COMPLEXES OF ZIRCONIUM AND HAFNIUM WITH SUBSTITUTED PHTHALOCYANINES

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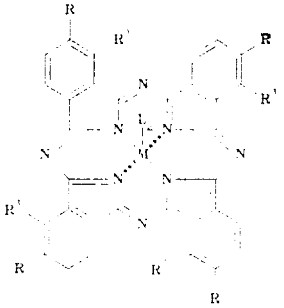
The syntheses and electronic spectra of complexes of zirconium and hafnium with halo-, tert-butyl-, nitro-, and amino-substituted phthalocyanines are described. The nature and location of the substituents are shown to affect the electronic absorption spectra. The changes in the spectra of the synthesized complexes on going from DMF to H_2SO_4 solution are analyzed.

The introduction of certain substituents into the benzene nuclei of phthalocyanine and its metal complexes affords compounds possessing increased solubility [1], catalytic activity [2, p. 110], new pigmenting potential [3, p. 211], and other properties of practical value [4]. Information about complexes of substituted phthalocyanines with divalent metals is widespread in the literature, but study of the corresponding complexes with metals in oxidation states above two and containing axial ligands, has been quite inadequate.

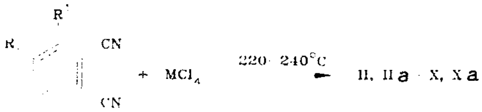
In continuing the investigation of complexes of Group IV elements with various tetrapyrrole ligands [5-7], we have synthesized and studied the electronic spectra of complexes of zirconium and hafnium with substituted phthalocyanines.



I, Ia-XIIa

I, Ia R=R^1=H; II, IIa R=Cl, R^1=H; III, IIIa, R=H, R^1=Cl; IV, IVa R=Br, R^1=H; V, Va R=H, R^1=Br; VI, VIa R=I, R^1=H; VII R=H, R^1=I; VIII, VIIIa R=*t*-Bu, R^1=H; IX, IXa R=NO_2, R^1=H; X, Xa R=H, R^1=NO_2; XI, XIa R=NH_2, R^1=H; XIIa R=H, R^1=NH_2; I, Ia—X, Xa L=Cl; XIa, XIIa L=OH; I—X *M*=Zr; Ia—XIIa *M*=Hf

To synthesize complexes of zirconium and hafnium, II and IIa-XIIa, with substituents at fixed positions, we began with the 3- or 4-substituted dinitriles of phthalic acid, obtained by known procedures [8; 9, p. 3]. We synthesized the metal complexes of II and IIa-X, Xa, in analogy with the unsubstituted metallophthalocyanines, I and Ia, by melting the corresponding dinitriles with zirconium or hafnium tetrachloride at 220-240°C [10].



The complex of zirconium with nitro-substituted phthalocyanine, IX, was also synthesized by the "urea" method [11], starting from 4-nitrophthalic acid, but with a smaller yield than by the "nitrile" method given above.

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TABLE 1. Complexes of Zirconium and Hafnium with Substituted Phthalocyanines

Complex	Empirical formula	λ_{max}, HM*		Complex	Empirical formula	λ_{max}, HM*	
		DMF	18M H_2SO_4			DMF	18M H_2SO_4
I	$C_{32}H_{16}Cl_2N_8Zr$	679	811	VI	$C_{32}H_{12}Cl_2I_4N_8Zr$	693	838
Ia	$C_{32}H_{16}Cl_2HfN_8$	682 (683)	808	VIa	$C_{32}H_{12}Cl_2HfI_4N_8$	693 (690)	833
II	$C_{32}H_{12}Cl_6N_8Zr$	685	817	VII	$C_{32}H_{12}Cl_2I_4N_8Zr$	696	856
IIa	$C_{32}H_{12}Cl_6HfN_8$	685 (687)	814	VIII	$C_{48}H_{48}Cl_2N_8Zr$	688	828
III	$C_{32}H_{12}Cl_6N_8Zr$	693	841	VIIIa	$C_{48}H_{48}Cl_2HfN_8$	687	831
IIIa	$C_{32}H_{12}Cl_6HfN_8$	691	839	IX	$C_{32}H_{12}Cl_2N_{12}O_8Zr$	715; 698	782; 756
IV	$C_{32}H_{12}Br_4Cl_2N_8Zr$	687	825	IXa	$C_{32}H_{12}Cl_2HfN_{12}O_8$	716; 696	759
IVa	$C_{32}H_{12}Br_4Cl_2HfN_8$	688 (688)	822	X	$C_{32}H_{12}Cl_2N_{12}O_8$	691	747
V	$C_{32}H_{12}Br_4Cl_2N_8Zr$	691	845	Xa	$C_{32}H_{12}Cl_2HfN_{12}O_8$	688	748
Va	$C_{32}H_{12}Br_4Cl_2HfN_8$	693	842	XIa	$C_{32}H_{22}HfN_{12}O_2$	731; 705 (732)	769; 740
				XIIa	$C_{32}H_{22}HfN_{12}O_2$	771	757

*Calculated values of λ_{max} are given in parentheses.

We did not succeed in synthesizing the amino-substituted complexes of zirconium and hafnium by the "nitrile" method. Thus, when 4-aminophthalodinitrile was melted with zirconium or hafnium tetrachloride, the resultant products were slightly soluble in DMF and other organic solvents and the solutions formed gave no spectroscopic evidence of the formation of phthalocyanine complexes. Probably, an acid—base reaction takes place during melting between $ZrCl_4$ or $HfCl_4$ (Lewis acids) and 4-aminophthalodinitrile with the formation of products with a noncyclic structure. Tetraaminophthalocyanine complexes XI and XIa were prepared by the reduction of nitro-substituted VIIIa and IXa with sodium sulfide by the procedure in [12]. During the synthesis and purification, the Zr—Cl bonds hydrolyze to form the corresponding dihydroxy derivatives, XIa and XIIa.

We checked the complete purity of compounds II and IIa-XIIa and their identity by means of elemental analysis and electronic and vibrational spectroscopy.

The insolubility of the synthesized complexes (except for VIII and VIIIa) in solvents transparent in the near-UV region, prevented, an analysis of the electronic absorption spectra over a wide range. As a consequence, Table 1 gives only the longwave absorption bands known [4, 13] to be the most sensitive to changes in functionality on the periphery of the phthalocyanine molecule.

The electronic absorption spectra of synthesized compounds II and IIa-XIIa (except for IX and IXa) are similar in nature to the spectrum of unsubstituted complexes I and Ia, with a single, intense band in the longwave region.

The splitting of the longwave band for 4-nitrosubstituted complexes IX and IXa may be due to the presence in them of isomers with different combinations of substituent locations.

Analysis of the experimental data (Table 1; Figs. 1 and 2) reveals that both electron-donating and electron-accepting substituents cause a bathochromic shift of the longwave absorption band with respect to the unsubstituted complexes. This shift is due to the polarization of the phthalocyanine macrocycle under the influence of substituents. As is known [13], this leads to a narrowing of the separation between the ground state and the excited state of the π-electrons.

For the unsubstituted hafnium complex Ia, and for complexes IIa, IVa, VIa, and XIa, containing halogen atoms or amino groups in the 4-position, we calculated the position of the longwave absorption band by the Hückel method in the π-electron approximation. Values of the coulombic and resonance parameters were chosen similar to the data in [14, p. 76; 15]. The method satisfactorily describes the shifts in the maximum of the longwave absorption under the influence of substituents on the benzene nuclei of the phthalocyanine fragment. The calculated data presented in Table 1 show the bathochromic character of the shift of the longwave absorption band in the series Ia → IIa → IVa → VIa → XIa. This is in good agreement with the absorption spectra in DMF.

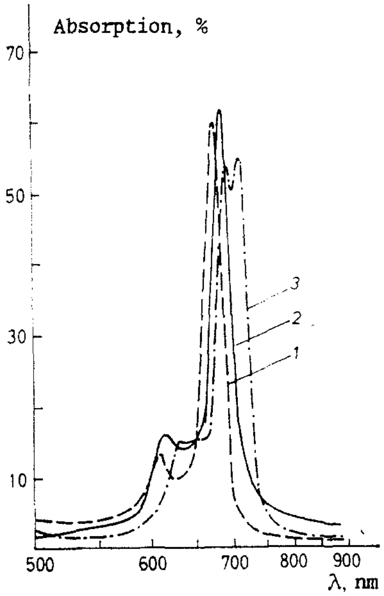


Fig. 1

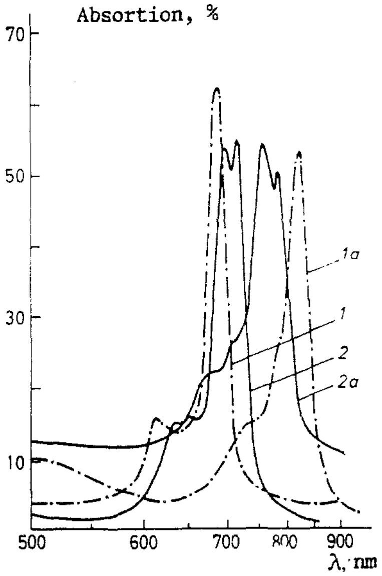


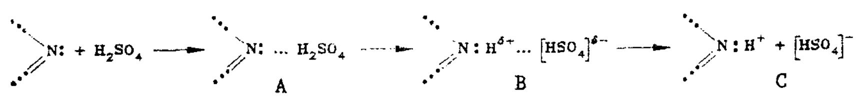
Fig. 2

Fig. 1. The electronic absorption spectra in DMF: 1) complex I; 2) complex II; 3) complex IX.

Fig. 2. The electronic absorption spectra in DMF (1, 2) and in 18 M H_2SO_4 (1a, 2a): 1, 1a) complex II; 2, 2a) complex IX.

On comparing the electronic spectra of complexes II, IIa-VII, VIIa, XIa, and XIIa, which contain halogen atoms or amino groups in the 3 and 4 positions, one finds, as noted in [16], that the first band is more sensitive to the introduction of substituents in position 3. In the case, however, of compounds IX, IXa, X, and Xa, the 3-nitro-substituted complexes show a smaller bathochromic shift than the 4-nitro-substituted ones (Table 1). This peculiarity is due to the lesser polarization of the macrocycle by nitro groups in the 3 position because they leave the plane of the molecules. This is confirmed by Stuart–Brieglieb steric models. Moreover, an interaction is not precluded between a nitro group in this position, it being a strong electron acceptor, and the p-electron pairs of the meso nitrogen atoms, leading to a reduced fraction of p-electrons passing from the nonbonding φ_N-orbitals of the N atoms to the vacant $\psi_{\pi}*$-orbitals of the phthalocyanine macrocycle [17]; i.e., they may be partially shut off from the overall chain of conjugation.

On comparing the positions of the first absorption bands in the electronic spectra of synthesized complexes II, IIa-VIII, and VIIIa in DMF and concentrated H_2SO_4, one can note the considerable bathochromic shift in sulfuric acid, which reaches 160 nm [Fig. 2; Table 1]. This shift results from the protonation of the meso nitrogen atoms [17], which is accompanied by the strong polarization of the phthalocyanine macrocycle. Tetrasubstituted complexes IX, IXa, X, and Xa have a lesser bathochromic shift (52-60 nm) on going from DMF to H_2SO_4. This peculiarity, noted earlier [9] for divalent complexes with tert-butyl derivatives of nitrophthalocyanines, must be explained by the reduction of the basicity of the meso nitrogen atoms because of the strong, electron-accepting influence on them of the nitro groups of the benzene nuclei. We hypothesize, based on the multistep acid–base interactions of tetraazaporphines (and phthalocyanine is a tetraazaporphine derivative) and sulfuric acid [18]:



that the nitro-substituted complexes with reduced basicity of the meso nitrogen atoms, form species B in sulfuric acid, with incomplete transfer of a proton from the sulfuric acid; i.e., a lesser degree of protonation compared with the limiting species C. A smaller degree of macrocycle polarization follows from this and leads to the previously mentioned smaller bathochromic shift.

In the case of amino-substituted complexes XIa and XIIa in sulfuric acid, the addition of protons takes place primarily at the amino group. Hence, the bathochromic shift of the longwave band for the 4-amino-substituted complex XIa is all of 38 nm, while for the 3-amino-substituted XIIa, the shift is hypsochromic (14 nm).

EXPERIMENTAL

The electronic absorption spectra of the compounds investigated were measured in DMF and 18 M H_2SO_4 on a Specord M 40 spectrophotometer at 20°C over the wavelength range of 500-900 nm. The concentration of the solutions was 10^{-5} M. Compounds I and Ia-XIIa were synthesized by the procedures in [9-11]. The unreacted dinitriles and linear condensation products were extracted with dry organic solvents (benzene, acetone). Excess zirconium or hafnium tetrachloride was removed by treating the synthesized compounds in vacuum (10^{-3} Pa) at 200-220°C. Complexes VIII and VIIIa with tert-butyl substituents, are quite soluble in organic solvents and were extracted with dry benzene and finally purified chromatographically on aluminum oxide. The elemental analyses for C, H, N, and halogen agreed with the calculated values.

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