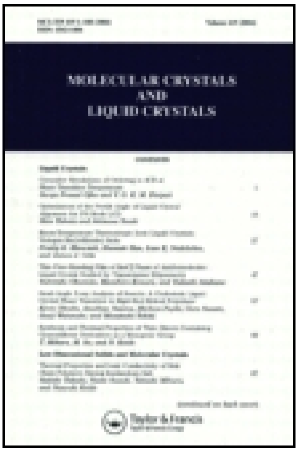

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THE MOLECULAR AND SUPRAMOLECULAR STRUCTURE OF METALLOORGANIC LYOTROPIC MESOGENS

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Abstract On the basis of data in literature and those obtained from our experiments we have analysed the influence of metal in the structure of rod-like and discoid amphiphilic molecules on their lyotropic mesomorphism.

Keywords: lyomesophase, phthalocyanine derivatives, discoid amphiphiles, porphine derivatives

INTRODUCTION

A study of the influence of different chemical structures of mesogen molecules on their liquid crystal properties has been one of the most important branches of research in the sphere of mesomorphism.

The structure of rod-like amphiphiles and their liquid crystal properties has been the subject of intensive study by different investigators for many years. The conventional mesogene of this type is represented by a polar head and a long hydrophobic tail. Cationgenic surface active substances in the polar part, usually contain Li^+, Na^+, K^+, Rb^+ or Cs^+, as counterion . These are all metals of the main subgroup of group I of the periodic system of chemical elements, known as the alkaline metals. All of them are monovalent and have one electron each in the external electronic layer. Nevertheless, replacing one cation from this type by another one in molecules with an identical hydrophobic fragment already exerts influence on the micelle stage of generation.

It has been established that for K^+, Na^+, Li^+, in carboxylates with identical length of the hydrocarbon fragment a decrease of cmc_2 is observed. This decrease also correlated with a change in the concencration of hexagonal phase formation[1].

When cooled, hydrated salts of fatty acids also behave in different ways: lithium and sodium soaps do not gel phases[2].

A comparison of the mesomorphic properties of Li and Cs salts, which in their structure contain a fluoride carbon chain, shows that caesium salts form bilayer aggregates in water, while lithium salts produce cylindrical aggregates. The difference is explained by the low energy hydration of caesium ions in contrast to the high energy hydration of lithium ions. This naturally leads to a difference in the magnitude of hydrophilic-hydrophobic balance[3].

Practically speaking, questions concerning the influence of the nature of the metal in the molecule of a discoid lyotropic mesogen on the manifestation of lyotropic mesomorphism have not been investigated. The object of our work has been to study the influence of the nature of metal, as complex generator, on the lyotropic mesomorphism of metal-complex derivatives of phthalocyanine and porphine.

MATERIALS AND METHODS

The synthesis of carboxide derivatives of phthalocyanine and their metal complexes was carried out according to B. Berezin[4]. The synthesis of sulphate derivatives of tetraphenyl porphines and their sodium salts was realised by the sulphatization of tetraphenyl porphines with a surplus of chlorsulphuric acid. We precipitated a mixture of tetra-, tri-, and possibly di- and monosulphoacids of tetraphenyl porphine in a 100 fold surplus of acetone[5].

The final isolation of tetrasulphophenyl porphine was carried out chromatographically. The product was identified according to spectral data and the results of paper chromatography.

Absorption spectra were studied on UV VIS Zeiss spectrophotometer. IR- spectra were recored on Specord 75 IR.

A sandwich-cell with thickness 1.0 mm was used for X-ray structural research. Samples were non-aqueous model systems and aqueous systems of carboxyderivatives phthalocyanine and sulphoderivative of porphine. Nickel filtered Cu Kα X-ray radiation (α = 0.154 nm) from a BSV- 24 X-ray tube (operating at 40 kV and 20 mA) was collimated by three slit collimators. The distances from sample to detector were 43.2 and 106.5 cm.

Optical polarization microscopy observations in the temperature region of 293-373 K were done with a MIN-8 microscope.

RESULT AND DISCUSSION

The number of lyotropic discoid mesogens synthesized up to the present time is not great. However, we share N. Boden's thesis that there is no dramatic difference between thermotropic and lyotropic mesogens. By introducing the hydrophylic group into the composition of thermotropic mesogens, it is possible to obtain new classes of lyotropic mesogens[6]. A survey of classes of synthesized thermotropic discoids shows that a considerable part are represented by metallorganic compounds[7,8].

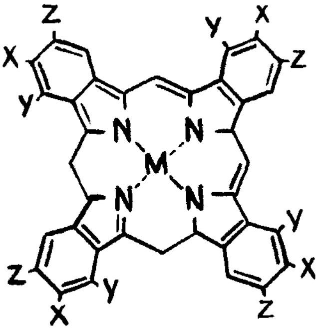
They are the following: derivatives of porphine , phthalocyanine , bis-p-n-alkylbenzoilmethanates of copper and bis-dithiolenes . On the whole the presence of a metal atom imparts interesting electrophysical properties to the mesophase [7] .

We chose to synthesize metal-complexes not containing extensive aliphatic or ethylenoxide tails, substituting them with carboxyl or sulphate clusters.

Potential mesogens of a phthalocyanine nature are represented in Table 1.

As the table indicates, derivatives differ in electronic structure and the valence of the metal-complex generator, and also in the number and position of the substitute.

Table 1 Potential mesogenes of a phthalocyanine nature.

STRUCTURAL FORMULA	N	METAL (M)	SUBSTITUTE			MESOGENIC PROPERTIES
			X	y	Z	
	I	Cu^{2+}	-COOH	-H	-H	+
	II	Cu^{2+}	-COONa	-H	-H	+
	III	Cu^{2+}	-COOH	-H	-COOH	+
	IV	Co^{2+}	-COOH	-H	-H	+
	V	Co^{2+}	-H	-COOH	-H	-
	VI	Al^{3+}	-COOH	-H	-H	-
	VII	Al^{3+}	-H	-COOH	-H	-
	VIII	Zn^{2+}	-COOH	-H	-COOH	+
	IX	Zn^{2+}	-COOH	-H	-H	+
	X	$2H^{+}$	-COOH	-H	-COOH	+
	XI	Cu^{2+}	-H	-COOH	-H	+

The basic structural element of the lyotropic mesophase is not a molecule, but a supramolecular ensemble. This is its essential difference from the thermotropic mesophase. One of the manifestations of the generation of such ensembles must be the associative processes in diluted solutions. They may be determined according to spectral characteristics. It was found that carboxy-derivatives of phthalocyanine disolve poorly in water (pH 6,5). Disolution improves with the addition of ammonia or alkaline NaOH. These additions increase the proton-acceptance properties of the solvent[9] .

We investigated the absorption spectrums of carboxy derivatives of phthalocyanine and its metal complexes in aqueous alkaline solutions with a concentration range of 10^{-5}- 10^{-7} mol/l. We studied the influence of temperature, in the range from 290 - to 353 K, non-ionogenic surfactants and urea on the processes of association. Further, we compared the results obtained with the spectra of these substances in organic solvents.

Working with dilute solutions made it possible to establish the fact that a metal-complex generator influences associative processes and the dependence of solubility on the pH of the solvent .

Taking the spectral investigation data as a basis, we constructed a summary diagram of the dependence of the intensity of the first absorbtion band on the pH of the aqua-ammonia system. The concentration of the substance was kept constant. This made it possible to reveal two types of behavior . Optimum solubility at pH 11 is observed in derivatives of ligand and copper complex of phthalocyanine, regardless of the number of carboxyl groups - four or eight (Figure 1)

A progressive increase of first band absorbtion with the growth of pH is observed in derivatives of phthalocyanine with coordinationally unsaturated and trivalent metals.

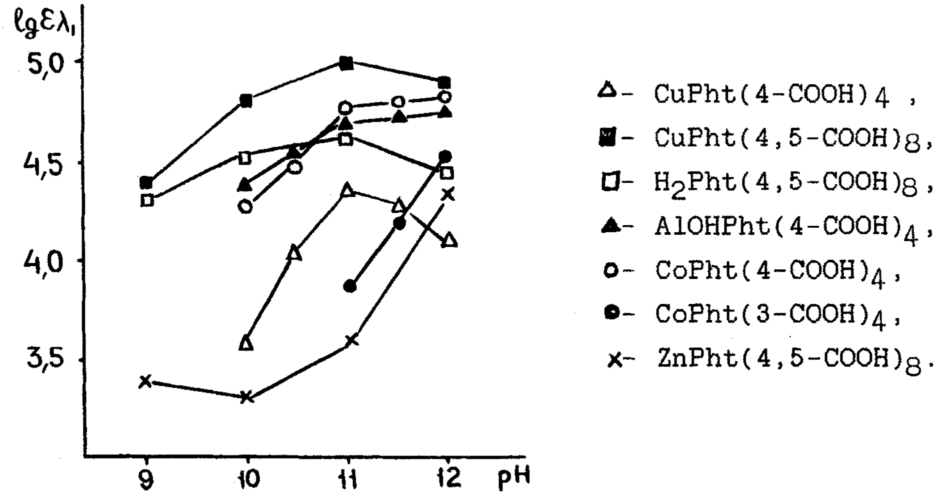


FIGURE 1 The influence of pH system $H_2O\text{-}NH_4OH$ on the intensity of the first absorption band of MPht-carboxy derivatives.

A substitution in the third position moves the range of solubility in the direction of high pH values.

Octasubstitution extends the range of solubility in comparison with tetrasubstitution at lower pH values.

The presence and stability of associates in diluted solutions depends to a considerable extent on the metal complex generator. Dimers and higher associated forms are observed in compounds I - IV and VII - XI in solution. These associates are particularly stable in copper complex. They are not destroyed by the action of temperature and the addition of surfactants.

A V - VII compound in solution is found in a monomolecular form or else forms oxodimers.

The most likely type of interaction of phthalocyanine derivatives in an associate is the interaction of plane - to plane. In this connection there is the possibility of ensemble formation of the columnar type (a stack of coins). The process of solvation takes place on account of the hydrophyl environment of the macrocycle. Intermolecular interaction is ensured by the overlapping of electron clouds of π- conjugated systems and the establishment of hydrogen bonds along the column of molecules.

In coordinationally unsaturated metal complexes, along with solubility due to disassociation of carboxylic groups, additional solvation of the metal complex generator (extracoordination) of the solvent takes place.

Probably precisely that contribution favors the transition $Co(II)Ph(4\text{-}COOH)_4$ and $Zn(II)Ph(4,5\text{-}COOH)_8$ to monomolecular form with high pH values. This contribution is the cause of an increase in the solubility of trivalent complexes Co^{3+} and Al^{3+}:$CoOH(III)Ph(3\text{-}COOH)_4$, $AlOH(III)Ph(4\text{-}COOH)_4$ and $AlOH(III)Ph(3\text{-}COOH)_4$ with an increase in pH value.

Together with the main longwave range in the series of systems inclined to association, there appears an additional stratum which testifies to the thread-like polymerization of pigment molecules.

The tendency to association and the spectral display of thread-like polymerization are the precondition for the existence of lyotropic mesophases in the systems of compounds I - IV and VII - XI.

Actually, in alkaline solution of the given substances in a definite concentration and temperature range, two types of textures are observed optically: nongeometrical grainy and schlieren.

On the basis of the structural similarity of the central part of a molecule with thermotropic discoids, a supramolecular packing of the stack - of - coins type was assumed.

The presence of schlieren and grainy texture raised the question of a possible similarity of supramolecular ensembles and lyomesophases of N- and M phases of the chromonictype as well.

As T. Attowood did with respect to lath form pigments[10] , we made a comparison of the textures, phases, transitions and the structure of the mesophases obtained with phases of disodium salts of chromoglycate for the purpose of proving the chromonic nature of the phases.

The structure of supramolecular ensembles was investigated in contrast to non-aqueous forms of mesogens. Their X-ray photographs featured five sharp circular reflexes varying in size, and a halo, with a 2.9-3.4 nm period.

The data of infra-red spectroscopy did not clarify the question of whether compounds are found in the α or β polymorphic form. This is connected with the fact that the new functional groups brought about a change in the IR-spectrum in comparison with nonsubstituted phtalocyanines. On the basis of an X-ray structural data analysis and the construction of a model of supramolecular packing, the preservation of the α- form was assumed. On the basis of this assumption, the calculation of the structural parameters of the crystalline grating for a copper complex of tetracarboxy phthalocyanine for example constituted a- 3.08, b- 0.38 and c- 2.76 nm. In the elementary cell there are four molecules of copper complex. During dissolution in an alkaline medium, there is a possible formation of associates on account of overlapping clouds of

π - conjugated systems and on account of hydrogen bonds along the column of molecules. Carboxyaniones take part in the formation of the latter.

Interaction along the stack of discoid molecules is considerably stronger then on the plane of the molecular network. The introduction of a solvent for the most part goes along the hydrophylic periphery of the columns assuring the preservation of supramolecular packing of the stack of coins type (Figure 2).

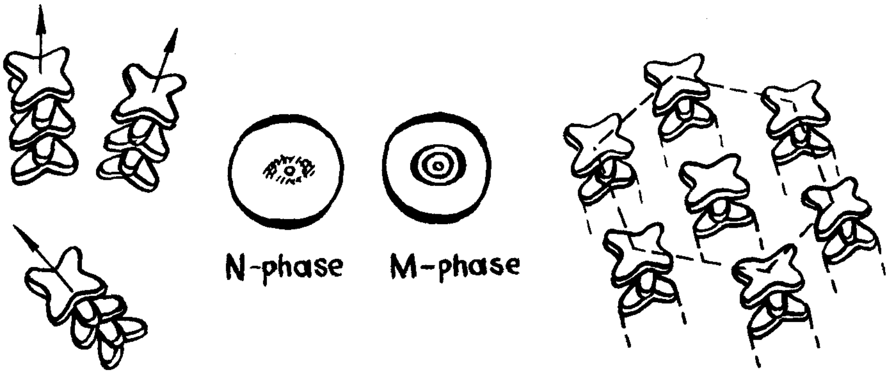
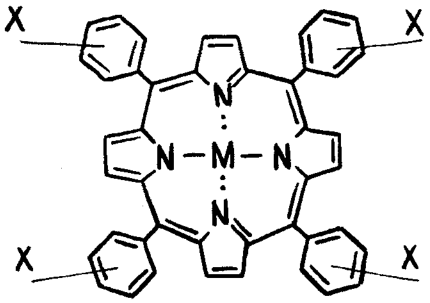


FIGURE 2 The scheme of X-ray data and supramolecular packing of carboxyphthalocyanine derivatives in lyotropic liquid crystal phases.

As a result, the conditions are created for the formation of large supramolecular aggregates having an orientational or orientational and translational order sufficient for the realization of a mesomorphic state.

The diffraction patterns obtained in the analysis of the lyomesophase proved to be analogous to the N- and M- phases of pigments of the chromonic type. In the case of the N- phase there are two ring reflexes: one acute with a period of 0.34 - 0.36 nm and one blurred internal reflex with a period of 4.0 - 6.0 nm. In the case of M- phases, there are two acute internal reflexes with the proportion of $1:1/\sqrt{3}$, which confirms the presence of a hexagonal network. With changes in concentrations and temperatures phase transition in systems of derivatives of phthalocyanines I-IV and VII-XI proved to be similar to those described for disodium salts of chromoglycate.

The sulphate derivatives of tetraphenylporphine that we investigated are represented in Figure 3. By analogy with derivatives of phthalocyanine, we made a selection of the optimal pH solvent, analyzed the absorbtion spectrums of diluted solvents and determined the structural characteristics in the lyomesophase and the solid phase.



X_1 - SO_3H,
X_2 - SO_3Na,
$M_1 = 2H^+$, $M_2 = Co^{3+}$,
$M_3 = Zn^{2+}$.

FIGURE 3 The structural formula of tetraphenyl porphine derivatives.

As a result of the investigations carried out, it was found that the ligand its sodium salts and Ni^{2+} complex form lyomesophases. A complex with Co^{3+} does not form lyomesophases.

Analogously with carboxy derivatives of phthalocyanine, it was determined initially that molecule packing in the solid phase is possible. The structural similarity of the central fragments of phthalocyanine and porphine molecules gives rise to the idea of a similarity in their supramolecular organization.

On the basis of the data obtained from X-ray structural analysis of the solid phase of tetraphenylporphine and its sodium salts and the construction of structural chemical models and their supramolecular packing, we established that sulfoderivatives of tetraphenylporphine resemble the β-form.

The lateral projection of the non-intersecting parts of molecules is represented in Figure 4 .

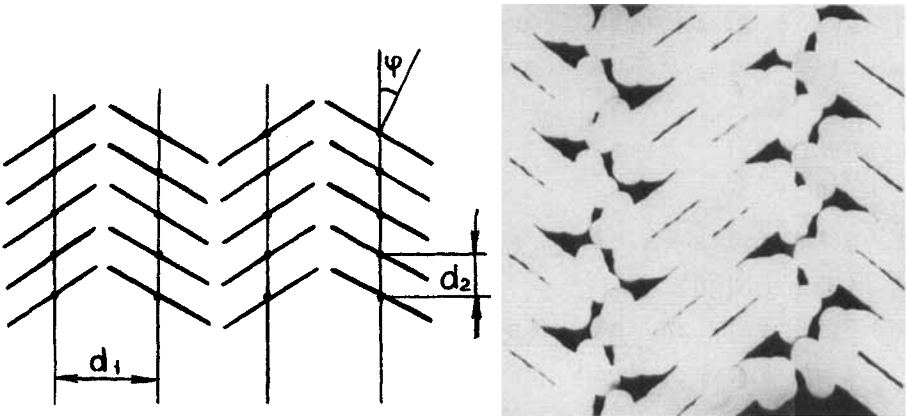


FIGURE 4 The scheme of supramolecular packing of tetraphenyl porphine derivatives.

With such a packing, similarly to phthalocyanines, the interaction of macrocycles along the columns is stronger than on their peripheries. In that case, the introduction of a solvent must also go along the hydrophyl periphery, supporting the structure of the columns, which are the basic units of lyomesophases, with hydrogen bonds.

In the case of a complex with Co^{3+} , the columnar structure is destroyed because of extracoordination, and the lyomesophase is not formed.

On the basis of the data of polarization microscopy and an X-ray structural analysis of the lyomesophase, the formation of sulphate derivatives of tetraphenylporphine may be regarded as N- and M phases of the chromonic type.

Thus, ligand and metal complexes of carboxy derivatives of phthalocyanines and of sulphate derivatives of tetraphenylporphine - (a molecule without extensive lateral substitutes) - may form lyomesophases of the chromonic type. The character of a metal-complex generator in the structure of molecule exert a decisive influence on lyomeso properties. Complexes with trivalent metals of lyomesophases are not formed.

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