

OPTICAL AND ELECTROPHYSICAL PROPERTIES OF METAL COMPLEXES  
OF TETRA(1,4-DITHIACYCLOHEXENO)PORPHYRAZINE

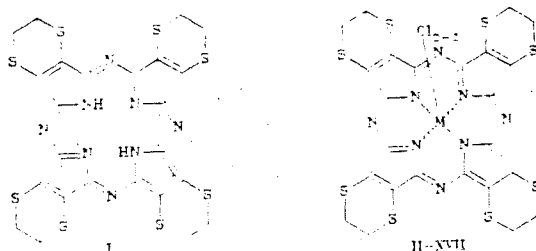
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The optical and electrophysical characteristics of metal complexes of tetra-(1,4-dithiacyclohexeno)porphyrzine were measured. The presence of 1,4-dithiacyclohexene rings in the molecules of the investigated compounds leads to the appearance of bands corresponding to an  $n \rightarrow \pi^*$  transition in the absorption spectra. The positions of the long-wave bands corresponding to a  $\pi \rightarrow \pi^*$  transition are determined by the nature of the metal. All of the complexes have semiconductor properties; the specific electrical conductivities range from  $10^{-11}$  to  $10^{-9} \Omega^{-1} \cdot \text{cm}^{-1}$ .

A study of complexes of porphyrzine derivatives with metals is extremely urgent, since it makes it possible to establish the effect and role of various structural elements of molecules with respect to their physicochemical properties.

We have previously synthesized complexes of tetra(1,4-dithiacyclohexeno)porphyrzine ( $\text{H}_2\text{TDTP}$ ) (I) with di-, tri-, and tetravalent metals ( $\text{ClO}_2\text{-}_2\text{MTDTP}$ ) (II-XVII):



II M=Cu<sup>2+</sup>; III M=Zn<sup>2+</sup>; IV M=Mg<sup>2+</sup>; V M=Cd<sup>2+</sup>; VI M=Fe<sup>2+</sup>; VII M=Co<sup>2+</sup>;  
VIII M=Ni<sup>2+</sup>; IX M=Pb<sup>2+</sup>; X M=Sn<sup>2+</sup>; XI M=Al<sup>3+</sup>; XII M=Cr<sup>3+</sup>; XIII M=Ga<sup>3+</sup>;  
XIV M=In<sup>3+</sup>; XV M=Ge<sup>4+</sup>; XVI M=Sn<sup>4+</sup>; XVII M=Zr<sup>4+</sup>

In the present communication we present the results of an investigation of their optical properties and electrical conductivities as compared with an extensively studied class of compounds, viz., phthalocyanines [3], which have a similar porphyrzine macroring.

Data from the electronic absorption spectra of the investigated I-XVII, which are presented in Table 1 and Fig. 1, show that replacement of the benzene rings in the phthalocyanine molecule by 1,4-dithiacyclohexene rings leads to a substantial change in the electronic-optical properties and, above all, to the appearance of a new band at 525-595 nm.

The electronic spectrum of free  $\text{H}_2\text{TDTP}$  in  $\alpha$ -chloronaphthalene (Fig. 1a) contains three absorption bands at 500-700 nm and a Soret band at 360 nm. As in the case of metal phthalocyanines [3], the formation of metal complexes II-XVII is accompanied by merging of two long-wave absorption bands to form one band; this is explained by an increase in the degree of molecular symmetry. The position of this band depends on the nature of the central metal atom. In contrast to the spectra of phthalocyanine and its metal complexes, the spectra of I-XVII are characterized by the presence in the visible region of an additional band at 525-595 nm, which does not show up sufficiently distinctly in the spectra of the complexes with divalent metals (II-X).

The appearance of this band in the spectra of  $\text{H}_2\text{TDTP}$  and its metal complexes makes it possible to assume that an  $n \rightarrow \pi^*$  transition is permitted due to excitation of the n electrons

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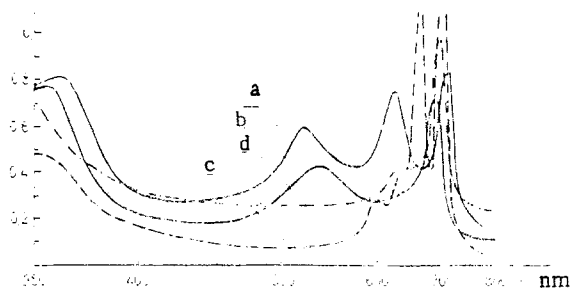


Fig. 1. Electronic absorption spectra in  $\alpha$ -chloronaphthalene: a) I; b) XVII; c) phthalocyanine; d) dichlorozirconium phthalocyanine.

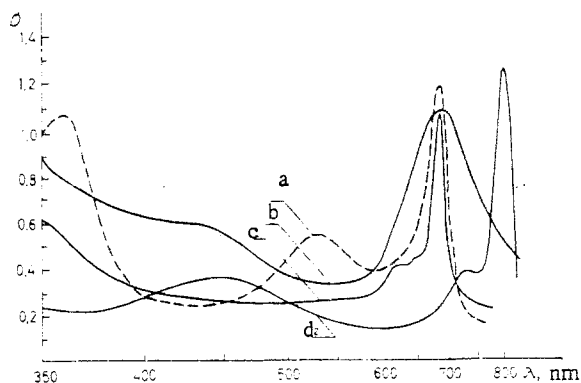


Fig. 2. Electronic absorption spectra of XVII (a, b) and dichlorozirconium phthalocyanine (c, d): a, c) in DMFA; b, d) in  $H_2SO_4$ .

of the sulfur atoms of the peripheral 1,4-dithiacyclohexene rings. The basis for this assumption is a comparison of the absorption spectra of metal complexes II-XVII in organic solvents and in concentrated sulfuric acid (Table 1 and Fig. 2).

It is known [3] that the character of the spectra of phthalocyanine and its metal complexes does not change on passing from organic solvents to sulfuric acid; however, one observes a strong bathochromic shift (80-120 nm) of almost all of the absorption bands, which is associated with protonation of the porphyrine ring at the exocyclic nitrogen atoms. According to our data (Fig. 2 and Table 1), the less intense band vanishes in the spectra of  $H_2TDTP$  and  $Cl_{0-2}MDTDP$  in solution in concentrated sulfuric acid, whereas, as compared with the corresponding metal phthalocyanines [2], the first long-wave band does not experience such a significant bathochromic shift, and one even observes a hypsochromic shift in the case of complexes IX-XI and XV-XVI. It is apparent that in the case of  $H_2TDTP$  and its metal complexes, in addition to protonation in the principal macroring, protons add to the peripheral 1,4-dithiacyclohexene rings through the  $n$  electrons of the sulfur atoms; this leads to disappearance in the electronic spectra of the additional band, which we ascribe to an  $n \rightarrow \pi^*$  transition. The hypsochromic or bathochromic shift of the first long-wave band, which corresponds to a  $\pi \rightarrow \pi^*$  transition, is probably the result of the combined manifestation of protonation in the macroring and in the 1,4-dithiacyclohexene rings; these processes, taken separately, should lead to opposite shifts.

As in the case of phthalocyanines [4], the coordination of metal ions with  $H_2TDTP$  leads to a hypsochromic shift of the long-wave absorption band, as evidenced by the results of measurements of the spectra of II-XVII in  $\alpha$ -chloronaphthalene (Table 1). Unfortunately, the insolubility of  $H_2TDTP$  in other organic solvents did not allow us to trace this tendency in DMFA and DMSO.

TABLE 1. Positions of the Absorption Bands in the Electronic Spectra and Conductivities of H<sub>2</sub>TDTP and Its Metal Complexes

Compound	$\lambda$ , nm				$\sigma$ , $\Omega^{-1} \cdot \text{cm}^{-1}$
	DMFA	DMSO	$\alpha$ -chloronaphthalene	H <sub>2</sub> SO <sub>4</sub>	
I	—	—	709; 625; 523; 360	698; 465	$1.0 \cdot 10^{-11}$
II	—	—	668; 525; 415	715; 435	—
III	665; 602; 525; 368	667; 546; 372	—	735; 437	$2.4 \cdot 10^{-11}$
IV	660; 602; 527; 385	667; 540; 371	670; 606; 535; 374	—	$4.5 \cdot 10^{-11}$
V	666; 602; 535; 385	671; 540; 385	668; 600; 525; 408	—	$1.9 \cdot 10^{-10}$
VI	—	637; 357	—	667; 465	$5.5 \cdot 10^{-10}$
VII	—	640; 345	645; 528; 352	705; 463	$3.0 \cdot 10^{-10}$
VIII	—	—	667; 589	676	$6.0 \cdot 10^{-10}$
IX	684; 570; 424	692; 570; 427	707; 637; 535; 422	705; 455	$3.4 \cdot 10^{-11}$
X	—	697; 557; 368	—	674; 460	$7.0 \cdot 10^{-9}$
XI	667; 547; 380	671; 550; 380	690; 544; 405	688; 450	$5.0 \cdot 10^{-11}$
XII	669; 578; 383	673; 581; 379	690; 667; 595; 385	705	$6.0 \cdot 10^{-11}$
XIII	662; 505; 357	666; 510; 375	—	700	—
XIV	678; 535; 382	680; 541; 383	690; 560; 370	705; 445	$1.6 \cdot 10^{-10}$
XV	675; 555; 377	670; 555; 380	—	655; 445	—
XVI	680; 553; 367	685; 550; 368	700; 575; 360	678; 450	$1.9 \cdot 10^{-9}$
XVII	680; 530; 360	672; 534; 366	687; 538	652; 435	—

The reason for the hypsochromic shift is probably the absence of degeneracy of the electronic transitions in the first absorption band of free H<sub>2</sub>TDTP [4].

It should be noted that in the case of concentrated sulfuric acid both a bathochromic shift and a hypsochromic shift of the long-wave absorption band are observed on passing from H<sub>2</sub>TDTP to its metal complexes (Table 1). This peculiarity should be explained by a difference in the manifestation of the electronic effects of coordination as a function of the nature of the ion-complexing agent [5].

The positions of the absorption bands in the spectra of metal complexes Cl<sub>0-2</sub>MTDTP in the same organic solvent are determined by the nature of the metal, viz., by the size of the atom and its electronic structure. Thus, as compared with the complexes of other metals, an appreciable bathochromic shift of the first long-wave absorption band (to 50 nm) is observed in the spectra of the complexes with lead, tin, indium, and zirconium. This should be explained by the special geometry of their molecules. It is known that the atomic radii of lead, tin, indium, and zirconium (1.5–1.6 Å) exceed the radius of the coordination "window" of the tetrapyrrole ligands (1.35 Å). In contrast to metal complexes, the radii of the metal atoms in which are commensurable with the coordination "window" of the macrocyclic ligand, the metal atoms in complexes IX, X, XVI, and XVII therefore deviate from the plane of the molecule. The special position of the metal, as well as the presence of extra ligands, promotes polarization of the  $\pi$ -electron cloud of the macroring and, consequently, draws together the energy levels of the  $\pi$  electrons in the ground and excited states.

One's attention is directed to the decrease in the degree of resolution of the spectra of H<sub>2</sub>TDTP and its metal complexes as compared with phthalocyanine and metal phthalocyanines (Fig. 1); this is a sign of the presence of associated molecules in solution. This fact, as well as the slight solubility and the inability of the complexes to melt and sublime, is a consequence of intensification of intermolecular interaction due to the presence of sulfur atoms along the periphery of the molecules.

Tetra(1,4-dithiacyclohexeno)porphyrzine and its metal complexes have semiconductor properties. As in the phthalocyanine series, the specific electrical conductivities of pellets of the compounds increase on passing from the free ligand H<sub>2</sub>TDTP to its metal complexes from  $10^{-11}$  to  $10^{-9}$   $\Omega^{-1} \cdot \text{cm}^{-1}$  (Table 1). The substantial increase in the electrical conductivity that is characteristic for metal phthalocyanines [6, 7] is not observed on passing to complexes of H<sub>2</sub>TDTP with tri- and tetravalent metals. This may be associated with a decrease in the degree of coplanarity of the molecules, as evidenced by the construction and analysis of Stuart-Briegleb models, and with the formation of looser packing as a consequence of this.

#### EXPERIMENTAL

The electronic absorption spectra of the investigated compounds in  $\alpha$ -chloronaphthalene, dimethylformamide (DMFA), dimethyl sulfoxide (DMSO), and sulfuric acid were recorded with a

Specord UV-vis spectrophotometer at 20°C over the range 330-760 nm. The concentration of the solutions was  $10^{-5}$  M. The specific electrical conductivities were determined from data obtained from measurements made with direct current. The measurements were made with pellets pressed under a pressure of  $10^8$  Pa, to which silver electrodes were applied by vacuum deposition. The configuration of the electrodes and the methods used for the measurements provided for the elimination of surface currents [6]. Prior to the measurements, the samples were heat treated at 420°K in vacuo ( $10^{-3}$  Pa) for 4 h.

Compounds I-XVII were obtained by the methods in [1]. Dichlorozirconium phthalocyanine was synthesized by a known method [8].

#### LITERATURE CITED

1. G. P. Shaposhnikova, V. P. Kulinich, Yu. M. Osipov, and R. P. Smirnov, Summaries of Papers Presented at the 4th All-Union Conference on the Chemistry and Application of Porphyrins [in Russian], Erevan (1984), p. 80.
2. B. P. Lever, *Inorg. Chem. Radiochem.*, 7, 68 (1965).
3. B. D. Berezin, Coordination Compounds of Porphyrins and Phthalocyanines [in Russian], Nauka, Moscow (1978), p. 68.
4. G. P. Gurinovich, A. N. Sevchenko, and K. N. Solov'ev, Spectroscopy of Chlorophyll and Related Compounds [in Russian], Nauka i Tekhnika, Minsk (1968), p. 189.
5. B. D. Berezin, V. N. Klyuev, and A. B. Korzhenevskii, *Izv. Vuzov. Khim. Khim. Tekhnol.*, 20, 357 (1977).
6. F. Gutmann and L. E. Lyons, *Organic Semiconductors* Wiley Interscience, New York (1967).
7. G. P. Shaposhnikov, V. F. Borodkin, M. I. Al'yanov, M. I. Fedorov, V. A. Shorin, and F. P. Snegireva, in: *Organic Semiconductors* [in Russian], M. V. Kurik (ed.), Kiev (1976), p. 44.
8. V. E. Plyushchev, L. P. Shklover, and I. A. Rozdin, *Zh. Neorg. Khim.*, 9, 125 (1964).

#### SYNTHESIS, STRUCTURE, AND TRANSFORMATIONS

##### OF 1-AZA-3-OXA-7-THIABICYCLO[3.4.0]NONAN-2-ONE

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1-Aza-3-oxa-7-thiabicyclo[3.4.0]nonan-2-one was obtained by reduction of 3,4-dimethoxycarbonyltetrahydro-1,4-thiazine. The reduction of this product with lithium aluminum hydride led to 3-hydroxymethyl-4-methyltetrahydro-1,4-thiazine. The molecular and crystal structures of 1-aza-3-oxa-7-thiabicyclo[3.4.0]nonan-2-one were investigated by x-ray diffraction analysis.

It has been previously shown that the reduction with sodium borohydride of diesters I and II, obtained by alkylation of methyl tetrahydro-1,4-thiazine-3-carboxylate with methyl chloroacetate and methyl acrylate, leads to the formation of the corresponding diols III and IV [1] (see scheme on following page).

However, the reduction of diester V, obtained from methyl tetrahydro-1,4-thiazine-3-carboxylate and methyl chloroacetate, with sodium borohydride under similar conditions did not lead to the formation of the corresponding diol. The PMR spectrum of the only product (VIII) did not contain the broad singlets that are characteristic for the protons of hydroxy groups. In addition, the IR spectrum of VIII does not contain bands of stretching vibrations

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