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Unsymmetrical Sandwich Diphthalocyanine and Similar Complexes

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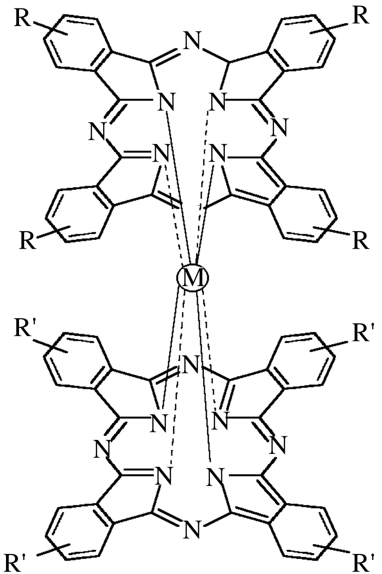
Abstract—Data on the synthesis and spectral and physicochemical properties of unsymmetrical sandwich diphathalocyanine and similar complexes are presented.

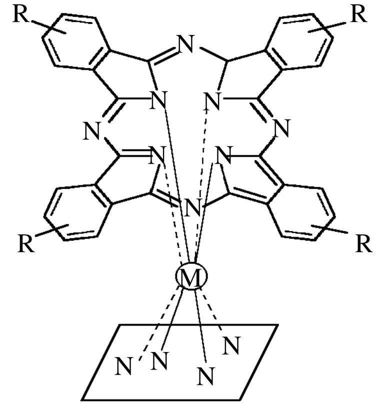
Among a plethora of metal complexes of phthalocyanine and porphyrins, particular researcher's attention from mid-1960s has been given to to sandwich complexes in which the metal atom is bound with two phthalocyanine ligands. Peculiar molecular and electronic structures of such complexes provide their unique physicochemical properties which, in combination with high chemical and thermal stability, as well as relative facility of synthesis, stimulate active investigations on these compounds [1–3]. Thus, owing to pronounced electrochromic properties, sandwich metal complexes hold promise for electrochromic display applications [4, 5]. The utility of metal diphthalocyanines as thin-film chemical sensors for ecologically harmful gases [6–8] and materials for ionizing radiation sensors [9]. Water-soluble sulfo- and crown-substituted metal diphthalocyanines can be selectively accumulated in living cells and have been studied as photosensitizers for photochemical cancer diagnostics and therapy [10, 11].

In recent years there have been developed a new direction in the chemistry of sandwich complexes, associated with the synthesis and properties of unsymmetrical compounds containing at one metal atom of two phthalocyanine ligands with various peripheral substituents ($R_4PcMPcR'_4$) or a phthalocyanine in combination with a porphyrin, tetraazaporphyrin, or another tetrapyrrole ligand (R_4PcML).

Here we present our data on the synthesis and some properties of diphthalocyanine and similar sandwich complexes of unsymmetrical structure.



$R_4PcMPcR'_4$



R_4PcML

R ≠ R'; M = Zr, Hf, rare-earth metals.

SYNTHESIS

Unsymmetrical sandwich complexes are basically prepared either by template synthesis of various substituted phthalonitriles [12, 13] or by substitution of hydrogen atoms in metal-free compounds [14] or alkali metal atoms in appropriate labile complexes on a rare-earth or another metal capable of coordinating two tetrapyrrole ligands [15–20].

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Thus, the mixed-ligand zirconium complex (OER)Zr(OETAR) was synthesized by the reaction of dichlorozirconium octaethylporphyrin (Cl_2ZrOER) with dilithium octaethyltetraazaporphyrin (Li_2OETAR) in boiling toluene [15]. The X-ray diffraction analysis of this complex showed that the zirconium ion resides between the porphyrin and tetraazaporphyrin planes and is bound with eight endocyclic nitrogen atoms.

A lot of unsymmetrical sandwich complexes were prepared by reactions of two different metal-free tetrapyrrole ligands or their dilithium complexes with metal salts [16–20].

Unsymmetrical sandwich complexes with 1 : 2 [(TRhP)Se(Pc)] and 2 : 3 [(TPhP)Se(Pc)Se(TPhP)] metal : ligand ratios were prepared by boiling cerium acetylacetonate $Ce(acac) \cdot 2H_2O$ and *meso*-tetraphenylporphyrin (H_2TPhP) in 1,2,4-trichlorobenzene under nitrogen, followed by treatment of the reaction mixture by dilithium phthalocyanine (Li_2Pc) and further boiling [16]. Complexes with octamethoxyphthalocyanine and octaethylporphyrin ligands were synthesized in a similar way.

The reaction of lutecium acetate with unsubstituted and substituted dilithium phthalocyanines at a 1 : 1 : 1 reagent ratio in boiling α-chloronaphthalene gave corresponding sandwich complexes.

$$Li_2Pc + Li_2PcR_n \xrightarrow{Lu(OAc)_3} (Pc)Lu(PcR_n),$$

$$n = 8,\ R = CH_3,\ OCH_3;\ n = 4,\ R = C(CH_3)_3.$$

A necessary condition of successful result in this synthesis is using dry solvents and inert gas.

Condensation of $Lu(OAc)_3$ with Li_2Pc and dilithium naphthalocyanine (Li_2NPc) gave the unsymmetrical complex NPcLuPc which was characterized by electronic, ^1H NMR, and IR spectroscopy [18]. This complex was shown to be a sandwich compound and has an unpaired electron localized between two macrorings.

So-called triple-decker complexes (Pc)M(L)M(Pc) were obtained by the reactions of neodymium, europium, and gadolinium acetylacetonates $M(acac)_3$ with *meso*-tetrakis(4-methoxyphenyl)porphyrin (H_2L) and H_2Pc in boiling 1,2,4-trichlorobenzene in inert atmosphere [19]. The X-ray diffraction analysis of the neodymium complex provide evidence for the proposed structure with two neodymium atoms in one molecule, each coordinated with eight nitrogen atoms of the two ligands between which it is located. The inner ligand (L) is almost planar, and all the three ligands are tuned relative to each other.

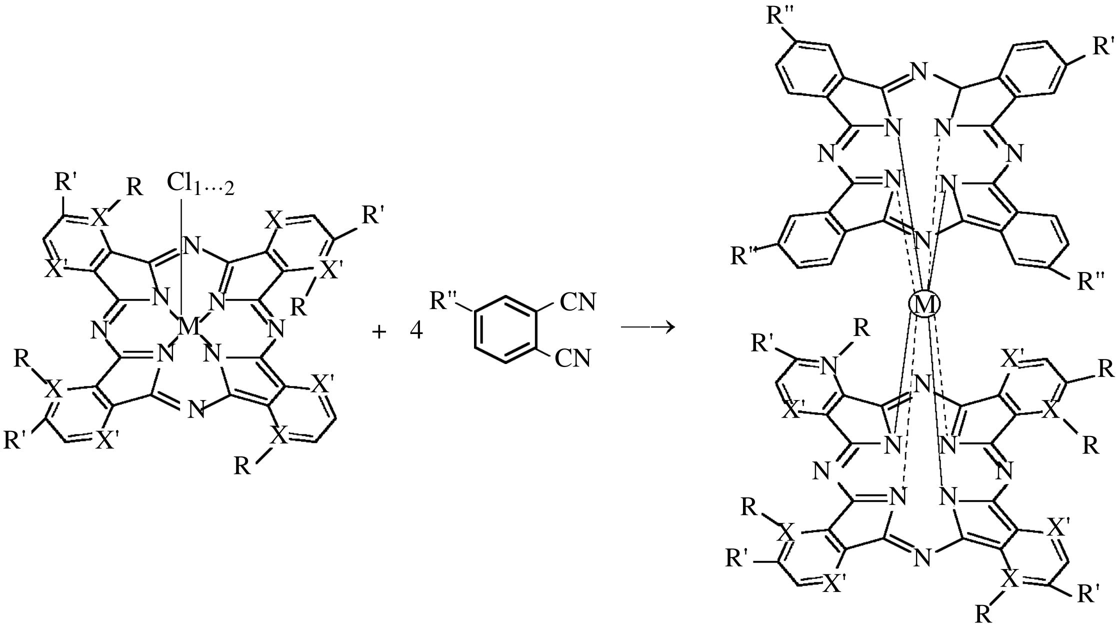
Analysis of the above-mentioned syntheses of unsymmetrical sandwich complexes reveals their major drawback, consisting in that along with target complexes the reaction mixtures always contain hardly separable admixtures. Thus, in the synthesis from various dinitriles, symmetrical monometal phthalocyanines and metal diphthalocyanines are formed as by-products. In the synthesis of labile dilithium complexes, the latter may undergo demetalation to give metal-free ligands as by-products.

The most efficient synthetic route to unsymmetrical sandwich metal complexes, developed by us [21–31], as well as other authors [32,33], involves reaction of monometal phthalocyanines or their structural analogs with *o*-phthalonitriles [21–31].

Unsymmmetrical sandwich complexes of zirconium and hafnium, containing two different tetrapyrrole ligands at one metal atom, were synthesized by reactions of dichlorometal tetrapyridine- or dichlorometal tetrapyridazine-porphyrazines ($Cl_2MTRyPa$ and $Cl_2MTRzPa$; M = Zr, Hf) with *o*-phthalonitrile [21]. Further on, by varying tetrapyrrole ligands in the monometal complex, as well as substituents in *o*-phthalonitrile, we could prepare unsymmetrical sandwich complexes of rare-earth metals, combining an unsubstituted phthalocyanine ligand with chloro- and nitro-substituted (M = Nd, Sm, Ho, Lu) [22, 28], as well as a *tert*-butyl-substituted phthalocyanine ligand with chloro-, bromo-, and nitro-substituted phthalocyanines (M = Lu, Ho, Y, Er) [23, 24, 31]. The syntheses were performed by the following general scheme (for X, X', R, R', and R", see Table 1).

Table 1. Synthesized sandwich complexes

X	X'	R	R'	R"	M	Abbreviated formula
C	CH	H	NO_2, Cl, Br, I, *t*-Bu	H	Zr, Hf, Nd, Sm, Ho, Lu	$PcMPc(4R')_4$
C	CH	NO_2, Cl, Br, I	H	H	Zr, Hf, Nd, Sm, Ho, Lu	$PcMPc(3R')_4$
C	CH	H	Cl, Br, NO_2	*t*-Bu	Lu, Ho, Y, Er	$(4R')_4PcMPc(4R'')_4$
C	N	H	H	H	Zr, Hf	PcMTPyPa
N	N	H	H	H	Zr, Hf	PcMTPzPa



Therewith, a peculiar molecular geometry of the starting complexes was taken into account, specifically, deviation of the metal atom from the tetrapyrrole ligand plane [34] and location of the chlorine atoms on one side of the molecular plane.

A mixture of a starting complex and a ~20-fold molar excess of *o*-phthalonitrile was heated at 305–310°C for some hours. The large excess of *o*-phthalonitrile is required since this compound serves simultaneously as a reagent and a reaction medium. Control experiments showed that with a smaller excess of *o*-phthalonitrile the yield of the target product is lower, whereas a larger excess has no yield effect but complicates product purification.

In the same way, starting from chlorolutecium octaphenyltetraazaporphyrin (ClLuOPhTAP), we prepared a sandwich complex with an octaphenyltetraazaporphine and a phthalocyanine ligands at the lutecium atom (OPhTAPLuHPc) [25]. Complexes comprising a phthalocyanine and a tetrabenzoporphyrin ligands (TBPMHPc, M = Lu, Gd) were synthesized by reactions of lutecium or gadolinium tetrabenzoporphyrins with excess phthalonitrile [27].

Analysis of experimental data on the synthesis of unsymmetrical sandwich metal complexes by the above procedure highlights a number of pecularities. Successful synthesis of zirconium and hafnium complexes is possible if the starting monometal complex contains chlorine extra ligands. Attempted conversion of dichlorometal complexes into dihydroxy derivatives to use the latter as starting materials was unsuccessful, i.e. no phthalocyanine ligand formed. At the same time, lanthanide diphthalocyanines under the above conditions form both from chlorometal phthalocyanines and from their corresponding hydroxymetal phthalocyanines.

Synthesis of sandwich metal complexes is complicated in the case of acoplanar tetrapyrrole ligands. Thus, attempted synthesis of a zirconium complex with a phthalocyanine and a tetra(1,4-dithiacyclohexene)porphyrazine ligands failed. The reaction of dichlorozirconium tetra(1,4-dithiacyclohexene)porphyrazine with *o*-phthalonitrile yields the metal-free phthalocyanine H_2Pc, whereas the reaction of Cl_2ZrPc with ethylenedithiomalenitrile, to the metal-free tetra(1,4-dithiacyclohexene)porphyrazine [21]. Probably, the nonplanarity of tetra(1,4-dithiacyclohexene)porphyrazine, associated with the presence of peripheral 1,4-dithiacyclohexene rings, creates steric hindrances to formation of a sandwich complex.

Similarly, lutecium di(octaphenyltetraazaporphyrin) could no be prepared from dichlorolutecium octaoctaphenyltetraazaporphyrin (ClLuOPhTAP) and diphenylmalenitrile. In this case, steric hindraces are produced by the phenyl rings deviating from the porphyrazine macroring plane. At the same time, heating ClLuO·PhTAP with excess *o*-phthalonitrile gave a new complex differing in properties both from the starting complexes and from known lutecium mono- and diphthalocyanines. This complex was identified as the unsymmetrical sandwich compound OPhTAPLuHPc [25].

The completeness of formation of unsymmetrical sandwich complexes was controlled spectrophoto-

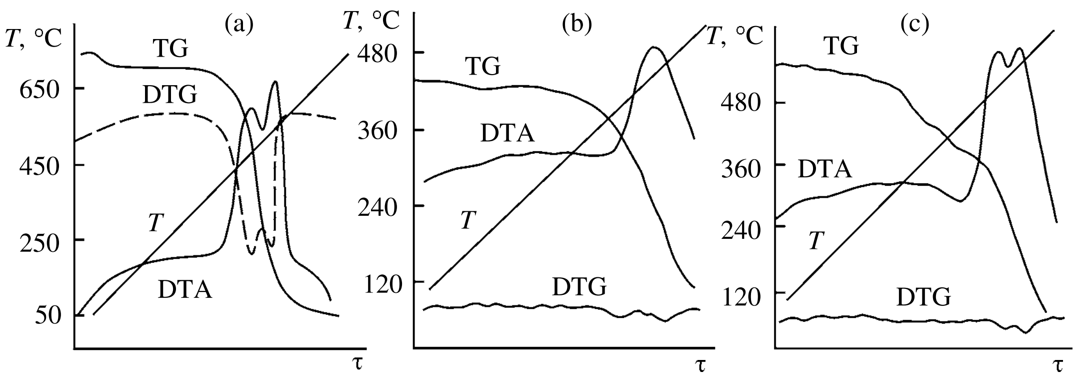


Fig. 1. Thermoanalytical curves of (a) PcZrTPyPa, (b) (4-Cl)$_4$PcErCl, and (c) (4-Cl)$_4$PcErHPc.

metrically by comparing the electronic absorption spectra of solutions of the starting monometal complex and the reaction mixture in an aprotic solvent, such as DMF. As the sandwich complex is formed, the spectrum acquires a new strong long-wave band shifted blue with respect to the corresponding band in the spectrum of the starting complex, as well as a red-shifted weaker band or a shoulder on the long-wave, descending branch of the principal band.

The resulting complexes were purified in several ways: extraction with organic solvents, column chromatography, vacuum distillation of excess *o*-phthalonitrile and other volatile admixtures, or thermal vacuum sublimation of the target products.

THERMAL STABILITY

It was found by differential thermal analysis, unsymmetrical diphthalocyanines and structurally similar compounds are more stable thermally than their parent extra complexes.

As seen from the thermoanalytical curves of PcZrTPyPa (Fig. 1a), strong thermal decomposition takes place at 500°C and is accompanied by an exothermic effect (DTA curve). At 562°C, the DTA curve shows one more exothermic peak whose shape points to a higher rate of thermolysis at this temperature. Probably, at 500°C, the complex decomposes with metal–nitrogen bond fission, whereas the decomposition at 562°C involves the tetrapyrrole ligands.

Table 2 and Figs. 1b and 1c compare the thermooxidative degradation data for unsymmetrical lutecium, holmium, and erbium diphthalocyanines and their parent extra complexes.

By and large, like with zirconium complexes, diphthalocyanines are more stable thermally than the phthalocyanine extra complexes from which they are derived. The DTA curves of the former have an intricate pattern, implying step thermooxidative processes involving metal–nitrogen bond fission followed by decomposition of the phthalocyanine ligands [24].

The higher thermal stability of unsymmetrical sandwich complexes, as well as symmetrical metal diphthalocyanines [35–39], compared with monometal phthalocyanines, can be explained in terms of their unusual structure in which the two ligands "clutch" the metal atom and protect it from air oxygen.

ELECTRONIC SPECTROSCOPY

Comparing the electronic absorption spectra of unsymmetrical sandwich complexes and their parent extra complexes in aprotic solvents, such as DMF, one can note similar spectral changes produced by metal diphthalocyanine formation. A strong absorption band appears in the spectrum, shifted blue with respect to the principal long-wave band of the parent metal phthalocyanines or similar extra complexes.

In the long-wave region of the spectrum, a weaker band or an ill-defined shoulder, depending of the

Table 2. Parameters of thermooxidative degradation of substituted rare-earth metal mono- and diphthalocyanines

Compound	Peak temperature from DTA, °C
ClLuPc(4-NO$_2$)$_4$	523
(4-NO$_2$)$_4$PcLuHPc(4-*t*-Bu)$_4$	558, 580
ClHoPc(4-Cl)$_4$	510
(4-Cl)$_4$PcHoHPc(4-*t*-Bu)$_4$	523, 551
ClHoPc(4-NO$_2$)$_4$	485
(4-NO$_2$)$_4$PcHoHPc(4-*t*-Bu)$_4$	523, 549
ClErPc(4-Cl)$_4$	469
(4-Cl)$_4$PcErHPc	502, 541

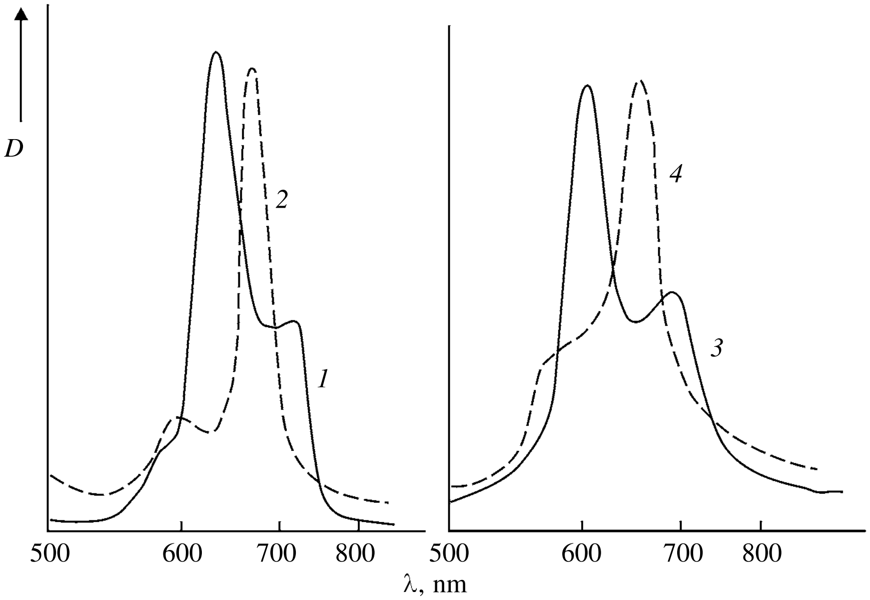


Fig. 2. Electronic absorption spectra of $(4\text{-Cl})_4\text{PcHoHPc}(4\text{-}t\text{-Bu})_4$ in (*1*) DMF and (*2*) acetone and of $(4\text{-Br})_4\text{PcErHPc}$ in (*3*) DMF and (*4*) thin film.

nature of the metal, appear on the long-wave branch of the prinicipal band (Table 3, Fig. 2).

The electronic absorption spectra of unsymmetrical sandwich complexes of tervalent metal strongly vary with solvent. As found in [23, 24], in going from DMF to benzene or acetone, the spectra of unsymmetrical lutecium, holmium, yttrium, and erbium diphthalocyanine complexes comprising *tert*-butyl-substituted and halogen- or nitro-substituted phthalocyanine ligands are no longer typically "diphthalocyanine" and become similar to the spectra of monometal phthalocyanines, having a single strong long-wave band.

Table 3. Electronic absorption spectra of unsymmetrical diphthalocyanine and similar complexes

Compound	$\lambda_{\max}$, nm		
	DMF	benzene	thin film
$\text{PcZrPc}(4\text{-Cl})_4$	630, 750	630, 751	640, 770
$\text{PcZrPc}(3\text{-Cl})_4$	630, 748	628, 750	642, 769
$\text{PcZrPc}(4\text{-Br})_4$	629, 751	630, 753	639, 778
$\text{PcZrPc}(3\text{-Br})_4$	631, 748	629, 751	640, 775
$\text{PcZrPc}(4\text{-I})_4$	629, 747	629, 749	645, 776
$\text{PcZrPc}(3\text{-I})_4$	630, 750	629, 751	649, 780
PcZrTPyPa	628, 747	627, 749	637, 760
PcZrTPzPa	628, 746	627, 749	639, 761
$\text{HPcLuPc}(4\text{-NO}_2)_4$	632, 715		
$(4\text{-Cl})_4\text{PcErHPc}\cdot(4\text{-}t\text{-Bu})_4$	630, 680	667	
$(4\text{-Br})_4\text{PcErHPc}\cdot(4\text{-}t\text{-Bu})_4$	630, 694	667	
$(4\text{-Cl})_4\text{PcYHPc}$	622, 683		615 sh, 674
$(4\text{-Br})_4\text{PcErHPc}$	620, 682		600, 672
OPhTAPLuHPc	613, 679 w	649, 662	
TBPLuHPc	625, 669		675

Similar changes were earlier observed with symmetrical diphthalocyanine complexes in going to DMF to weaker nucleophilicity solvents, as well as to solutions with lower pHs [40, 41]. Depending on these factors, the imine hydrogen atom is either localized on an endocyclic nitrogen atom ("green" form) or is transferred as a proton on the aprotic solvent molecule ("blue" form). With diphthalocyanine complexes with tetravalent metals (Zr, Hf), no analogous changes occur, i.e. the spectrum changes neither with changing organic solvent nor with changing solution pH.

With unsymmetrical rare-earth metal diphthalocyanine complexes, the shape of the long-wave part of the spectral curve depends on the size of the complet-forming ion [23]. For example, the spectra of chlorine- and nitro-substituted complexes of neodymium and samarium (ionic radii larger than 0.9 Å) contain a broadened band and lack of a well-defined long-range maximum, whereas related holmium and lutecium diphthalocyanines (ionic radii smaller than 0.9 Å) give an additional long-wave band.

It is known [1] that the character of the electronic absorption spectra of sandwich complexes, particularly metal diphthalocyanines, depends on the state of the two chromophores. Their resonance dipole coupling splits the *Q* band into two components, and this splitting the larger, the smaller the distance between the chromophores. In the case of unsymmetrical diphthalocyanine complexes of rare-earth metals, this trend is observed, as the ionic radius of the metal decreases.

The splitting of the two long-wave maxima of an unsymmetrical sandwich complex in which lutecium is bound with a phthalocyanine and an octaphenyltetraazaporphyrin ligands was found [15] to be 15 nm smaller compared with the respective value for lutecium diphathalocyanine [25]. This decrease may be explained by the fact that the distance between the two ligands in the unsymmetrical complex is increased by the deviation of phenyl rings of the octaphenyltetraazaporphyrin ligand from the macroring plane.

As noted in [42], the electronic absorption spectrum of a sublimed film of a zirconium complex with a phthalocyanine and a tetraphenylporphyrazine ligands (PcZrTPyPa) is similar, except for slight shifts of absorption bands, to that of the symmetrical zirconium diphathalocyanine [43]. Such spectral similarity can be explained in terms of leveling of the electronic structures of the tetrapyridineporphyrazine and phthalocyanine ligands.

At the same time, analysis of the electronic absorption spectra of unsymmetrical lutecium sandwich complexes in benzene [32] showed that the molecular asymmetry much affects the spectra. Thus, if a molecule comprises two structurally similar phthalocyanine ligands, a long-wave band appears in an intermediate position compared with symmetrical compounds. Therewith, the band at 460 nm characteristic of rare-earth metal diphthalocyanines in benzene is preserved.

If λ_{max} of monometal phthalocyanines and their structural analogs are sufficiently far from each other, then they do not coalesce in the hydbrid sandwich compound and shift only slightly with respect to the λ_{max} of the corresponding monometal phthalocyanines (Table 4).

The above data show that if two ligands strongly differing from each other in structure are combined in one molecule, their long-wave absorption bands move way from each other. The nature of the metal affects the intensity ratio of these bands.

Table 4. Positions of the long-wave absorption bands in the electronic absorption spectra of lutecium complexes

Compound	λ_{max}, nm (in benzene)
PcLuPc(*t*-Bu)$_4$	660
PcLuPc	658
(*t*-Bu)$_4$PcLuPc(*t*-Bu)$_4$	662
PcLuNPc(*t*-Bu)$_4$	776, 654
(OAc)LuPc	674
(OAc)LuNPc	765
PcLuPc	658
NPcLuNPc	761

Two λ_{max} (649 and 662 nm) were observed in the spectrum of a benzene solution of a lutecium complex with a phthalocyanine and an octaphenyltetraazaporphyrin ligands [25].

Spectral evidence for the relative autonomy of the tetrabenzoporphyrin and phthalocyanine ligands in the unsymmetrical gadolinium complex TBPGdHPc was reported in [27]. The spectrum of a DMF solution of this complex in the range 500–800 nm contains three absorption bands at 690, 654, and 604 nm. The band at 604 nm, lacking in the spectrum of the related lutecium sandwich complex and characteristic of the tetrabenzoporphyrin ligand, points to a relative autonomy of the tetrabenzoporphyrin and phthalocyanine ligands. In the gadolinium complex, the ligands interact weaker than in the lutecium complex, which can be explained by the larger radius of Gd^{3+} compared with Lu^{3+}. The weaker π–π interaction is also confirmed by the smaller resonance splitting of the *Q* band in the spectrum of the gadolinium complex in DMF compared with the lutecium complex.

The ability of certain unsymmetrical diphthalocyanines to sublime in a vacuum without decomposition allowed preparation of thin films for studying the electronic and optical properties of the complexes. The electronic absorption spectra of solid films obtained by subliming unsymmetrical halogen- and nitro-substituted diphthalocyanine complexes on spectrally pure quartz supports, unlike the spectra of the same compounds in DMF (Fig. 2), show a single strong long-wave band shifted red with respect to the respective bands of DMF solutions [24]. In view of the above-described spectral changes produced by migration of imine protons, one can conclude that the spectra of solid films of unsymmetrical halogen- and nitro-substituted diphthalocyanines are indicative of a neutral (“green”) form having the proton localized on the endocyclic nitrogen atom of the phthalocyanine

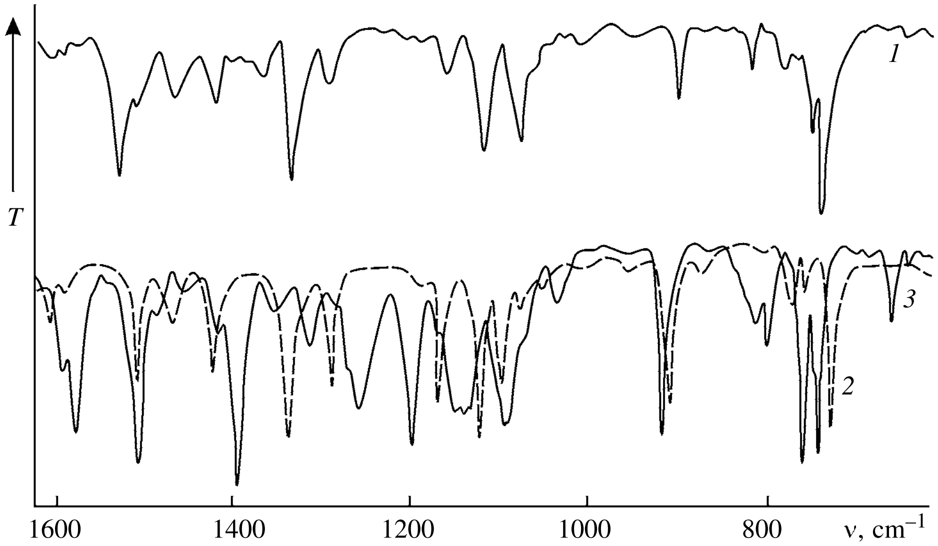


Fig. 3. IR spectra of (*1*) PcZrTPyPa, (*2*) CuPc, and (*3*) CuTPyPa.

ligand. An unsymmetrical lutecium complex with a phthalocyanine and a tetrabenzoporphyrin ligands, too, prefers the "green" form in the solid state (λ_{max} 675 nm) [27].

The spectra of solid films of unsymmetrical halogen-containing yttrium and erbium diphthalocyanine complexes are better resolved compred with those of metal phthalocyanine extra complexes [44].

The electronic absorpion spectra of unsymmetrical zirconium and hafnium diphthalocyanine and related complexes are almost identical to the spectra of the same compounds in solutions, except that bands are shifted red by 20–30 nm, depending on the structure of the complex.

VIBRATIONAL SPECTROSCOPY

Vibrational spectroscopy was primarily used for structural assessment of unsymmetrical sandwich complexes, particularly for confirmation of the presence of certain functional groups or molecular fragments in them. Thus, the IR spectra of nitro-substituted diphthalocyanine complexes [22–24] display a very strong band at 1500 cm^{-1}, associated with asymmetric stretching vibrations of the N–O bond in nitro groups attached to aryl residues, as well as a strong band at 1350 cm^{-1}, associated with symmetric stretching vibrations of this bond.

The medium-intensity band at 1100 cm^{-1} in the IR spectra of unsymmetrical chloro-substituted diphthalocyanine complexes was assigned to Ar–Cl stretching vibrations [22–24].

The bands at 1527 and 1535 cm^{-1} in the IR spectrum of PcZrTRyPa [42] arise from pyridine ring vibrations. These bands can be related to the bands at 1577 and 1592 cm^{-1} in the IR spectrum of CuTPyPa [45, 46], which have no analogs in the spectra of metal phthalocyanines. The observed shifts of these bands are explained, as already mentioned, by leveling of the electronic structures of the tetrapyridineporphyrazine and phthalocyanine ligands.

The IR spectra of *tert*-butyl-substituted unsymmetrical diphthalocyanine complexes [23, 24] contain well-defined bands in the range 2800–3000 cm^{-1}, belonging to symmetric and asymmetric vibrations of CH_3 groups, as well as a characteristic doublet at 1360–1370 cm^{-1}, belonging to deformation vibrations of bonds in *tert*-butyl groups.

According to IR evidence [22–25], unsymmetrical diphthalocyanine complexes and related compounds contain no metal-free phthalocyanine H_2Pc. In particular, the IR spectra of the complexes show no band at 1000 cm^{-1}, whereas in the spectrum of H_2Pc this band is very strong [47].

The unsymmetrical zirconium diphthalocyanine complexes $PcZrPc(4\text{-}NO_2)_4$ and $PcZrPc(3\text{-}NO_2)_4$ give bands at 192 and 294 cm^{-1}, which relate to the bond of zirconium with endocyclic phthalocyanine nitrogen atoms.

Analysis of the IR spectra of unsymmetrical sandwich complexes revealed structural features of these compounds. Figure 3 compares the thin-film IR spectra of PcZrTPyPa [42] and copper phthalocyanine

Table 5. X-ray photoelectron spectra of nitro-substituted zirconium complexes

Complex	Binding energies (E_b, eV) and band half-widths (δ, eV)											
	N1*s*				Zr3*d*				O1*s*		Cl2*p*	
	E_b	δ	E_b	δ	E_b	δ	E_b	δ	E_b	δ	E_b	δ
$Cl_2ZrPc(3\text{-}NO_2)_4$	398.4	2.7	405.1	2.5	183.7	2.2	185.2	2.0	531.1	3.0	200.9	3.5
$Cl_2ZrPc(4\text{-}NO_2)_4$	399.0	3.3	405.1	2.8	182.9	2.1	184.7	2.0	531.2	3.0	200.2	3.8
$PcZrPc(3\text{-}NO_2)_4$	398.8	2.3	404.0	2.2	182.1	1.8	184.7	1.8	531.8	2.7		
$PcZrPc(4\text{-}NO_2)_4$	398.8	2.1	403.7	2.1	182.2	1.7	184.8	1.8	531.8	2.6		

and tetrapyridineporphyrazine complexes [45, 46]. As seen, the IR spectrum of the unsymmetrical sandwich complex stronger resembles the spectrum of CuPc that of CuTPyPa, and is not, under any circumstances, a superposition of the spectra of the two different ligands, as would be expected. Neither splitting nor broadening of absorption bands in the IR spectrum of PcZrTPyPa, associated with the presence of two structurally different ligands is observed. Thus, the bands at 900 cm^{-1} in the spectrum of CuPc and at 908 cm^{-1} in the spectrum of CuTPyPa correspond to a single band near 893 cm^{-1} in the spectrum of the unsymmetrical sandwich complex. The ν(CH) bands at 722 and 739 cm^{-1} in the spectra of CuPc and CuTPyPa, respectively, correspond to a single band in the spectrum of PcZrTPyPa at 730 cm^{-1}. The fact that the IR spectrum of this unsymmetrical sandwich complex is uncomplicated compared with the spectrum of monometal phthalocyanine [42] suggests that the electronic structures of the two ligands in the latter complex are leveled by interaction through the coordinating metal atom and become almost identical to each other. The molecular asymmetry of PcZrTPyPa is reduced to the asymmetry of nuclear configurations of the ligands.

The IR spectra of sublimed films of unsymmetrical lutecium and gadolinium complexes with a phthalocyanine and a tetrabenzoporphyrin ligands in the range 200–400 cm^{-1} were reported in [27]. In the mentioned spectral range, two strong absorption bands are observed, confirmatory of the presence of two different ligands in the complexes. Evidence for the unsymmetrical structure of the latter was found in the IR spectra measured at 400–4000 cm^{-1}. In the 1700–1300 cm^{-1} range, splitting of the C=N and C=C stretching absorption bands was observed, uncharacteristic of symmetrical metal diphthalocyanines. Moreover, the IR spectra contained strong absorption bands at 1330–1340 cm^{-1}, characteristic of the "green" forms of metal diphthalocyanines [48]. The above findings gave evidence for the conclusion that the lutecium and gadolinium complexes in the solid state exist in the "green" form with the proton localized on an endocyclic nitrogen atom, drawn from the electronic spectra of sublimed films of these compounds.

The IR spectra of PcZrTPyPa and its mono- and dicationic forms obtained by exposure of the complex to iodine vapors [42] are similar to each other, on account of the similarity of nuclear configurations of the three forms, and, at the same time, each have certain peculiar features. Similarity of the spectra of the cationic forms of PcZrTPyPa and MPc was also noted. On this basis, a conclusion was drawn that the excess cationic charge, rather than being concentrated on one of the two ligands, is distributed between them. Thus, the electronic structures both of the cation and of the neutral molecule prove symmetrical with respect to the coordinating metal atom.

X-RAY PHOTOELECTRON SPECTROSCOPY

To gain further evidence for the composition and structure of unsymmetrical sandwich complexes, some of them were studied by means of X-ray electron spectroscopy. This method is suitable for compounds of any complexity, including phthalocyanines.

Comparative study of the zirconium extra complexes $Cl_2ZrPc(3\text{-}NO_2)_4$ and $Cl_2ZrPc(4\text{-}NO_2)_4$ and their derived unsymmetrical nitro-substituted zirconium diphthalocyanines $PcZrPc(3\text{-}NO_2)_4$ and $PcZrPc\cdot(4\text{-}NO_2)_4$ gave information on the presence of nitro groups, electron density distribution, and other structural features [49].

Their X-ray photoelectron spectra measured at 0–1400 eV contain bands characteristic of N1*s*, O1*s*, Zr3$d_{3/2}$, and Zr3$d_{5/2}$ electrons. In addition, the spectra of the parent extra complexes show Cl2*p* bands. In the N1*s* spectrum of $Cl_2ZrPc(3\text{-}NO_2)_4$ (Table 4), there is a double band with its maxima at E_b 405.1

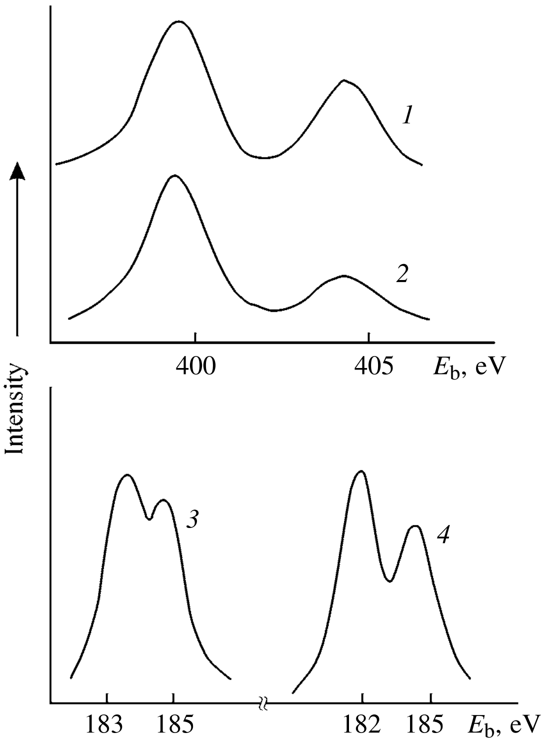


Fig. 4. X-ray photoelectron spectra of (*1*) $Cl_2ZrPc \cdot (4\text{-}NO_2)_4$ (N1*s* electrons), (*2*) $PcZrPc(4\text{-}NO_2)_4$ (N1*s* electrons), (*3*) $Cl_2ZrPc(3\text{-}NO_2)_4$ (Zr3*d* electrons), and (*4*) $PcZrPc(3\text{-}NO_2)_4$ (Zr3*d* electrons).

and 398.4 eV and intensity ratio 1 : 2.2. The complex $Cl_2ZrPc(4\text{-}NO_2)_4$ has a similar N1*s* spectrum (E_b 405.1 and 399.0 eV, intensity ratio 1 : 2.1). The N1*s* spectra of the diphthalocyanine complexes $PcZrPc \cdot (3\text{-}NO_2)_4$ and $PcZrPc(4\text{-}NO_2)_4$, too, contain a double band with its maxima at E_b 404.0, 398.8 and 403.7, 398.8 eV and intensity ratio 1 : 4.2 (Table 5, Fig. 4).

Thus, nonequivalence of at least two types of nitrogen atoms in the complexes studied was revealed. The N1*s* bands at E_b 398.4–399.0 eV and with half-widths of 2.1–3.3 eV are assignable to the phthalocyanine ligand whose electron density is uniformly distributed between endocyclic and *meso*-bridging nitrogen atoms. The high-energy band in the N1*s* spectrum of the extra complexes and their corresponding diphthalocyanines belongs to the nitro groups. The intensity ratio of the high- and low-energy spectral bands is 1 : 2.1, which can be considered close to theoretical (1 : 2) on the assumption that the zirconium extra complexes contain four nitro groups. The respective ratios for the zirconium diphthalocyanines are 1 : 4.1 from experiment and 1 : 4 on the assumption that these complexes, too, have four nitro groups.

The Zr3*d* spectra are differently resolved depending on the structure of the complexes. The spectra of the extra complexes are poorly structured broad bands with two maxima (Fig. 4). The Zr3*d* spectra of the diphthalocyanines have a well-defined structure whose low-energy component may be associated with zirconium $3d_{3/2}$ electrons.

From a comparison of the X-ray photoelectron data we can draw the following conclusions. The electron-acceptor nitro groups take part in electron density distribution over the whole molecule. Therewith, the $4\text{-}NO_2$ group exerts a stronger effect in the $Cl\text{–}Zr \cdot Pc(4\text{-}NO_2)_4$ chain, compared with $3\text{-}NO_2$. Evidence for this conclusion comes from the fact that the electron density of the chlorine and zirconium atoms is decreased and on the phthalocyanine nitrogen atoms is increased. Therewith, in the nitro group itself no electron density redistribution between the oxygen and nitrogen atoms is observed.

Compared with the extra complexes, the diphthalocyanines feature increased electron density on the metal and nitro nitrogen atoms (Table 5). This is explained by the replacement of the chlorine by phthalocyanine ligand which exerts a weaker electron-acceptor effect on the metal atom and its organic ligand.

REACTION WITH HALOGEN VAPORS

Like phthalocyanine metal complexes [50], unsymmetrical sandwich complexes can react with halogen vapors. Thus, the reaction of PcZrTPyPa with iodine vapors was found to occur in two stages [42]. Exposure of sublimed films of this complex to iodine vapors (in air) at low (~10^{-3} mm) partial pressures gives the "green" form. In saturated iodine vapors the latter gradually (from several minutes to several hours, depending on layer thickness) acquires a brown color. The "brown" form is unstable and converts into the "green" form under the action of iodine vapors. The latter, in its turn, splits off iodine and passes into the parent (blue) complex PcZrTPyPa when heated in a vacuum at 200–220°C.

The spectrum of the "green" form (Fig. 5) is similar to the that of the monocationic salt, whereas the spectrum of the "brown" form is similar to the spectrum of the dicationic salt of a symmetrical zirconium diphthalocyanine [41]. The spectrum of the "brown" form contains a band near 690 nm, which obviously belongs to an admixture of the "green" form. Both form give a broad absorption band (300–600 nm) having no defined maximum. This band is lacking in the spectrum of the cationic form of zirconium diphthalocyanine, obtained electrochemically [43]. This band was assigned [42] to the iodine

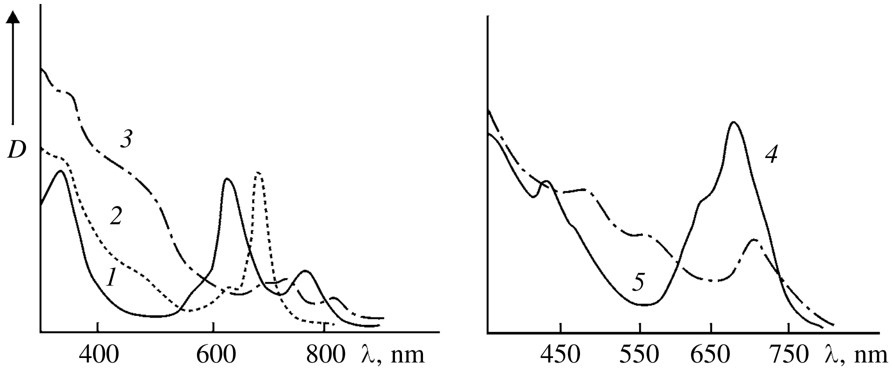


Fig. 5. Electronic absorption spectra of sublimed films. (*1–3*) PcZrTPyPa [(*1*) initial film, (*2*) the same film exposed to saturated iodine vapor (dication), and (*3*) the latter film exposed to air for 1 h in the absence of I_2 (monocation)], and (*4*, *5*) PcLuTBP [(*4*) initial film, and (*5*) the same fim exposed to Br_2 vapors).

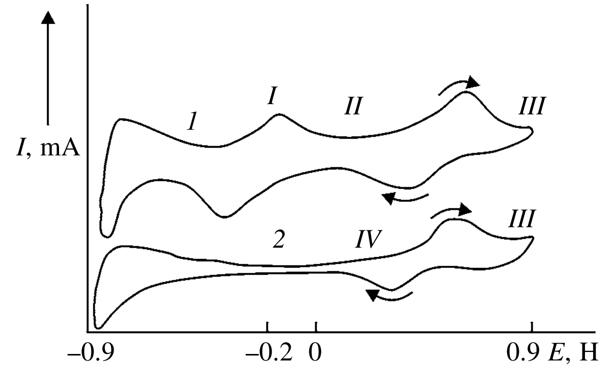


Fig. 6. Potentiodynamic curves of platinum electrodes with deposited electrochromic films in 1 N KNO_3 at *V* 0.1 V/c. (*1*) Pc_2Lu, (*2*) $PcHfPc(4\text{-}Cl)_4$. (*I*) Blue, (*II*) bluish-green, (*III*) reddish brown, and (*IV*) blue.

counterion, and it is more intense in the case of the dication compared with monocation.

Evidence for the assessment of the reaction products of PcZrTPyPa with iodine (mono- and dications) comes from the ESR spectra. The “green” form has 100% of paramagnetic molecules: A singlet signal with *q* 2.002 is observed. The number of paramagnetic centers in the “brown” form comprises 10–20% of the total number of molecules. These centers probably belong to the “green” form admixture which is also seen in the electronic spectrum.

Exposure of the sublimed film of the unsymmetrical lutecium complex TBPLuNPc to bromine vapors leads to one-electron oxidation of the complex, and the oxidation product in its spectral characteristics to the “red” form of lutecium diphthalocyanine, obtained electrochemically [51]. Subsequent treatment of the film with hydrazine vapors recovers the initial color and spectral characteristics of the film. This finding suggests that TBPLuNPc is susceptible to reversible redox processes accompanied by color changes.

ELECTROCHROMIC PROPERTIES

Since certain diphthalocyanine metal complexes possess electrochromic properties, we considered it of interest to study the electrochromic properties of the synthesized unsymmetrical diphthalocyanines.

Figure 6 presents the potentiodynamic curves of $PcHfPc(4\text{-}Cl)_4$ and lutecium diphthalocyanine (potent electrochromic material) in 1 M KNO_3.

In a neutral medium (1 M KNO_3) at a positive p otential (+0.5 V) we observed current gain. Simultaneously, the $PcHfPc(4\text{-}Cl)_4$ film changed color. As the potential was raised from +0.5 to +0.9 V, the color of the film changed from blue to brown. It should be noted that the color change is reversible and reproducible. At a negative potential of the working electrode (up to –0.9 V), the color of the film does not change and remains blue. Unlike $PcHfPc(4Cl)_4$, lutecium diphthalocyanine in the range –0.9 to +0.9 V changes its color from blue through green to brown. The green–brown transition occurs at +0.6 V, which is 0.1 V higher than the potential of the blue–brown transition in the unsymmetrical hafnium diphthalocyanine studied.

In an acid medium (1 M HNO_3) in the range –0.2 to +0.9 V, $PcHfPc(4\text{-}Cl)_4$, too, changes its color from blue to brown. This color transition occurs at +0.3 V, which is 0.1 V lower than the potential of the green–brown transition of lutecium diphthalocyanine. At a negative potential, the film of the unsymmetrical hafnium phthalocyanine does not change color and remains blue. Analogous results were obtained with other unsymmetrical hafnium phthalocyanines.

Thus, unsymmetrical sandwich complexes can be considered as promising electrochromic materials.

It should be noted that unsymmetrical halogen-substituted hafnium diphthalocyanines, unlike lutecium diphthalocyanines, undergo no redox reactions in the cathodic range, leading to film degradation. This allows one to increase the number of recoloring cycles and thus prolong the life of the film. Of importance is that halogen-containing zirconium and hafnium complexes sublime on heating in a vacuum. This opens the way to preparing films for electrochromic studies by thermal vacuum deposition rather than by mechanical rubbing, which makes the process more efficient and the resulting films more uniform and reliable in operation.

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