

Cobalt tetraphenol-substituted phthalocyanine. A spectroscopic study of its redox properties in solution

Elena R. Milaeva* and Gábor Speier**

Department of Organic Chemistry, University of Veszprém, 8201 Veszprém (Hungary)

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Abstract

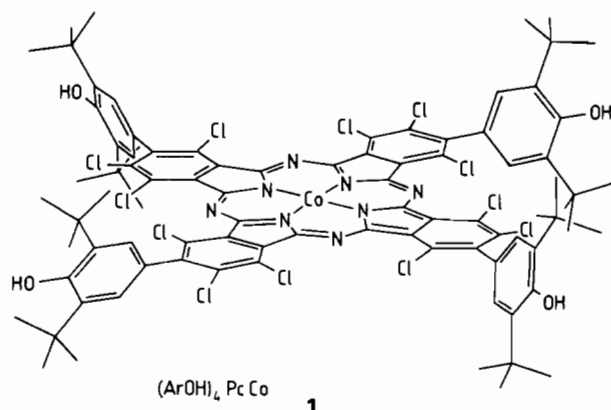
The redox properties of tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)dodecachlorophthalocyaninatocobalt(II), $(\text{ArOH})_4\text{PcCo}$ (**1**) have been studied in solution using electron spectroscopy and electron spin resonance. For **1** two reduced species, the yellow $(\text{ArOH})_4\text{PcCo}^{\cdot-}$ (**2**) and the pink $(\text{ArOH})_4\text{Pc}^{3-}\text{Co}^{\cdot}$ (**3**), and two oxidized species, the green $(\text{ArOH})_4\text{PcCo}^{\text{III}}$ (**4**) and the red-brown $(\text{ArOH})_4\text{Pc}^{\cdot+}\text{Co}^{\text{III}}$ (**5**), are observed representing the oxidation state changes of the cobalt and phthalocyanine ring. By using PbO_2 or $\text{K}_3\text{Fe}(\text{CN})_6$ the oxidation occurs at the peripherally substituted phenolic group and leads to the phenoxy radical $(\text{ArO}^{\cdot})(\text{ArOH})_3\text{PcCo}$ (**6**).

Introduction

In recent years there has been considerable interest in the redox chemistry of phthalocyanines. Redox species of metallophthalocyanines have been observed as intermediates in various processes, such as organic catalysis, electrocatalysis, photocatalysis, electrochromism, etc. [1–5].

Here we report a spectrochemical study on the cobalt derivative of tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)dodecachlorophthalocyanine $(\text{ArOH})_4\text{PcCo}$ (**1**)[†] in various redox processes. The presence of phenolic groups with bulky alkyl substituents makes the phthalocyanines described here highly soluble in organic solvents. This allowed us to study their properties in solution.

The redox processes of phthalocyanines bearing redox active transition metal atoms can occur either at the metal or at the phthalocyanine ligand [6]. Both cases occur with the cobalt phthalocyanine presented here. Moreover, the presence of redox-active substituents, such as hindered phenols, allows a third possible way in the redox reactions, namely, the phenolic fragment may also be oxidized and new types of phthalocyanine species can be formed. Our ultimate goal was to determine how the well-defined phenolic and phthalocyanine redox behaviour is manifested in this type of



system. In this paper we describe our spectroscopic investigation of the various redox reactions of **1** and present the features of its redox properties.

Experimental

The synthesis of tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)dodecachlorophthalocyaninatocobalt(II) (**1**) from the corresponding 4-(3',5'-di-tert-butyl-4'-hydroxyphenyl)-3,5,6-trichlorophthalonitrile [7] was described previously [8]. **1** was purified by TLC on silica gel with methanol–hexane (10:1) and Soxhlet extraction with acetonitrile. Solvents were dried by standard procedures and distilled before use. Anhydrous copper(II) chloride was made from $\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$ (Reanal) by heating at 180 °C in vacuum for 8 h. Tetrachloro-1,2-benzoquinone (Fluka AG), triphenylphosphine (Fluka

*On leave from the Department of Organic Chemistry, Moscow State University.

**Author to whom correspondence should be addressed.

[†]Pc = phthalocyanine dianion. Axial ligands and counter ions are omitted for clarity [6].

AG), triethylamine (Loba Chemie), KO_2 (Pierce Inorganic B.V.) and KOH (Reanal) were used as supplied. Iodosylbenzene was prepared according to the literature [9]. The solutions for spectroscopic measurements were prepared under argon and samples for ESR were prepared in vacuum. Electronic spectra were recorded with a Specord M-40 (Carl Zeiss, Jena) spectrophotometer. The ESR spectra were obtained with a Jeol JES-FE/3X and X band Varian E-12 spectrometer with 100 kHz field modulation at room temperature.

Results and discussion

$(\text{ArOH})_4\text{PcCo}$ (1)

The cobalt phthalocyanine complex **1** containing hindered phenolic fragments shows the typical electronic spectrum of phthalocyanines [1, 2]. The principal feature in the visible region is the Q band near 700 nm and the Soret band near 300 nm. The Q band indicates the transition from HOMO to LUMO orbitals, $1a_{1u}(\pi) \rightarrow 1e_g(\pi^*)$, and the Soret band the $1a_{2u}(\pi) \rightarrow 1e_g(\pi^*)$ transition [10]. There are also intense transitions in the UV region (e.g. N, L, C-bands of the phthalocyanine ring [11]), which are omitted here. The electronic absorption spectrum of **1** in DMF is shown in Fig. 1. The presence of phenolic groups with bulky alkyl substituents in the molecule makes this complex highly soluble in different organic solvents.

$(\text{ArOH})_4\text{PcCo}^I$ (2)

It is known that in phthalocyanines with transition metals reduction can occur either on the metal or at

the ligand [6]. By the conversion of PcCo to PcCo^I in DMF the first step of reduction with the additional electron in the d_{z^2} orbital of cobalt [12] is facile [13–16]. The appearance of a new absorption band in the region of 400–500 nm in all reduced species containing Co^I has been assigned to the metal to ligand charge transfer (MLCT) transition [12].

We have carried out the one-electron reduction of the phenol-containing cobalt(II) phthalocyanine (**1**) in DMF by KOH , Et_3N and O_2^- . In all cases the reduction results in a colour change from blue to yellow–green (Fig. 1). The spectrum observed by the reduction with KOH and Et_3N is typical for a PcCo^I species, characterized by the appearance of a new band at 492 nm assigned to MLCT, and a slight red shift and decrease in intensity of the Q band. These spectroscopic data are in agreement with those found in non-coordinating or weakly coordinating solvents (e.g. DMF) for other phthalocyanine cobalt(II) compounds [14–16].

$(\text{ArOH})_4\text{Pc}^{3-}\text{Co}^I$ (3)

The phthalocyanine compounds can be reduced in four stepwise additions of electrons to the low, unoccupied $1e_g$ molecular orbital of the ring. For cobalt phthalocyanines the first one-electron reduction occurs at the metal, the next reduction involves the ring orbitals of the ligand [6, 17].

The reduction of $(\text{ArOH})_4\text{PcCo}$ (**1**) by NaBH_4 in different solvents (DMF, THF, Et_2O , MeCN) leads to the formation of the dinegative ion $(\text{ArOH})_4\text{Pc}^{3-}\text{Co}^I$ (**3**) with a drastic change in the colour from blue to red, which is characteristic for this kind of species [17]. The electronic absorption spectrum of **3** consists of a

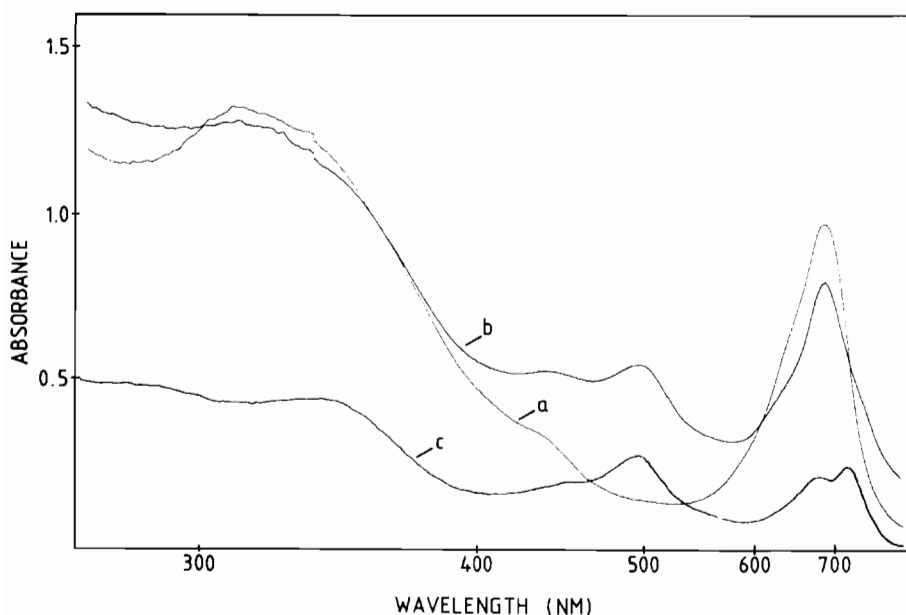


Fig. 1. The electronic spectra of (a) $(\text{ArOH})_4\text{PcCo}$ (**1**); (b) $(\text{ArOH})_4\text{PcCo}^I$ (**2**); (c) $(\text{ArOH})_4\text{Pc}^{3-}\text{Co}^I$ (**3**) in DMF.

very intense band at 490 nm, which can be assigned to MLCT. The absorption in the Q region is interpreted [6] in terms of the appearance of two new Q bands, which arise from the partially filled $1e_g$ molecular orbital: 671, 725 nm (DMF), 682, 748 nm (Et_2O), 650, 716 nm (THF), 678, 740 nm (MeCN). The electronic absorption spectrum of **3** in DMF is shown in Fig. 1. The ESR spectrum of **3** in THF shows a signal at $g=2.0038$ near the g value of the free electron, which is characteristic for an anion radical with the unpaired electron delocalized in the phthalocyanine ring.

The solution of **3** is stable under inert atmosphere for several days, but it can be easily oxidized to the starting complex $(\text{ArOH})_4\text{PcCo}$ by molecular oxygen.

$(\text{ArOH})_4\text{PcCo}^{\text{III}}$ (**4**)

The first step of chemical oxidation of cobalt(II) phthalocyanines in weakly coordinating solvents occurs at the central metal as has been shown previously [15, 16, 18]. We have found that $(\text{ArOH})_4\text{PcCo}$ (**1**) is converted quantitatively to $(\text{ArOH})_4\text{PcCo}^{\text{III}}$ (**4**) by various oxidants in coordinating as well as in non-coordinating solvents. This may be explained by the presence of the strongly electron-withdrawing chloro substituents on the macrocyclic ring. This facilitates the one-electron oxidation of Co^{II} . The spectral changes are in all cases identical if various oxidants e.g. bromine (in DMF, C_6H_6 , $\text{C}_6\text{H}_5\text{Br}$, CCl_4), tetrachloro-1,2-benzoquinone (in DMF, $\text{C}_6\text{H}_5\text{Br}$), iodosylbenzene (in DMF) or copper(II) chloride (in DMF, DMSO) are used. The development of the absorption spectra by the titration of **1** (at the concentration 1×10^{-4} M) with CuCl_2 in DMF is given in Fig. 2. The colour changes from blue to green. **4** is

stable in solution in air and can be easily reduced to **1** by adding triphenylphosphine. The absorption spectrum of the cobalt(III) complex is characterized by a red shift and an increase of intensity ($\epsilon=7.88 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and sharpening of the Q band compared with that of the starting Co^{II} compound ($\epsilon=3.69 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Similar features were observed for other cobalt(III) phthalocyanines [13].

$(\text{ArOH})_4\text{Pc}^{\cdot+}\text{Co}^{\text{III}}$ (**5**)

A further oxidation of $(\text{ArOH})_4\text{PcCo}^{\text{III}}$ (**4**) can be substantiated in non-coordinating solvents by the use of bromine as the oxidizing agent. In this process the molecule loses one electron from the phthalocyanine ligand producing a phthalocyanine cobalt(III) cation radical (**5**). For this kind of cation radical changes in the absorption spectrum will reflect the existence of a 'hole' in the $1a_{1u}$ orbital and therefore it will allow new, additional transitions to this level of higher energy [13]. Indeed, the quantitative oxidation of $(\text{ArOH})_4\text{PcCo}^{\text{III}}$ (**4**) by bromine in C_6H_6 or $\text{C}_6\text{H}_5\text{Br}$ gives rise to the appearance of two new additional bands. One is a broad band at c. 510 nm and the other is a sharp intense band at 775 nm. These are in good agreement with those observed for cation radical species of cobalt(III) phthalocyanines [6, 17, 18]. The changes in the Q band region of the absorption spectrum are given in Fig. 3, showing a decrease in intensity of the Q band and concomitant appearance of a new red-shifted band with an isobestic point at 735 nm. The identification of a radical cation is supported by ESR data. During the oxidation of **4** to **5** a signal at $g=2.0012$ could be detected. This low g value is very similar to

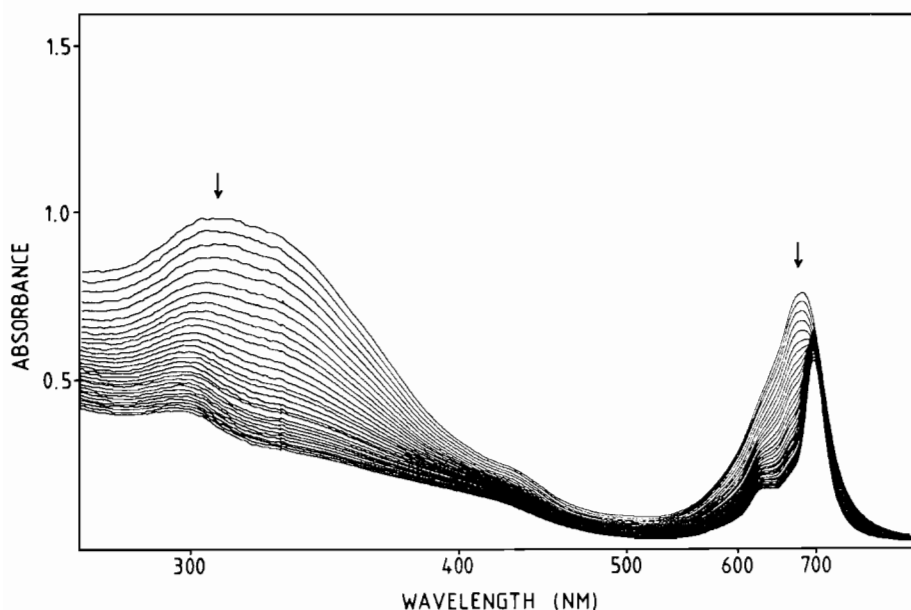


Fig. 2. The evolution of electronic spectra during the oxidation of $(\text{ArOH})_4\text{PcCo}$ (**1**) to $(\text{ArOH})_4\text{PcCo}^{\text{III}}$ (**4**) by CuCl_2 in DMF.

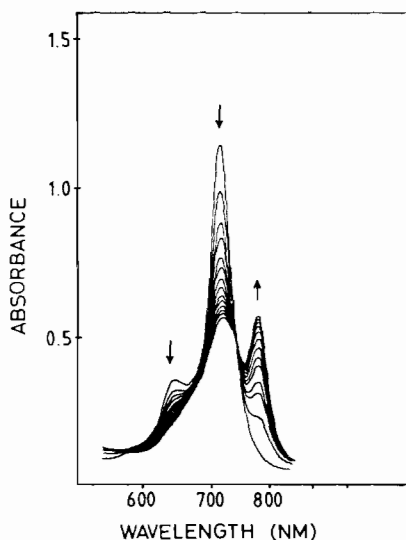


Fig. 3. The changes in the electronic spectra of $(\text{ArOH})_4\text{PcCo}^{\text{III}}$ by the titration with Br_2 in PhBr ; the formation of $(\text{ArOH})_4\text{Pc}^{\text{I}}-\text{Co}^{\text{III}}$ (5).

that found for the uncharged free radical phthalocyanine species of PcLi^\cdot ($g = 2.0015$) [19]. This anomalously low g value may be related to the high delocalization of the unpaired electron in the phthalocyanine ring [20].

Phenoxy-type free radical, $(\text{ArO}^\cdot)(\text{ArOH})_3\text{PcCo}$ (6)

The hindered 2,6-di-*tert*-butylphenol derivatives can be easily oxidized by various one-electron oxidizing agents (transition metal salts and oxides [21–25], quinones [26], potassium ferricyanide in the presence of potassium hydroxide [21, 27], etc.). The stability of the phenoxy radicals formed depends on the nature of substituents in the *para*-position of the phenoxy ring [28]. Recently we have discovered the increase of stability of phenoxy radicals by coordination to transition metals [29, 30]. As a result we have expected that the oxidation of metallophthalocyanines with hindered phenolic fragments should result in a reasonable stable phenoxy radical phthalocyanine species. The oxidation of **1** with reagents such as PbO_2 or $\text{K}_3\text{Fe}(\text{CN})_6/\text{KOH}$ in organic solvents at the concentration 1×10^{-8} M leads to a phenoxy-type phthalocyanine radical. By using metal salts (CuCl_2) or quinones (tetrachloro-1,2-benzoquinone) the oxidation occurs at the cobalt (see above) but the involvement of phenoxy radical species as intermediates cannot be excluded. Figure 4 shows the ESR spectrum of $(\text{ArO}^\cdot)(\text{ArOH})_3\text{PcCo}$ (**6**), a triplet centered at $g = 2.0045$ with hyperfine coupling constant of $a_{2\text{H}} = 1.8$ G due to the two *meta*-protons in the phenoxyl ring. There is now evidence for the interaction of the unpaired electron spin density with the other nuclei (nitrogen, cobalt). On the other hand these data differ from those obtained by oxidizing of the starting phthalonitrile ($a_{2\text{H}} = 2.2$ G) [7]. This seems to support

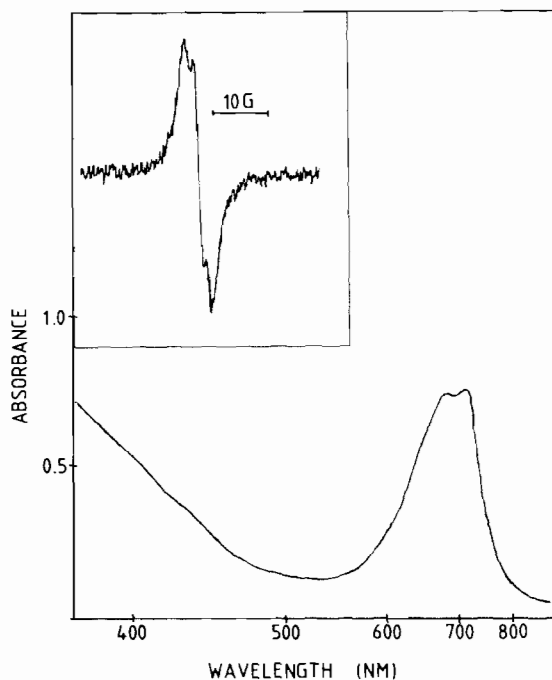


Fig. 4. The ESR and electronic spectra of $(\text{ArO}^\cdot)(\text{ArOH})_3\text{PcCo}$ (**6**) in DMF.

the assumption that the unpaired electron is slightly delocalized at least within the corresponding benzene ring of the phthalocyanine unit [31]. It is of interest to note that by adding more oxidants or by lowering the temperature no change in the ESR signal can be seen. From that the conclusion may be drawn that the oxidation leads to the monoradical species, which is reasonably stable in solution.

The spectroscopic investigation of the oxidation process of **1** (at the concentration 1.2×10^{-4} M) under identical conditions shows differences in the spectral data (Fig. 4). The spectrum of **6** with the additional new band blue-shifted by *c.* 20 nm of the Q band is similar to that observed for binuclear cobalt phthalocyanines [18] or phthalocyanine dimers [32]. Aggregation is a well-known phenomenon in the chemistry of metallophthalocyanines [1].

We believe that the tendency to the aggregation of the cobalt phthalocyanine radical **6** might be the explanation of the observed spectral data. The change in the Soret band region is insignificant. The Soret band is slightly blue-shifted. There are, however, two weak, broad bands at *c.* 403 and 430 nm, which can be assigned to new $\pi-\pi$ transitions in the radical species [13].

Conclusions

The cobalt(II) phthalocyanine with hindered phenolic fragments described here gives rise to various redox

TABLE 1. Spectral data for 1-6^a

Compound	λ_{\max} (nm), DMF ($\epsilon 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)			Colour
	Soret band	CT bands	Q bands	
(ArOH) ₄ PcCo ^{II} (1)	312(4.80)		625(sh); 680(3.69)	blue
(ArOH) ₄ PcCo ^I (2)	318(4.78)	492(2.08)	620(sh); 682(3.03)	yellow-green
(ArOH) ₄ Pc ³⁻ Co ^I (3)	334(1.80)	490(1.09)	671(0.85); 725(0.98)	red
(ArOH) ₄ PcCo ^{III} (4)	303(5.17)		625(sh); 695(7.88)	green
(ArOH) ₄ Pc ¹⁻ Co ^{III} (5) ^b	289(4.80)		510(6.50); 775(6.70) ^c	brown
(ArO)(ArOH) ₃ PcCo ^{II} (6)	308(4.60)	403(2.10); 430(1.50)	678(3.03); 698(3.07)	green-blue

^aIn DMF. ^bIn C₆H₅Br. ^c π - π transition [7].

species by its oxidation or reduction as evidenced by spectroscopic methods. Almost all of them are fairly stable in solution in air. The presence of sterically hindered phenolic groups in the periphery of the phthalocyanine ligand makes novel electron transfer reactions possible.

Experimental data were obtained for the direct observation of different redox species in the following redox processes: (i) oxidation or reduction of the central metal atom, (ii) oxidation or reduction of the phthalocyanine ring, (iii) oxidation of the peripherically substituted redox-active (phenolic) groups (Table 1).

Further studies on the redox behavior of other metallophthalocyanines with hindered phenols are in progress and will be published in due course.

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