

## Co(II) Phthalocyanine Complex with Pyridine Bonded to Silica and Its Interaction with Oxygen

KRISTYANA TASHKOVA

*Higher Institute of Chemical Technology, 8010 Bourgas, Bulgaria*

and ATANAS ANDREEV

*Institute of Kinetics and Catalysis, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria*

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*The formation of mono- and bi-pyridine complexes of Co(II) phthalocyanine is possible on the surface of silica, depending on the concentration of pyridine chemically bonded on the support. Super-oxo- and  $\mu$ -peroxodicobalt complexes are identified by esr and reflection spectroscopy on silica containing different concentrations of Co(II) phthalocyanine pyridine complexes chemically bonded on the surface. Besides supported surface complexes, physically sorbed particles of Co(II) phthalocyanine exist, due to the high adsorption capacity of the support.*

### Introduction

Cobalt chelates with porphyrin-like structure are known to form reversible complexes with oxygen [1–4]. The complexes are of interest due to their activity in catalytic and electrochemical redox reactions and as oxygen carriers. The application of these

complexes in a solid state offers particular advantages, but a problem arises connected with molecular dispersion on a solid surface. It is clear that Co(II) phthalocyanine [Co(II)PhC] cannot be molecularly dispersed on silica surface when physically adsorbed.

In the present paper the interaction of oxygen with Co(II) phthalocyanine pyridine complex, chemically bonded to the silica surface, is studied. Pyridine is chosen as a surface-bonded ligand owing to its ability to act both as a complex-forming agent and as an activator for the interaction with oxygen.

### Experimental

The chemical bonding of pyridine with the surface of 'aerosil' (300 m<sup>2</sup>/g) was carried out according to the following procedure [5]. Triethoxyvinylsilan interacts with surface hydroxyl groups followed by

TABLE I. Characteristics of the Samples.

Samples	Double bond content, mmol/g	Co(II) phthalocyanine, incorporated in the samples	
		mmol/g	N, mol PhC/mol Py
1	0.20	0.24	1.20
2	0.20	0.09	0.45
3*	0.20	0.09	0.45
4	1.37	0.09	0.07
5	2.05	0.09	0.04
6	SiO <sub>2</sub>	0.79	—

\*Prepared at 393 K.

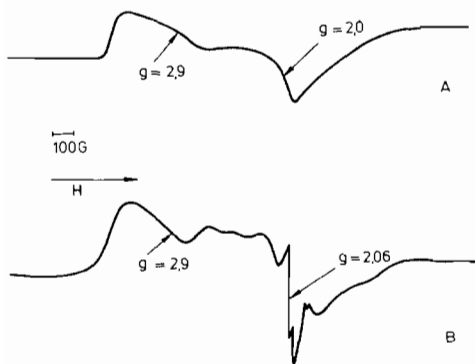
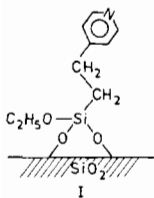


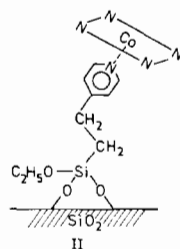
Fig. 1. EPR spectra of Co(II)PhC/SiO<sub>2</sub> samples. A, air dry sample 1; B, air-dry sample 3.

incorporation of hydrogen bromide in the double bond and attachment of pyridine by Würtz synthesis. The surface compound obtained in this way can be schematically presented by Scheme (I). The double



bond content (Table I), determining the surface compound formed by interaction of surface hydroxyl groups with triethoxyvinylsilane, was used for estimation of the amount of surface pyridine (assuming the pyridine yield to be quantitative).

The deposition of Co(II)PhC on the modified silica was carried out from solution in *n*-octane at 373 K. The surface complex is schematically represented by Scheme (II). The amount of the Co(II)PhC used and the Co(II)PhC/pyridine ratio are presented in Table I.



The synthesized surface complexes and their interaction with oxygen were studied by electron paramagnetic resonance (JEOL-3BSX spectrometer) and reflection spectroscopy in the UV and visible ranges (Carl Zeiss VSU-2P spectrometer).

## Results and Discussion

The properties of the samples under consideration should depend to a great extent on the Co(II)PhC/pyridine ratio. Fig. 1-A represents the EPR spectrum of sample 1, which contains the greatest amount of Co(II)PhC (the maximum Co(II)PhC/Py ratio). Two intensive broad lines at  $g = 2.0$  and  $g = 2.9$  are observed. These lines are identical with lines observed in the spectrum of Co(II)PhC diluted in  $\beta$ -PhC matrix [6]. A similar spectrum is obtained for sample 6, which contains Co(II)PhC supported on pure silica. It can be concluded that the EPR lines are due to the highly dispersed Co(II)PhC particles [7]. They were present in considerable amounts in the samples with high Co(II)PhC/Py ratio or Co(II)PhC on pure silica. There were no adsorption lines in the samples which can be assigned to reversible oxygen adducts.

EPR data were confirmed by reflection spectroscopy studies. Figure 2-A presents the reflection spectrum of sample 6 in the UV and visible ranges. The following bands are observed: Soret bands at 310–380 nm and three bands at 600, 630 and 680 nm, typical of Co(II)PhC [7]. Sample 1 shows a similar spectrum.

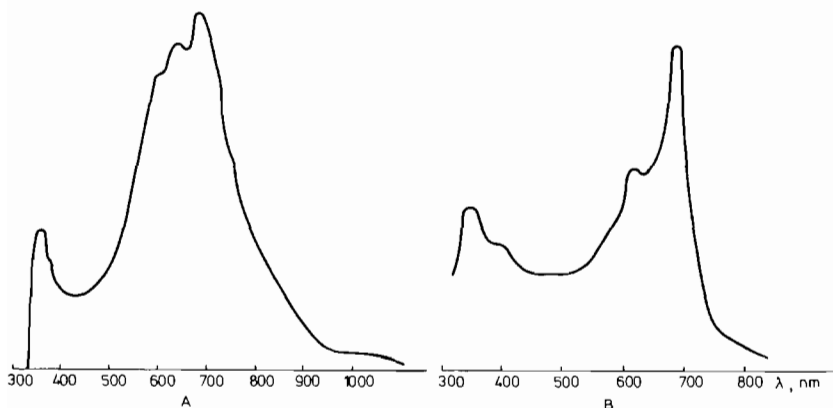


Fig. 2. Reflection spectra of Co(II)PhC/SiO<sub>2</sub> samples. A, air-dry sample 6; B, air-dry sample 2.

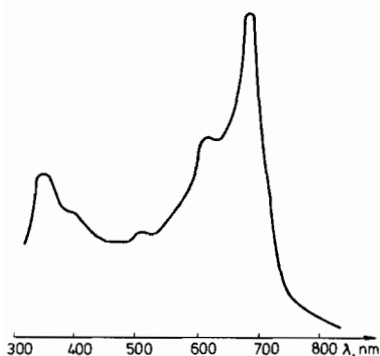
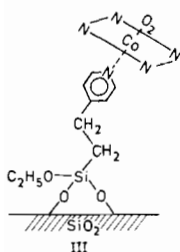


Fig. 3. Reflection spectrum of Co(II)PhC/SiO<sub>2</sub> (air-dry sample 3).

The decrease in Co(II)/PhC/Py ratio in sample 2 allows us to identify bands typical of a surface Co(II)PhC-pyridine complex (Fig. 2-B). The band at 630 nm disappears, but new bands appear at 615 and 675 nm. The band at 615 nm is the most intensive band in the spectrum of nitrogen-containing Co(II) complexes with C<sub>4v</sub> symmetry [8], and is attributed to a pentacoordinated surface complex of Co(II), Co(II)PhC·Py. The next intensive band in the spectrum of Co complexes coordinated with five nitrogen atoms appears at about 400 nm [8]. This band is also observed in the spectrum of sample 2 (Fig. 2-B). Evacuation of sample 2 does not cause any change in the reflection spectrum.

Figure 1-B presents the EPR spectrum of the air dry sample 3. Along with the above discussed absorption at  $g \approx 2.0$  and  $g \approx 2.9$ , a narrow band (band width of about 30 G) is observed. According to its spectral characteristics this line can be attributed to the oxygen adduct formed on the cobalt-pyridine complex with an electron transfer to the oxygen molecule under the activating action of the axially coordinated pyridine [9]. The structure of the complex can be expressed by Scheme (III).



The oxygen adduct is found only for the samples containing the lowest amount of phthalocyanine, which is incorporated at high temperature (conditions providing better dispersion). When the sample contains more Co(II)PhC, not all pyridine rings form complexes and the particles of physically sorbed phthalocyanine create an intensive paramagnetic background which suppresses the O<sub>2</sub><sup>-</sup> signal.



Fig. 4. EPR spectra of Co(II)PhC/SiO<sub>2</sub> (sample 4). a, air-dry; b, after evacuation ( $1 \times 10^{-4}$  Torr); c, after oxygen adsorption ( $P_{O_2} = 480$  Torr).

The results discussed above reveal that only a part of the introduced CoPhC forms surface complexes with the pyridine, even in the presence of sufficient amounts of pyridine rings on the surface. Due to the higher polarity and molecular weight of CoPhC a part of it remains physically sorbed on the surface as crystal aggregates.

The thermal stability of the adducts can provide further information about their structure. With gradual heating of the sample in the chamber of the EPR resonator, the signal intensity gradually decreases and reaches zero at 388 K. After cooling to room temperature a 90% recovery of the initial intensity is observed, in agreement with literature data about the behavior of reversible oxygen adducts of nitrogen-containing cobalt complexes [9].

In addition the formation of adducts with oxygen is proven using reflection spectroscopy data. The spectrum of the air-dry sample 3 (Fig. 3) shows absorption at about 510 nm, typical of superoxo-cobalt complexes [10]. No absorption at 510 nm is observed after evacuation.

The increase in supported pyridine content leads to considerable changes in the EPR spectrum of the samples. Figure 4a presents the spectrum of sample 4 after evacuation (sample 4 contains considerable amount of chemically attached pyridine). The spectrum shows a superfine structure caused by cobalt with nuclear spin  $I = 7/2$  and  $g = 2.4$ . This structure disappears on oxygen adsorption (Fig. 4b) and recovers after repeated evacuation. Taking into account the known spectra of CoPhC and its complexes [11], as well as other cobalt complexes of similar struc-

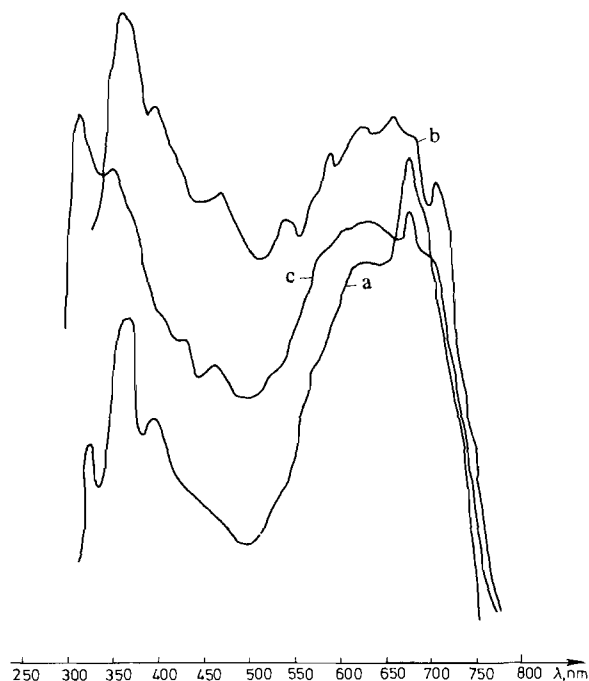
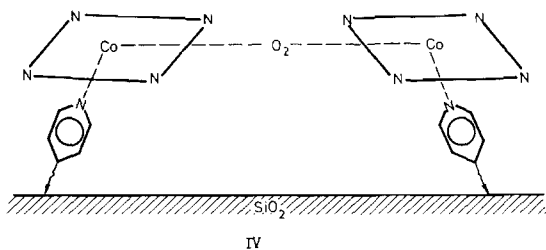


Fig. 5. Reflection spectra of Co(II)PhC/SiO<sub>2</sub> (sample 4). 1, air-dry sample; 2, after evacuation ( $1 \times 10^{-4}$  Torr); 3, after oxygen adsorption ( $P_{O_2} = 480$  Torr).

ture [12], one can assume an equilibrium between the species, shown in Scheme (IV).



The higher concentration of supported pyridine provides the possible existence of adjacent complexes (Scheme II), which form  $\mu$ -peroxodicobalt complexes with oxygen (Scheme IV). Evacuation destroys the oxygen complex and an absorption band of the phthalocyanine molecule in (Scheme II) appears in the EPR spectrum.

Evidence of the presence of bridged peroxodicobalt structures is given by the band at about 300 nm [10] in the spectrum of the air-dry sample 4 (Fig. 5a). After evacuation only the two Soret bands remain in this range – Fig. 5b. Characteristic bands of crystal phthalocyanine are observed in the other ranges of the spectrum.

Conditions are available for formation of bipyridine complexes (Scheme V) in sample 5, which contains the largest number of bonded pyridine rings. The EPR spectrum of sample 5 (Fig. 6) has absorp-

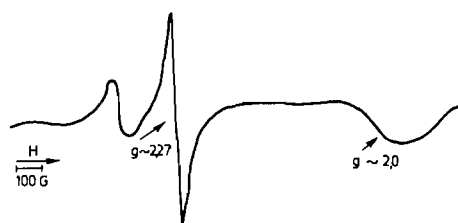
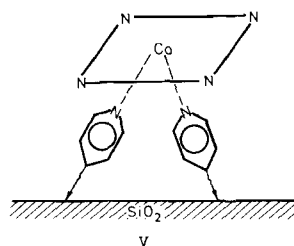


Fig. 6. EPR spectrum of Co(II)PhC/SiO<sub>2</sub> (air-dry sample 5).



tion bands at  $g_{\perp} \approx 2.27$  and  $g_{\parallel} \approx 2.00$ , which correspond to the EPR spectrum of Co(II)PhC in pyridine solution [13]. Evacuation decreases irreversibly the signal intensity, which is probably due to changes in the complex (Scheme V) structure – aggregation, distortion *etc.* Structure V is confirmed by the presence of absorption bands at 430 nm and a shoulder at 525 nm in the reflection spectrum of sample 5 (Fig. 5c), which is in agreement with data in [14].

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