Alkylation of cobalt and lutetium tetra(3,5-di-*tert*-butyl-4-hydroxyphenyl)dodecachlorophthalocyanine complexes initiated with current

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Electrochemical properties of tetra(3,5-di-*tert*-butyl-4-hydroxyphenyl)dodecachlorophthalocyanine complexes of cobalt(II) and lutetium(III) in DMF solutions have been studied. It was suggested that in the presence of *n*-butyl bromide, the electrochemically generated monoanionic complexes undergo alkylation at the metal atom. The geometries of the neutral and anionic complexes were calculated by the ZINDO/1 semiempirical method.

Key words: cobalt, lutetium, tetra(3,5-di-*tert*-butyl-4-hydroxyphenyl)dodecachlorophthalocyanines, calculation of molecular structures; electrochemical reduction; alkylation of reduced forms.

Previously,[1] it has been demonstrated that when the direction of electrode polarization was changed from cathodic to anodic, the reaction of mercury metal with *n*-butyl bromide in the presence of a catalyst (a monoanionic Co^I dimethylglyoximate complex, which was formed from the corresponding neutral Co^{II} complex upon cathodic polarization of the electrode) afforded salts of butylmercury. It is known that the first stage of this process (cathodic alkylation of a catalyst) is typical of various chelate complexes of transition metals (for example, cobalamin, phthalocyanine, salene, and dithiocarbamate complexes of Co, Fe, Ru, Rh, Ni, and Cr), which form rather stable compounds containing the alkyl—metal σ-bond.[2] These compounds contain a metal atom, which can occur in three successive oxidation states (for example, +3, +2, and +1 for Co), and have an external π-system of the ligand, which favors stabilization of the anionic complex. However, the ability of the metal atom to occur in three oxidation states, $(n + 1)$, n, and $(n - 1)$, and the presence of the chelating ligand are not necessarily sufficient conditions for alkylation of metallocomplex anions. For example, the dimethylglyoximate complex of Ir, unlike the analogous complexes of Co and Rh, does not undergo chemical or electrochemical alkylation.[3]

The potential of formation of the nucleophilic anion, which reacts with alkyl halides, is an important factor of this process. If this potential is more negative than the potential of reduction of the alkylation product, the latter compound is not formed because it undergoes irreversible reduction with cleavage of the metal—alkyl bond. The potential of formation of the metal complex anion and the potential of reduction of the alkylation product depend on the nature of the metal atom, chelating ligand, solvent, and the σ-bonded organic group.[4] For example, it is known that most of the processes of reduction of metalloporphyrins, which contain an organic group linked to the metal atom through the σ-bond, occur at more negative potentials than reduction of metalloporphyrins, which contain coordinated ligands. However, some Fe porphyrins, which contain the Fe—Alk bond, are reduced more readily than the corresponding complexes, which contain ionic ligands.[5]

In this work, we studied alkylation of the electrochemically generated anionic tetra(3,5-di-*tert*-butyl-4-hydroxyphenyl)dodecachlorophthalocyanine complexes of Co^{II} (**1**) and Lu^{III} (**2**) whose reduction potentials on a cathode are substantially different. *n*-Butyl bromide was used as an alkylating agent.

Experimental

Complexes **1** and **2** were synthesized according to a known procedure.[6] Electrochemical studies were carried out in DMF in the presence of a 0.05 *M* Bu_4NBF_4 solution on a mercury-film electrode. The potentials were measured relative to a silver-chloride electrode. Cyclic voltammetry and the rotating disk electrode method were used.

DMF was purified by successive boiling and distillation *in vacuo* over anhydrous $CuSO_4$ and P_2O_5. The mercury-film electrode was prepared by electrolysis of a 0.05 *M* $Hg(OCOMe)_2$ solution in aqueous acetonitrile on a platinum cathode at −0.7 V during 10 min.

Electrochemical studies were performed using a PI-50-1.1 potentiostat. All measurements were carried out under an atmosphere of argon.

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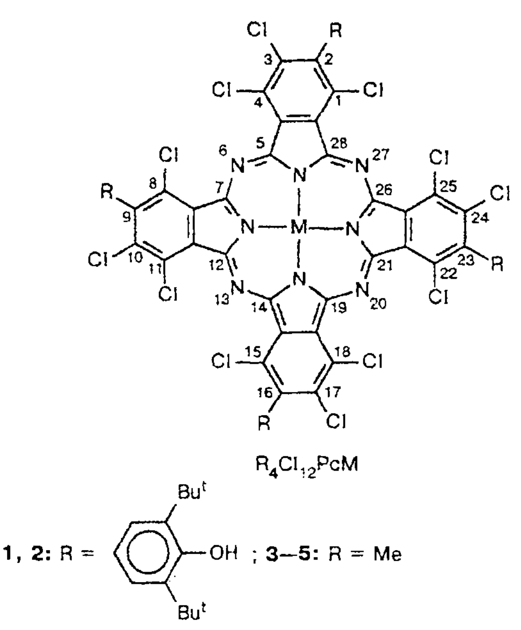
Results and Discussion

The choice of complexes was determined by the possibility of their use in anodic redox catalysis. It can be suggested that the condensed benzene rings of the phthalocyanine ligand in complexes **1** and **2** are not in a single plane due to repulsion between the electron shells of the Cl atoms at positions 4/8, 11/15, 18/22, and 1/25.

X-ray structural data on these complexes are unavailable. Therefore, to gain an idea of their structures, we calculated the geometries of model compounds **3**, **4**, and **5**, which differ from complexes **1** and **2** in that all 4-hydroxy-3,5-di-*tert*-butylphenyl groups are replaced by methyl groups. Compound **3** is used as a model of complex **1**. Compounds **4** and **5** in which M = Y are used as models of complex **2** because the Y atom is similar in properties to the Lu atom.[7]

Calculations were carried out by the ZINDO/1 semiempirical method,[8] which has been specially developed to calculate complexes of transition metals. To estimate the validity of the prediction of the structure by the ZINDO method, we calculated also the geometry of the cobalt complex of unsubstituted phthalocyanine PcCo whose structure has been studied by X-ray structural analysis at 115 K[9] and 295 K[10] and by diffraction of polarized neutrons at 4.3 K.[11] Selected results of our calculations are given in Table 1.



$R_4Cl_{12}PcM$

1, **2**: R = [4-hydroxy-3,5-di-Bu^t-phenyl]—OH ; **3**—**5**: R = Me

M = Co^{II} (**1**, **3**), Lu^{III}OAc (**2**), Y^{II} (**4**), Y^{III}OAc (**5**)

A comparison of the calculated and experimental values of the bond lengths and bond angles in PcCo demonstrated that, on the whole, the ZINDO/1 method adequately describes the geometry of the molecule, which is planar in the region of the coordination Co unit with the pyrrole N atoms as well as in the region of the benzene rings. However, the calculated $M-N_a$ bond length is 0.06 Å larger than the corresponding experimental value. The elongation of the Co—N bond causes an increase in the bond lengths between the azomethine N atom and the C atoms of the pyrrole rings (N_b-C_a) by 0.03 Å and an increase in the C—C bond lengths in the pyrrole rings (C_b-C_b) by 0.02 Å.

As expected, the complexes that contain the dodecachloro-substituted phthalocyanine ligand are nonplanar due to the steric repulsion between the Cl atoms at positions 4/8, 11/15, 18/22, and 1/25. Cobalt complex **3** adopts a saddle-like conformation in which the coordination unit retains a planar-square configuration but the

Table 1. Experimental and calculated (ZINDO/1 method) average bond lengths (*d*) and bond angles (ω) in PcCo and complexes **3**—**5**

Compound, anion	Bond lenght, *d*/Å					Bond angle, ω/deg				
	$M-N_a$[a]	N_a-C_a[b]	N_b-C_a[c]	C_a-C_b[d]	C_b-C_b	N_a-M-N_a	$M-N_a-C_a$	$C_a-N_b-C_a$	$C_a-N_a-C_a$	$N_b-C_a-N_a$
					Experiment[e]					
PcCo	1.919	1.380	1.325	1.457	1.398	90	126.5	121.1	107	127.9
	1.912	1.380	1.319	1.449	1.397	90	126.6	121.2	106.9	127.8
	1.907	1.375	1.317	1.450	1.384	90	126.6	121.5	106.7	127.6
					Calculations for neutral molecules					
PcCo	1.974	1.383	1.347	1.452	1.423	90	126.7	125.0	106.7	125.9
3	1.949	1.383	1.345	1.451	1.423	90	126.8	123.6	106.3	126.2
4	2.430	1.384	1.351	1.453	1.427	74.6	124.4	127.9	109.2	126.6
5	2.445	1.383	1.349	1.452	1.428	74.0	124.0	128.5	109.2	126.3
					Calculations for anions					
$PcCo^-$	1.965	1.377	1.348	1.455	1.424	90	126.7	124.0	106.7	126.3
3^-	1.965	1.376	1.347	1.454	1.425	90	126.4	123.5	107.1	126.6
4^-	2.484	1.378	1.349	1.455	1.427	72.2	123.8	126.7	109.1	127.2

[a] M is the central metal atom (Co or Lu); N_a is the atom of the pyrrole ring. [b] C_a is the atom at the α position of the pyrrole ring. [c] N_b is the azomethine atom. [d] C_b is the atom, which is shared by the pyrrole and benzene rings. [e] The structure was determined by X-ray diffraction study at 115 K[9] and 295 K[10] and by diffraction of polarized neutrons at 4.3 K.[11]

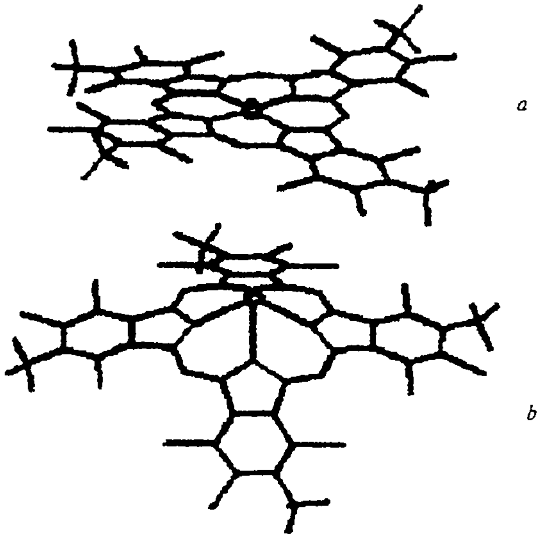


Fig. 1. Structures of molecules **3** (*a*) and **4** (*b*) calculated by the ZINDO/1 method.

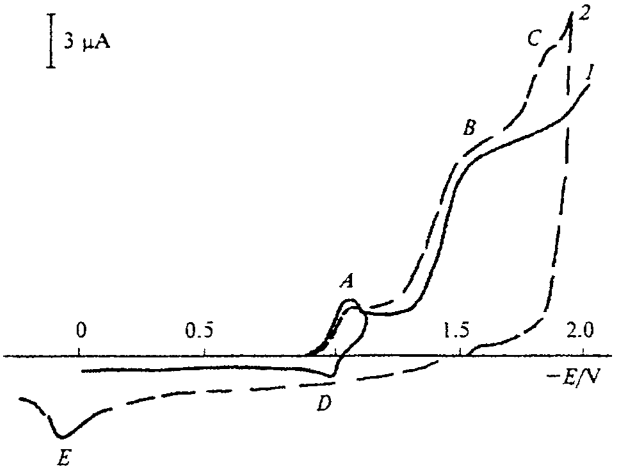


Fig. 2. Cyclic voltammograms of reduction of complex **1** in DMF (0.05 *M* Bu_4NBF_4, Ag/AgCl/KCl (saturated), mercury-film electrode, 20 °C): *1*, 10^{-3} *M* **1**; *2*, 10^{-3} *M* **1** and $5 \cdot 10^{-3}$ *M* Bu^nBr.

isoindole fragments of the phthalocyanine ligand deviate from the plane of the chelate unit by ~10°. In this case, one pair of isoindole fragments is bent upward, and the opposite pair is bent downward (Fig. 1 *a*).

According to calculations, in yttrium complexes **4** and **5**, the ligand is also nonplanar. However, in these complexes, unlike the cobalt complex, the ligand adopts a tent-like conformation with four isoindole fragments bent downward. The coordination unit is nonplanar. According to the results of calculations, the deviation of the Y atom from the plane of the pyrrole N atoms is 1.2 Å (see Fig. 1 *b*). Apparently, this is due to the fact that the orbital radius of the Y atom is larger than that of the Co atom (1.693 and 1.181 Å, respectively). In complex **5**, the axial acetate ligand is oriented so that the distances between the Y atom and the O atoms are equal (2.687 Å), *i.e.*, the Y—O bonds are ionic (according to our calculations, the Y—O distance in $Y(OH)_3$ is 2.30 Å). Apparently, complex **2** has an analogous structure.

We calculated the molecular orbitals of complex **3** by the ZINDO/1 method. The results of calculations demonstrated that in the $(R_4Cl_{12}PcCo)^-$ anion, the highest occupied molecular orbital (HOMO, $\varepsilon = -0.02$ eV) is localized on the Co atom and on the ligand. The next lower lying MO (HOMO-1; $\varepsilon = -1.46$ eV) is essentially the d_{z^2}-AO of the cobalt atom. The geometries of the $(R_4Cl_{12}PcCo)^-$ anion and the neutral molecule are very similar. The main difference is that the Co—N_a bonds are 0.01 Å shorter (see Table 1).

The HOMO of the monoanion of yttrium complex **4** ($\varepsilon = -0.96$ eV) is the hybridized orbital located on the metal atom. The total negative charge in this anion is to a large extent also localized on the Y atom. According to our calculations, $q(Y) = -0.68$, whereas in the anion of complex **3**, $q(Co) = -0.37$. Therefore, in the case of charge control, the anion of the yttrium complex should be a stronger nucleophile and, therefore, should undergo alkylation more readily. On the other hand, in the anion of complex **3**, the HOMO energy is by 0.94 eV higher than that in the anion of complex **4**. Therefore, in the case of the orbital control, the Co atom should undergo alkylation more readily. If it is assumed that compound **3** is an adequate model of complex **1**, and complex **4** is an adequate model of the reduced form of complex **2** (with elimination of the acetate group), the above-mentioned concepts can be extended to structures **1** and **2**, which we have studied experimentally.

Two reduction peaks are observed on the cathodic branch of the polarization curve of complex **1** (Fig. 2). The first peak (*A*) with $E_p^{Red} = -1.04$ V corresponds to the reversible process (the potential of the reverse anodic peak is −0.96 V, the ratio of the heights of the anodic peak I^a/I^c is equal to 1 at the rate of the potential scan of 0.2 V s^{-1}). This peak belongs to the well-known transition:[12]

$$R_4Cl_{12}PcM^{II} \overset{\bar{e}}{\rightleftharpoons} (R_4Cl_{12}PcM)^-.$$

The second peak at −1.54 V is 3.6 times higher than the first peak (*B*, see Fig. 2) and corresponds to the irreversible process. Usually, the second peak on the polarization curves of reduction of phthalocyanine complexes of transition metals is reversible and is caused by the transfer of one electron[12] to form a dianion:

$$(PcM)^- \overset{\bar{e}}{\rightleftharpoons} (PcM)^{2-}.$$

It can be suggested that in our case, the transfer of one electron to the macrocyclic ligand also occurs at the potential of the second peak. However, it should be taken into account that Cl^- anions can then be eliminated, and additional electrons can be transferred to the dechlorinated metal complex of phthalocyanine that formed (the eceheceh ... process) (Scheme 1):

Scheme 1

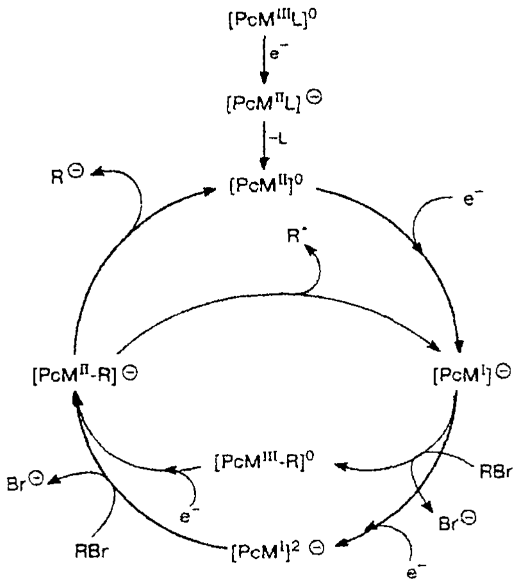
$$
\begin{aligned}
&[R_4Cl_{12}PcCo]^- \xrightleftharpoons{+e} [R_4Cl_{12}PcCo]^{2-} \xrightarrow[-Cl^-]{} \\
&\longrightarrow [R_4Cl_{11}PcCo]^- \xrightleftharpoons{+e} [R_4Cl_{11}PcCo]^{2-} \xrightarrow{+H^+} \\
&\longrightarrow [R_4Cl_{11}HPcCo]^- \xrightleftharpoons{+e} [R_4Cl_{11}HPcCo]^{2-} \xrightarrow{-Cl^-} \\
&\longrightarrow [R_4Cl_{10}HPcCo]^- \xrightleftharpoons[+e]{} [R_4Cl_{10}HPcCo]^{2-} \xrightarrow{+H^+} \\
&\longrightarrow [R_4Cl_{10}H_2PcCo]^- \longrightarrow \textit{etc.}
\end{aligned}
$$

The presence of the peak of oxidation of the chloride anion on the anodic scan of the cyclic voltammogram ($E_p \sim +0.1$ V on a mercury-film electrode; peak *E* in Fig. 2) as well as the presence of the irreversible multiple-electron peak of the free phthalocyanine ligand (M = H, H in **1** or **2**) at −1.52 V on the cathodic branch of the voltammogram support this mechanism.

When *n*-butyl bromide was added to a solution of complex **1** in DMF, a new cathodic peak appeared in the cyclic voltammogram (peak *C*, Fig. 2), and the height of anodic peak *D*, which corresponds to transformation of neutral form **1** to the monoanion, decreased. Apparently, cathodic peak *C* corresponds to formation of the complex that contains the Co—Alk σ-bond. This complex may be of composition $Cl_{12}PcCo^{III}$-Bu [if after the transfer of the first electron to $Cl_{12}PcCo^{II}$ (see Fig. 2, peak *A*), alkylation occurs rather rapidly] or $Cl_{12-n}H_nPcCo^{III}$-Bu (if alkylation occurs after reductive dechlorination).

Reduction of the phthalocyanine complex of *n*-butylcobalt occurs at −1.88 V. If electrolysis was carried out at a higher cathodic potential (for example, at −2.0 V), the current increased so that the experimental number of transferred electrons changed from 1 to 10. This effect was observed previously for the porphyrin and dimethylglyoximate complexes of Co and was called "chemical catalysis of electrochemical reduction of alkyl halides."[13] This process can be described by the catalytic cycle shown in Scheme 2.

Scheme 2



This scheme is common to many chelate compounds of transition metals and rare-earth elements, including complexes of Co^{II}. It is evident that electrolysis at a cathodic potential higher than the potential of reduction of the Co—Alk bond resulted in regeneration of the reactive $[PcCo]^-$ anion. The latter readily undergoes alkylation with Bu^nBr, which is present in a solution, and then is reduced due to which the chain of conversions is resumed. If after electrolysis at −2.0 V the electrode was polarized in the anodic region, the height of the peak of oxidation of this anion in the cyclic voltammogram increased.

For complex **2**, a more complex pattern was observed. In the absence of Bu^nBr, the cathodic branch of the cyclic voltammogram at potentials from −1.3 to −2.0 V is divided into a series of poorly pronounced steps (Fig. 3). We believe that the transfer of the first

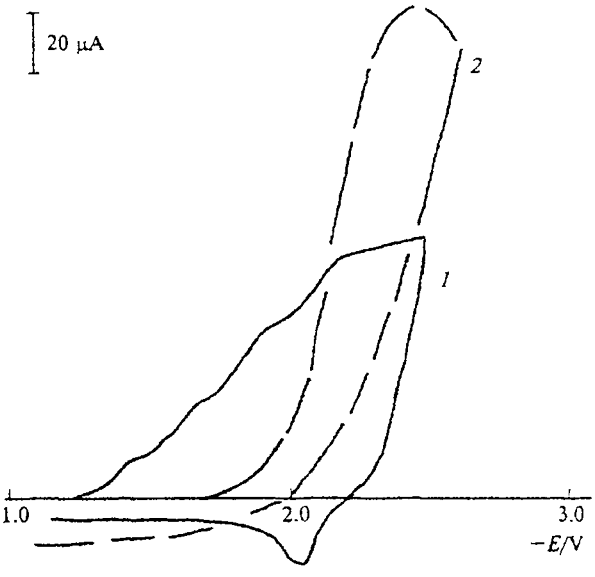


Fig. 3. Cyclic voltammograms of reduction of complex **2** in DMF (0.05 *M* Bu_4NBF_4, Ag/AgCl/KCl (saturated), mercury-film electrode, 20 °C). *1*, 10^{-3} *M* **2**; *2*, 10^{-3} *M* **2** and 5×10^{-3} *M* Bu^nBr, within 2 min after the beginning of electrolysis.

electron to molecule **2** occurs at negative potentials so high that reductive dechlorination of the phthalocyanine ligand can occur. Most probably, the anodic peak at -2.02 V on the reverse slope corresponds to oxidation of one of the products of reductive dechlorination to form a stable complex $(R_4Cl_{12-x}H_xPcLu)^-$ anion. Apparently, this anion can undergo alkylation with Bu^{n}Br because electrolysis ($E = -2.2$ V) in its presence is accompanied by an effect similar to that observed previously in the case of complex **1** (within 10 min after the beginning of electrolysis, the peak height at -2.2 V increased tenfold). It can be suggested that we failed to observe an individual peak of reduction of the $R_4Cl_{12-x}H_xPcLu^{III}$—Bu complex because the anion of complex **2**, unlike the anion of complex **1**, was formed at substantially higher cathodic potentials. This is indirect evidence in favor of the alkylation of the electrochemically generated anion of complex **2**.

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