group  $\nu$  (CO). Low value this frequency indicates the bridging function of the carbonyl groups in these complexes.

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