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## LETTER

### ESR Study of the Interaction of Tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl)dodecachlorophthalocyaninatocobalt(II) with Dioxygen

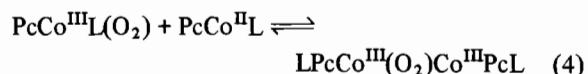
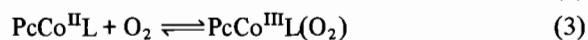
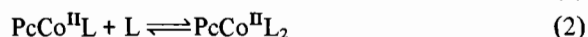
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The nature of the interaction between metallo-phthalocyanines (PcM) and dioxygen in solution is of considerable interest because of its relevance to dioxygen activation and homogeneous catalytic oxidation in biological systems [1].

In general, cobalt(II) phthalocyanines in non-coordinating solvents, e.g. in toluene, may participate in the following reactions in the presence of a ligand (L) and dioxygen [2]



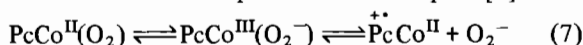
The five-coordinate complex (eqn. (1)) may fail to show an ESR signal due to dimerization [3, 4]. The product of reaction (4) is a binuclear O<sub>2</sub>-adduct of the μ-peroxo type, which is ESR silent [2, 5]. Moreover, if an excess of strong base is present, formation of six-coordinate complexes according to eqn. (2) is favoured [6]. These processes are typical for square-planar cobalt(II) complexes. However, in metallophthalocyanines, direct interaction with molecular oxygen may result in one-electron oxidation of the phthalocyanine ring [7]



For cobalt(III) phthalocyanines, the formation of cation-radicals was depicted as an intramolecular electron transfer between the ring and central cobalt atom [8]



By analogy, for cobalt(II) complexes this radical formation could involve an intramolecular electron transfer within the superoxocobalt complex [9]



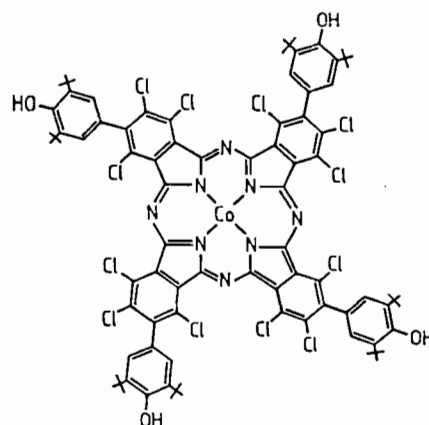
These relatively stable cation-radicals [10] usually show a narrow ESR signal at the *g*-value of the free electron (*g* = 2.003–2.004).

Recently, we have synthesized the highly soluble R<sub>4</sub>PcCo<sup>II</sup> complex containing sterically hindered phenol substituents on the periphery of the phthalocyanine ring [11, 12]. In this paper, we report on the behaviour of R<sub>4</sub>PcCo<sup>II</sup> under dioxygen, which was investigated by the ESR method in non-coordinating (toluene) and weakly coordinating (DMF) solvents.

### Experimental

Tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl)dodecachlorophthalocyaninatocobalt(II), R<sub>4</sub>PcCo<sup>II</sup>, was synthesized by standard procedures [1] from the corresponding 4-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)-3,5,6-trichlorophthalonitrile [11] and purified by TLC on silica gel with methanol/hexane (10:1), followed by Soxhlet extraction with acetonitrile.

ESR spectra were obtained on a JEOL JES-FE/3X instrument in the X-band with 500 kHz field modulation at room temperature and 77 K in quartz tubes.



R<sub>4</sub>PcCo<sup>II</sup>

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## Results and Discussion

The ESR spectrum observed by us for  $1 \times 10^{-2}$  M  $R_4PcCo^{II}$  in the presence of pyridine in air-saturated toluene glass at 77 K is the superposition of three signals (Fig. 1, Table 1). The first signal may be assigned to  $R_4PcCo^{II}py_2$  formed in excess pyridine. The parallel components show superhyperfine splittings due to coupling with two  $^{14}N$  nuclei of pyridine molecules coordinated to the cobalt(II) centre. The spectrum is typical for square-planar Co(II) complexes and shows eight hyperfine lines due to a single  $^{59}Co$  nucleus ( $I = 7/2$ ). The parameters are analogous to those of other cobalt phthalocyanine and porphyrin complexes containing two pyridine molecules in axial positions [13–15]. At a  $g$  value of 2.0031, there is a narrow singlet without hyperfine structure, assignable to a phthalocyanine cation-radical. Its position and bandwidth ( $c. 5$  G) are typical for  $PcCo$  [10]. The third signal, which shows anisotropy at 77 K, appears at a very low  $g$  value of  $c. 1.985$ . This signal, with a linewidth of  $c. 30$  G, resembles those observed for cobalt(II) porphyrins containing aromatic substituents on the ring, in the presence of pyridine and  $O_2$  [15]. Despite the general lack of superhyperfine splitting [16], it seems reasonable to assign this signal to a 1:1  $O_2$ -adduct of  $R_4PcCo^{II}$  (eqn. (3)). The relative intensity of this signal increases at the expense of the signal of

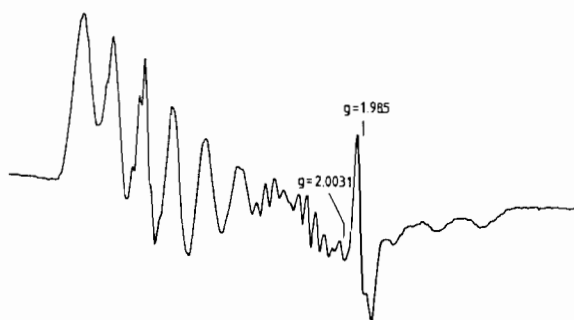


Fig. 1. ESR spectrum of  $R_4PcCo^{II}$  in toluene in the presence of pyridine and air;  $T = 77$  K;  $[R_4PcCo^{II}]_0 = 0.01$  M.

$R_4PcCo^{II}py_2$  when the solution is saturated with pure oxygen.

At room temperature, the signal corresponding to  $R_4PcCo^{II}py_2$  becomes poorly resolved and loses its intensity, whereas the two others (belonging to the cation radical and the  $O_2$ -adduct) remain unchanged. The difference in chemical behaviour of these species can be further explored by titrating the air-saturated solution of  $R_4PcCo^{II}$  with a strong acid. Cation-radicals of metallophthalocyanines, when formed in acids, are known [10] to be stabilized by the counterion and to show an ESR signal at the same  $g$  factor but with a bandwidth twice as large as that exhibited in non-acidic solutions. The increase in intensity and bandwidth ( $c. 10$  G) of the cation-radical signal can be actually observed when a solution of  $R_4PcCo^{II}$  is treated with different amounts of sulfuric acid. Under the same conditions, the superoxo adduct ( $R_4PcCoO_2$ ) undergoes irreversible oxidation to a Co(III) species, which leads to disappearance of the ESR signal of  $R_4PcCoL(O_2)$ . The ESR spectrum of  $R_4PcCo^{II}$  in DMF shows the same set of signals. Since in weakly coordinating solvents such as DMF, equilibria (1) and (2) are shifted toward the five-coordinate mixed complex ( $R_4PcCo^{II}DMF$ ) or its dimer [17], the relative amount of the superoxo complex must be higher than in the presence of pyridine. Indeed, the intensity of the signal assignable to the superoxocobalt species is about four times greater in DMF, compared with the signal observed in toluene/pyridine at the same initial concentration of  $R_4PcCo^{II}$ .

The nature of the axial ligand L (solvent) also influences the linewidth of the superoxo signal ( $c. 38$  G in DMF). The cation-radical signal in DMF appears at  $g = 2.0049$  in DMF.

When oxidizable compounds (such as 2-aminophenol or hydroquinone) are added to an air-saturated DMF solution of  $R_4PcCo^{II}$ , the relative intensity of the superoxo signal decreases, due to probable involvement of the superoxo species in catalytic substrate oxidation. In addition, 2-aminophenol can displace the DMF molecules in axial positions, yielding new mixed complexes (cf. Table 1).

TABLE 1. ESR parameters of various  $R_4PcCo$  complexes at 77 K ( $A$  values are in G; error  $\pm 0.0005$  G)

Compound	$g_{\perp}$	$g_{\parallel}$	$ A_{\perp} $	$ A_{\parallel} $	$a_{N_{\perp}}$	$a_{N_{\parallel}}$	Solvent
$R_4PcCo^{II}py_2$	2.182	2.016	59.7	73.6	11.1	16.2	toluene
$R_4PcCo^{II}(DMF)_2$	2.229	1.977	30.5	40.3			DMF
$R_4PcCo^{II}(AP)_2^a$	2.246	<sup>b</sup>	44.4	<sup>b</sup>			DMF
$R_4PcCo(py)(O_2)$	1.983	1.970					toluene
$R_4PcCo(DMF)(O_2)$	1.985	1.973					DMF
$R_4PcCo(AP)(O_2)$	1.985	1.972					DMF

<sup>a</sup>AP is 2-aminophenol.

<sup>b</sup>Not observed because of poor resolution.

The linewidth of the signal of the superoxo species containing 2-aminophenol in the axial position is c. 10 G smaller than that observed for the DMF complex.

Work is in progress on the catalytic oxidation of 2-aminophenol.

### Acknowledgement

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