Translated from *Uspekhi Khimii*, 54, 239-251 (1985) U.D.C. 541.49; 546.15; 547.682.1

Conducting Compounds Based on Phthalocyanine Derivatives

V.B.Zhukhovitskii, M.L.Khidekel', and K M.Dyumaev

The methods of synthesis and the physicochemical properties of partly oxidised metallophthalocyanines and porphyrins are surveyed and described systematically. Special attention has been devoted to the electrical conductivities of these compounds and also to the analysis of the influence of various factors on the latter.
The bibliography includes 93 references.

CONTENTS

I. Introduction 144
II. Synthetic metals based on partly oxidised phthalocyanines 145
III. Synthetic metals based on partly oxidised porphyrins 146
IV. Film and polymeric conducting materials based on phthalocyanines 147

I. INTRODUCTION

The first organic metals, compounds in which electron transfer in the solid phase takes place via the organic component of the molecule, were first obtained in the 1960's. These substances are of considerable scientific and practical interest[1,2] and naturally a new field devoted to them, combining the methods of organic chemistry and solid state physics, has developed rapidly. The principal requirements which must be met in the specific synthesis of organic metals, the methods of their preparation, as well as their properties and structure have been examined in a number of investigations (see, for example, Refs.3–9).

The presence of the metallic state was first demonstrated rigorously for the quinolinium–TCNQ and *N*-methylphenazinium-TCNQ compounds, where TCNQ is tetracyanoquinodimethane.[10] The electrical conductivities σ of these complexes at room temperature are approximately $10^2\ \Omega^{-1}\ cm^{-1}$ and their temperature variation in the range 200–300 K is of the same character as for metals. A remarkable property of these complexes is an anomalously high dielectric constant.[11] Even higher values of σ, amounting to $2 \times 10^3\ \Omega^{-1}\ cm^{-1}$, have been observed in the tetrathiofulvalene–TCNQ[12] and (tetrathiotetracene)$_2$ I_3 [13] systems. In this case the metallic state is stable down to 40–60 K. It has been possible to stabilise the metallic state to the very lowest temperatures for the first time in the hexamethylenetetraselenofulvalene–TCNQ,[14] (tetraselenotetracene)$_2$Br, and (tetraselenotetracene)$_2$Cl [15–17] compounds. An important advance in this field has been the synthesis of organic superconducting systems: $(TMTSF)_2PF_6$, $(TMTSF)_2AsF_6$, and $(TMTSF)_2ClO_4$, where TMTSF is tetramethylenetetraselenofulvalene, and also bis(ethylenedithiolo)-tetrathiofulvalene iodides.[6,18–21] The conduction in all these compounds takes place in the organic component of the complexes. The organic component is also conducting in partly oxidised polymers with a system of covalent bonds.[5,22]

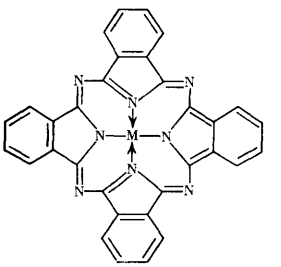
On the other hand, a class of partly oxidised inorganic complexes, exhibiting a conductivity of the metallic type [for example, $K_2Pt(CN)_4Br_{0.3}.3H_2O$] is known.[1] The molecules of these compounds have a square-planar structure and electron transfer in their specimens takes place via the metal–metal bond.

It has been found in recent years that conductivity of the metallic type obtains also in coordination compounds–partly oxidised phthalocyanines and their analogues. There are several possibilities for electron transfer in these substances: via the organic ligand with a branched system of conjugated bonds, via the complex-forming metal ion, and via the oxidant.

The aim of the present review is to survey the available data on the metal complex phthalocyanines and porphyrins exhibiting metallic properties and also to discuss the possibilities for further research in this field in order to obtain complexes with a high conductivity.

The electrical properties of phthalocyanines began to be investigated a fairly long time ago. In 1947 Eley and Vartanyan found independently that metal derivatives of phthalocyanines are semiconductors.[23] Extensive studies on the physicochemical properties of these macrocyclic compounds were then initiated. Interesting data in this field have already been obtained at the present time, particularly as regards the dark conductivity and photoconductivity of phthalocyanines and the influence on the latter of various chemical and physical factors.[24–29] The dependence of the conductivity on the temperature and pressure[22,30] and the role of the metal and of the adsorption of oxygen[31–37] and other gases[28,36] have been investigated and the infrared, ultraviolet, and EPR spectra of phthalocyanines have been examined; many of them have been studied by X-ray diffraction;[23,24,27,38–44] the electronic structure of phthalocyanines and the mechanism of the conduction in the latter have been discussed.[23,24,28,44–46] Phthalocyanines have been proposed as promising photoconductors for use in photocells with a blocking layer, as sensitisers for inorganic semiconductors, and as thin-film electrodes.[45,47]

The synthesis of phthalocyanines with metallic and not semiconducting properties has arisen as a new stage; this was achieved by synthesising partly oxidised phthalocyanines and their analogues.[48–50]



metallophthalocyanine

Partial oxidation of various phthalocyanines and porphyrins leads to a new class of highly conducting organic compounds. A characteristic feature of their crystal structure is the presence of regular stacks consisting of electron donors and

acceptors. The distances between the molecules in the stacks comprising the donors are significantly smaller than the van der Waals distances and considerably smaller than the distances between the stacks themselves. As a result, the conducting electron system in such compounds is quasi-one-dimensional. The electrical conductivity is markedly anisotropic; it is a maximum along the long axis of the crystal and is smaller by several orders of magnitude in the transverse direction.

The salts $NO(BF_4)$ and $NO(PF_6)$,[51] tetracyanoquinodimethane,[52] chloranil, bromanil, and molecular bromine and iodine[53–59] have been used as reagents for the partial oxidation of phthalocyanines and porphyrins. Elemental iodine proved to be the most suitable oxidant; the reason for this selectivity is that iodine forms a large number of reduced species (I^-, I_3^-, I_5^-), which enables the donor systems to acquire the most favourable degree of partial oxidation. In addition, all three forms of reduced iodine are comparatively easy to identify by Raman spectroscopy.[60,61]

Metallophthalocyanines (MPc) and metalloporphyrins are oxidised under identical conditions. The reactions are reversible and the equilibrium is displaced towards the starting materials on heating the dry product *in vacuo*.[62]

$$MPc + (x/2)I_2 \rightleftharpoons MPcI_x$$

M = Fe, Co, Ni, Cu, Pt, H_2, Al, Ga, Ge, Sn, Si, Pb, REE

(lanthanide elements)

Table 1. The conductivities of pressed polycrystalline $MPcI_x$ specimens at 300 K.[49,53,62]

Compound	x	σ, Ω^{-1} cm^{-1}	E_a, eV
$CuPcI_x$	1.71	4.2	0.0121
$PtPcI_x$	0.93	2.4	0.016
H_2PcI_x	2.2	2.3	0.040
$NiPcI_x$	0.00	$1\cdot10^{-11}$	1.6
$NiPcI_x$	0.56	0.7	0.024
$NiPcI_x$	0.58	2.2	—
$NiPcI_x$	1.00	0.7	0.036
$NiPcI_x$	1.07	7.7	—
$NiPcI_x$	1.44	7.7	—
$NiPcI_x$	1.68	0.8	0.021
$NiPcI_x$	3.81	0.6	—
$CoPcI_x$	0.00	$2\cdot10^{-10}$	1.6
$CoPcI_x$	0.60	0.1	0.065
$CoPcI_x$	1.00	0.06	0.082
$FePcI_x$	0.00	$2\cdot10^{-10}$	—
$FePcI_x$	1.93	$4\cdot10^{-3}$	0.127
$FePcI_x$	2.74	$2\cdot10^{-3}$	0.070
$FePcI_x$	3.85	$1\cdot10^{-4}$	0.254
H_2Pc-chloroanil	—	10^{-2}	—

II. SYNTHETIC METALS BASED ON PARTLY OXIDISED PHTHALOCYANINES

Methods of synthesis of polycrystalline and single crystal specimens of partly oxidised phthalocyanines have now been developed. In order to obtain the polycrystalline forms, powdered metallophthalocyanines are mixed with iodine in chlorobenzene; iodinated phthalocyanines are collected by centrifugation, washed with hexane, and dried in an inert atmosphere. The products are black polycrystalline substances with different stoichiometries; the conditions of synthesis have been described.[62]

$NiPcI_{1.0}$ single crystals are grown in an H-shaped tube by the diffusion method from solutions of NiPc and iodine either in 1,2,4-trichlorobenzene or in 1-chloronaphthalene.[50] The iodination of NiPc single crystals does not lead to $NiPcI_x$ single crystals, since the formation of a complex entails the impairment of the structure and decomposition of the crystal. The Raman spectra of $NiPcI_x$ exhibited an intense absorption at 107 cm^{-1}, which is characteristic of the polyiodide I_3^-. Bands due to I_2 or I_5^- (212 and 167 cm^{-1} respectively) were not detected in the spectra, which indicates the absence of these forms from the products.[49,50,60] This finding has also been confirmed by ^{129}I Mössbauer spectroscopy.[49]

The results of measurements of the conductivities of the polycrystalline specimens are presented in Table 1. Such conductivities include effects due to intraspecies contact resistance, but they are nevertheless comparable with those of other organic metals. It is noteworthy that the single crystal conductivities of the organic metals obtained at the present time usually exceed the conductivities of the powder by a factor of 10^2–10^3. In view of this, the data in Table 1 show that the phthalocyanines are promising electron donors for the formation of highly conducting organic molecular crystals.

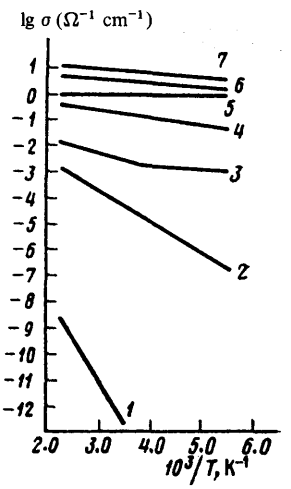


Figure 1. Variation of the electrical conductivities of pressed polycrystalline specimens with $1/T$: 1) CuPc; 2) $FePcI_{3.85}$; 3) $FePcI_{2.7}$; 4) $CoPcI_{0.6}$; 5) $NiPcI_{0.59}$; 6) $PtPcI_{0.93}$.

The temperature variation of the electrical conductivities of the pressed polycrystalline specimens is illustrated in Fig.1, which shows for comparison also the variation of the conductivity of unoxidised polycrystalline copper-phthalocyanine.

The interaction of iodine with $PcLnPc_{ox}$, where Pc_{ox} is the oxidised phthalocyanine ligand and Ln represents tervalent lanthanide elements such as Lu, Y, La, etc., has been investigated. The addition of iodine leads to a sharp increase of the electrical conductivity of the powder. Thus, for Ln = Pr, Sm, or Eu, the conductivities of the pressed specimens of the iodine complexes are higher by one order of magnitude relative to the unoxidised specimens and, in the case where Ln = Tb, Er, Tm, or Lu, the conductivity is higher by 3–4

orders of magnitude.[63,64] Iodinated complexes of di(phthalocyaninato)neodymium(III), i.e. $H[Nd^{III}(Pc)_2I_x]$, exhibit a high conductivity. When $x = 1,3$, the conductivity of the pressed polycrystalline specimen at room temperature is $6.4 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$, whereas for $x = 1.8$ it amounts to $8 \times 10^{-1}\ \Omega^{-1}\ cm^{-1}$.[65] On the basis of these results, the authors[63,64] suggested that iodide ions penetrate into the crystal lattice and form charge-transfer complexes having added to the nitrogen mesoatom of the macroring of the phthalocyanine ligand.

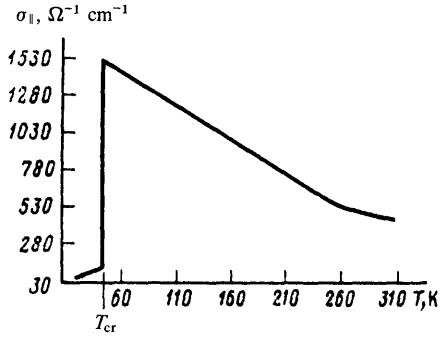


Figure 2. Temperature variation of the electrical conductivity of $NiPcI_{1.0}$ single crystals.[62]

Data on electrochemical transformations and on the conductivity of the products have been reported in the literature.[66,67]

Fig. 2 illustrates the temperature dependence of the electrical conductivity of $NiPcI_{1.0}$ single crystals in the direction of the stacks. At room temperature the conductivity of 65 specimens varied in the range 260–750 $\Omega^{-1}\ cm^{-1}$, the mean amounting to 550 $\Omega^{-1}\ cm^{-1}$. The temperature T_{cr} varies only slightly for different crystals and usually amounts to 90–100 K, although it reaches 52 K for some specimens.[62] When the specimen is cooled to a temperature below T_{cr}, the conductivity falls sharply. Such behaviour is comparable to that of the temperature dependence of the conductivity of the tetrathiofulvalene–TCNQ organic metal and shows that there is a Peierls transition or a first-order transition. The Raman spectra of the specimens show that in this transition the average degree of oxidation of NiPc remains unchanged down to 4 K.[62] The conductivity of the crystals cooled to a temperature below T_{cr} does not return to the initial value when they are reheated to the initial room temperature. On repeated cooling of the specimens, the Peierls transition takes place at a higher temperature T_{cr}.[62]

Later investigations showed that microcracks appear in the $NiPcI_{1.0}$ crystals on cooling. The sharp decrease of conductivity, which has been attributed to the Peierls transition, is in fact associated precisely with this phenomenon. When $NiPcI_{1.0}$ crystals, mounted without mechanical stresses on thin silvered graphite filaments, are cooled, the conductivity increases to a maximum value of $5 \times 10^3\ \Omega^{-1}\ cm^{-1}$ at 25 K (Fig. 3). On further cooling, the conductivity gradually falls, but its value does not tend to zero even at 0.1 K, in contrast to other molecular crystals.[68]

Whereas both in conducting complexes of this kind and in the Krogmann salt $[K_2Pt(CN)_4Br_{0.3}.3H_2O]$ [69] the transport properties may be almost fully attributed to the metal while the ligands play only an indirect role in the electron transfer, in organic metals of the phthalocyanine series the ligands are actually responsible for conduction. The metal ion in such a complex modifies markedly the properties of the ligand but is not involved directly in the transport process itself.[49,60] In the synthesis of a conducting complex the ligand and not the metal is oxidised; electron transport takes place mainly via the highly conjugated π-electron clouds of the ligand. The delocalisation of the charge carriers along the stack of phthalocyanine molecules is indicated by the appearance in the EPR spectrum of a band, narrowed by the exchange interaction between the ligand π orbitals, with a g-factor of 2.032, i.e. close to the g-factor for the free electron.[70,71]

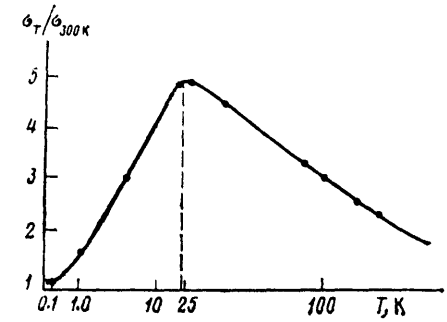


Figure 3. Temperature variation of the electrical conductivity of $NiPcI_{1.0}$ single crystals.[68]

The cross-sectional area of the phthalocyanine molecule is 2.5 times greater than that of the conducting stacks of known organic metals.[49] It is therefore of interest to compare the properties of individual charge carriers in $NiPcI_x$ and other conducting compounds obtained within the framework of the one-electron band theory of activity. According to this theory, the conductivity is related to the free path length λ and to the cross-sectional area of the conducting stack a by the equation[50,62]

$$\sigma = 2e^2\lambda/\pi\hbar a$$

where e is the electronic charge. For $NiPcI_{1.0}$ at room temperature, $\lambda = 3.3$–8.2 Å, which is equivalent to 1.0–2.3 intermolecular distances. These values are comparable to those for other highly conducting quasi-one-dimensional systems; 2.1–2.8 intermolecular distances for (tetrathiotetracene)$_2I_3$; 1.6–2.5 for hexamethylenetetraselenofulvalene–TCNQ; 0.4–0.6 for tetrathiofulvalene–TCNQ; 0.6 for $K_2Pt.(CN)_4Br_{0.3}.3H_2O$; 0.15 for quinoline–$(TCNQ)_2$.[62] Hence one may conclude that the large cross-sectional area of the $NiPcI_{1.0}$ molecules is not the cause restricting the attainment of a conductivity higher than the value obtained.

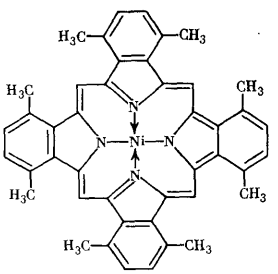
In conclusion one must note that at present there are no literature data for the influence of the crystalline modification of phthalocyanines on the electrical conductivities of their partially oxidised forms, although they would be of considerable theoretical and practical value.

III. SYNTHETIC METALS BASED ON PARTLY OXIDISED PORPHYRINS

The study of organic metals based on porphyrins is of great interest, since their structural wide variety permits a whole series of important conclusions and generalisations. Here we

shall discuss synthetic metals based on nickel 1,4,5,8,9,12, 13,16-octamethyltetrabenzoporphyrinate Ni(OMTBP), nickel tetrabenzoporphyrinate Ni(TBP), metallo-octaethylporphyrins M(OEP), and nickel tetramethylporphyrinate Ni(TMP).

The oxidation of Ni(OMTBP) with iodine in 1,2,4-trichlorobenzene yields, in particular, dark red Ni(OMTBP)$I_{1.08}$ crystals. Oxidation with iodine in chlorobenzene results in the formation, apart from the above crystals, of bronze needles having the composition Ni(OMTBP)$I_{2.0}$. The stoichiometric ratio of these complexes apparently depends on the solvent and the crystal growth conditions, but Ni(OMTBP)$I_{1.08}$ crystals almost always predominate.[60,72,73] The mixture of crystals is separated by physical methods on the basis of the colour and shape of the crystals.



Nickel 1,4,5,8,9,12,13,16-octamethyltetrabenzoporphyrinate

The Raman spectra of these compounds contain bands corresponding to the resonance absorption by the polyiodide I_3^-.[50] The degree of oxidation is 0.36 for Ni(OMTBP)$I_{1.08}$ and 0.97 for Ni(OMTBP)$I_{2.9}$.

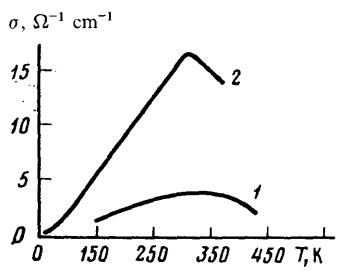
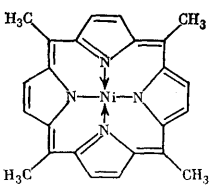


Figure 4. Temperature variation of the electrical conductivity of Ni(OMTBP)I_x single crystals.[50]

The temperature variation of the conductivity in the direction of the stacks is illustrated in Fig. 4 for Ni(OMTBP)$(I_3)_{0.36}$ and Ni(OMTBP)$(I_3)_{0.97}$. On decrease of temperature below 350 K, the conductivity of the complex Ni(OMTBP)$(I_3)_{0.36}$ resembles that of metals. It increases slowly, reaching a maximum at 300 K; when the specimen is cooled, the conductivity diminishes. The temperature variations of the conductivities of Ni(OMTBP)$(I_3)_{0.97}$ and Ni(OMTBP)$(I_3)_{0.36}$ are analogous. Thus a change in the degree of partial oxidation for the Ni(OMTBP) systems leads only to a quantitative alteration of the function $\sigma(T)$ without changing at the same time its qualitative character.[50] The values of σ at room temperature and the shapes of the $\sigma(T)$ curves for NiPc$I_{1.0}$ and Ni(OMTBP)I_x differ markedly from one another, which shows that slight structural changes in the macroring can alter significantly the properties of the organic metal.

Both compounds having the composition Ni(OMTBP)I_x are, as shown above, conducting materials whose crystals are made up of stacks of partly oxidised macrorings in which electron transport is ensured by the ligands. The EPR spectra of the single crystals at different temperature have a line with a g-factor of 2.012.[62] This value is comparable with the analogous parameter for radicals and demonstrates the delocalisation of π electrons in the direction of the ligand stacks. $\lambda = 0.C6$ of the intermolecular distance has been obtained for Ni(OMTBP)$(I_3)_{0.36}$; magnetic susceptibility data and the results of X-ray diffraction analysis have been discussed in two investigations.[50,60] Since only very small crystals of Ni(OMTBP)$(I_3)_{0.97}$ are at present available, it has not been possible to carry out crystallographic studies on this substance.

Diffusion oxidation of Ni(TMP) with iodine leads to acicular Ni(TMP)$I_{1.0}$ crystals.[74] This substance is stable up to 70 °C, losing iodine at a higher temperature. It has been established by Raman spectroscopy that the degree of oxidation of Ni(TMP)$I_{1.0}$ is 0.33.



nickel tetramethylporphyrinate

The iodine chains in the Ni(TMP)$I_{1.0}$ crystals are arranged parallel to the axes of the porphyrin stacks and are located within the channels formed by the methyl and pyrrole hydrogen atoms. The EPR spectrum consists of a narrow anisotropic signal with $g = 2.0067$. The narrow line in the spectrum indicates the oxidation of the ligand:

$$Ni(TMP)I_{1.0} = [Ni(TMP)]^+ + [Ni(TMP)]_2(I_3)^- .$$

The free path length for Ni(TMP)$I_{1.0}$ is equal to 0.5 of the intermolecular distance.[74]

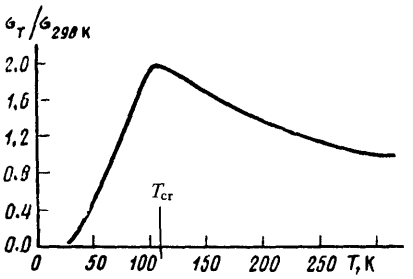


Figure 5. Temperature variation of the electrical conductivity of Ni(TMP)$I_{1.0}$ single crystals.[74]

The temperature dependence of the conductivity of the Ni(TMP)$I_{1.0}$ crystals is illustrated in Fig. 5. The plot shows that, with decrease of temperature from room temperature to $T_{cr} = 110$ K, the conductivity acquires a metallic character; on further reduction of temperature, the conductivity

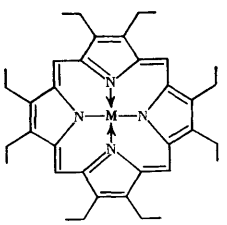
becomes thermally activated. On reheating and recooling of the specimen, hysteresis is not observed.[74]

Apart from the $Ni(TMP)I_{1.0}$ crystals, yet another complex of tetramethylporphyrin has been described, namely Ni(TMP)–TCNQ. Its crystals are made up of alternating donor and acceptor stacks. It has been observed that the infrared spectrum of the complex consists of a superposition of the spectra of the individual compounds. The conductivity of the Ni(TMP)–TCNQ crystals in the direction of their long axis has not been established accurately. It is only known that it does not exceed 10^{-5} Ω^{-1} cm^{-1} at room temperature.[75]

Table 2. The conductivities of polycrystalline $M(OEP)I_x$ specimens at 300 K.[76]

x	σ, Ω^{-1} cm^{-1}	E_a, eV
	$H_2(OEP)I_x$	
5.8	$3\cdot10^{-7}$	—
3.3	$2\cdot10^{-7}$	0.51
3.0	$1\cdot10^{-7}$	—
2.1	$2\cdot10^{-8}$	—
1.1	$1\cdot10^{-8}$	—
	$Cu(OEP)I_x$	
3.5	$6\cdot10^{-3}$	0.16
2.9	$4\cdot10^{-3}$	—
1.3	$4.4\cdot10^{-3}$	0.13
1.2	$3\cdot10^{-3}$	—
0.5	$2\cdot10^{-7}$	—
	$Ni(OEP)I_x$	
5.7	$2.8\cdot10^{-2}$	0.08
3.8	$1.8\cdot10^{-2}$	0.09
1.7	$2.8\cdot10^{-2}$	0.11
1.4	$1.4\cdot10^{-2}$	0.12
1.2	$6\cdot10^{-3}$	0.19
0.4	$1.5\cdot10^{-4}$	0.18

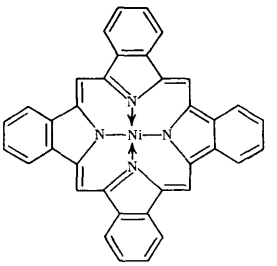
The products of the partial oxidation of metallo-octaethylporphyrins having the composition M(OEP), where M = Ni, Cu, or H_2, are of considerable interest.



metallo-octaethylporphyrin

They are important because the macroring (OEP) has a much less strained structure than in Pc and TBP. The complexes $M(OEP)I_x$ have been obtained by two procedures: the first by heating the complex M(OEP) with a (2–8)-fold excess of iodine for 24 h in an evacuated sealed tube and the second by mixing cooled solutions of M(OEP) and I_2 in chloroform; the product is obtained in the form of bright red single crystals.[76] The Raman spectra demonstrated the presence of iodine in the form of I_5^- (band at 167 cm^{-1}); consequently the degree of oxidation is $\rho = x/5$. The conductivity data for pressed polycrystalline $M(OEP)I_x$ specimens are presented in Table 2. In the course of the partial oxidation of M(OEP) an electron can be removed either from the *d* orbital of the metal or from the π orbital of the porphyrin ligand. ERP data have shown that the preferential oxidation of the ligand takes place,[76] which apparently means that the metals (Ni and Cu) do not play the main role in the conduction process.

A striking example of the fact that insignificant chemical transformations in the molecule entail a significant change in the physical properties of the synthetic metals is provided by the complex $Ni(TBP)I_{1.0}$, which differs from $Ni(OMTBP)I_{1.08}$ by the absence of eight methyl substituents and from $NiPcI_{1.0}$ by the replacement of the nitrogen mesoatoms by methylidyne groups.



nickel tetrabenzoporphyrinate

Raman spectra revealed the presence of an absorption at 107 cm^{-1}, which corresponds to I_3^- and the absence of the bands at 212 and 167 cm^{-1} characteristic of I_2 and I_5^- respectively. Thus the degree of oxidation is $\rho = 0.33$. The temperature dependence of the conductivity of $Ni(TBP)(I_3)_{0.33}$ single crystals is illustrated in Fig. 6. The compounds exhibit metallic properties in the temperature range from 300 to 95 K with a conductivity maximum of 600 Ω^{-1} cm^{-1}. On decrease of temperature below 95 K, $Ni(TBP)I_{1.0}$ becomes a semiconductor. Measurements of the conductivity of 200 $Ni(TBP)I_{1.0}$ single crystals at room temperature showed that $\sigma = 150-330$ Ω^{-1} cm^{-1}.[77] The free path length for $Ni(TBP)\cdot I_{1.0}$ single crystals is 2.1–4.3 Å or 0.66–1.3 intermolecular distances; for comparison, we may note that $\lambda = 60$ Å or 24 intermolecular distances for metallic nickel.[77]

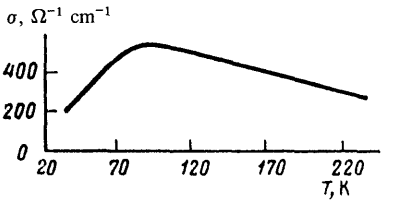


Figure 6. Temperature variation of the electrical conductivity of $Ni(TBP)I_{1.0}$ single crystals.[77]

In contrast to $Ni(OMTBP)I_{1.08}$ and $NiPcI_{1.0}$, in which charge transfer is associated with the delocalised π orbitals of the macroring, $Ni(TBP)I_{1.0}$ is a partly oxidised complex in which charge transport takes place via both the ligands and the complex-forming metal ions. The $[Ni^{II}(TBP)^+]$ cation can undergo electronic tautomerism, being converted thereby into $[Ni^{III}(TBP)]$. Thus the complex $Ni(TBP)I_{1.0}$ is a "connecting link" between purely organic and inorganic conducting coordination compounds. This is confirmed by EPR data. For the majority of the iodinated metalloporphyrins,

the g-factor is independent of temperature and is approximately equal to that for the free electron; the EPR signal is narrow and its width is also independent of temperature, which shows that the charge transfer in $NiPcI_{1.0}$, $Ni(OMTBP).I_x$, and $Ni(TMP)I_{1.0}$ takes place via the ligand. In contrast to this, the g-factor and ΔH for $Ni(TBP)I_{1.0}$ are greater at room temperature and depend markedly on temperature.[78]

IV. FILM AND POLYMERIC CONDUCTING MATERIALS BASED ON PHTHALOCYANINES

The deposition of films of conducting dyes such as phthalocyanines can alter significantly the electronic-optical properties of various materials. Thus the metal-free phthalocyanine is used to sensitise amorphous selenium in xerography and silicon dioxide in the preparation of phototransistors. The efficiency of the operation of solar batteries can be increased by depositing a film of phthalocyanine or porphyrin. The only factor which limits at the present time the employment of these films is their low intrinsic conductivity.[79,80] Oxidation with iodine increases appreciably the conductivity of the film.[79] Fig.7 illustrates the temperature dependence of the conductivity of an $NiPcI_x$ film. Evidently, both after cooling and heating from room temperature, the $NiPcI_x$ film becomes more of an insulator. The decrease of conductivity on heating can be accounted for by the diffusion of iodine; the cause of its decrease on cooling is so far obscure. These data are inconsistent with the temperature variation of the conductivities of analogous complexes measured by Martinsen et al.[68] Iodination of thin PcCo, PcCu, and PcPb films increases their conductivity to 10^{-3}–10^{-1} Ω^{-1} cm^{-1}.[81]

The polymerisation of $M(OH)_2Pc$, where M = Si, Ge, or Sn, at 300–400 °C in a high vacuum (10^{-3} mmHg) (Fig.8) leads to the corresponding phthalocyaninato-polysiloxanes and the corresponding polygermoxanes, and polystannoxanes in satisfactory yields.[82,83] The polymers are stable in air; iodine can be removed by heating *in vacuo* above 100 °C. The degrees of polymerisation are $n_{SiPc} \geq 120$, $n_{GePc} \geq 60$, and $n_{SnPc} \geq 115$. Raman spectroscopy demonstrated the presence of the alloying component in the form of I_3^- together with a small amount of I_5^-. The conductivities of the $\{[M(Pc)O]I_x\}$ polymers vary in the sequence $\sigma_{Si} > \sigma_{Ge} > \sigma_{Sn}$, which is apparently associated with increasing interplanar distances, amounting to 3.33 Å for Si–O–Si, 3.51 Å for Ge–O–Ge, and 3.95 Å for Sn–O–Sn.

The conductivities of the specimens obtained depend on the concentration of the alloying component (Fig.9) and temperature.[82,84] The conductivities of the $\{[M(Pc)O]I_x\}$ polycrystalline species at 300 K are listed in Table 3; they are comparable to the analogous parameters for $MPcI_x$, $M(OMTBP)I_x$, and $M(TBP)I_x$.

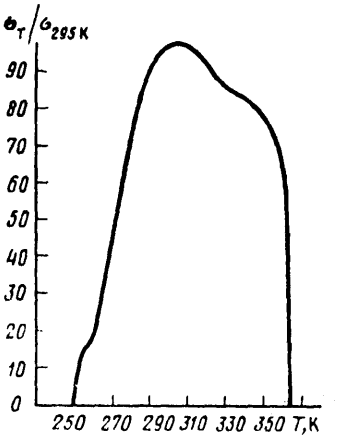


Figure 7. Temperature variation of the electrical conductivity of an $NiPcI_x$ film.[77]

The EPR spectra show that the partial oxidation involves the ligand orbitals without affecting the metal atom.[84] It is known that the single crystal conductivity of quasi-one-dimensional materials in the direction of molecular stacks is usually 10^2–10^3 times greater than the conductivity of polycrystalline specimens. It is therefore possible that the complexes $\{[M(Pc)O].I_x\}_n$, where M = Si or Ge, have metallic properties in the form of single crystals.

Partial oxidation of the quasi-one-dimensional complexes $[Al(Pc)F]_n$ and $[Ga(Pc)F]_n$ with iodine ensures a high conductivity (0.01–0.1 Ω^{-1} cm^{-1}). The iodination of $[M(Pc)F]_n$ was carried out at room temperature, or by keeping $[M(Pc)F]_n$

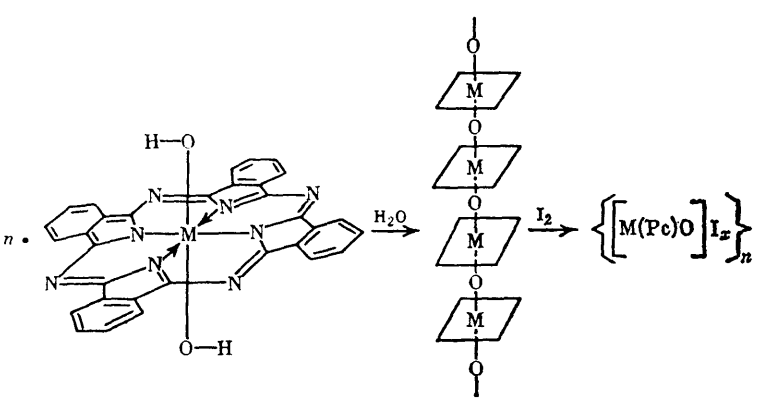


Figure 8. Schematic illustration of the preparation of $\{[M(Pc)O]I_x\}_n$.

in I_2 vapour for 7–21 days until the attainment of constant weight, or by stirring a suspension of $[M(Pc)F]_n$ in a solution of I_2 in hexane for 24 h. Raman spectroscopy demonstrates the presence of I_3^- (the band at 106–108 cm^{-1}) and the absence of I_2 and I_5^-.[85,86] The conductivities of the specimens obtained were measured on discs at 295 K (Table 4).

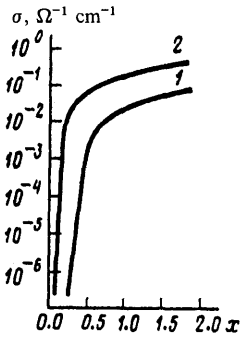


Figure 9. Dependence of the electrical conductivity of $\{[M(Pc)O]I_x\}_n$ on the iodine concentration: 1) M = Si; 2) M = Ge.[84]

Table 3. The electrical conductivities of polycrystalline $\{[M(Pc)O]I_x\}_n$ specimens at 300 K.[84]

Compound	σ, Ω⁻¹ cm⁻¹	E_a, eV
$[Si(Pc)O]_n$	$3\cdot10^{-8}$	—
$\{[Si(Pc)O]I_{0.5}\}_n$	$2\cdot10^{-2}$	—
$\{[Si(Pc)O]I_{1.4}\}_n$	$2\cdot10^{-1}$	0.04
$\{[Si(Pc)O]I_{4.6}\}_n$	$1\cdot10^{-2}$	—
$\{[Si(Pc)O]Br_{1.0}\}_n$	$6\cdot10^{-2}$	—
$\{[Ge(Pc)O]_n$	$<10^{-8}$	—
$\{[Ge(Pc)O]I_{1.8}\}_n$	$3\cdot10^{-2}$	0.08
$\{[Ge(Pc)O]I_{1.9}\}_n$	$5\cdot10^{-2}$	0.06
$\{[Ge(Pc)O]I_{1.94}\}_n$	$6\cdot10^{-2}$	0.05
$\{[Ge(Pc)O]I_{2.0}\}_n$	$1\cdot10^{-1}$	—
$\{[Sn(Pc)O]\}_n$	$<10^{-8}$	—
$\{[Sn(Pc)O]I_{1.9}\}_n$	$1\cdot10^{-6}$	—
$\{[Sn(Pc)O]I_{5.5}\}_n$	$2\cdot10^{-4}$	0.68

The conductivities of $\{[Al(Pc)F]I_x\}_n$ are higher than those of the gallium derivatives for high values of x, which is correlated with the greater interplanar spacings in the Ga polymer compared with the Al derivative and constitutes apparently yet another piece of evidence showing that the conductivity is ensured by the inter-ring overlap of the π orbitals. The highest conductivity obtained is 5 Ω^{-1} cm^{-1} for $\{[Al(Pc)F]I_{3.3}\}_n$; the conductivity of $\{[M(Pc)F]I_x\}_n$ is equal to or even greater than that of the SiO analogues. It is believed,[85,86] that this can be accounted for by the higher purity of $[M(Pc)F]_n$ compared with $[Si(Pc)O]_n$.

A characteristic feature of the structure of $\{[Ga(Pc)F]I_x\}_n$ is that the phthalocyanine rings cover one another, while in other structures they are displaced by an angle of 40° and above (Fig. 10). For this arrangement of the ligands in the stack of $\{[Ga(Pc)F]I_x\}_n$ molecules, a greater degree of overlap of the π orbitals between them should be ensured. This is apparently the explanation of the conductivity of 0.12 Ω^{-1} cm^{-1} of pelleted $\{[Ga(Pc)F]I_{0.93}\}_n$, which is extremely high even when account is taken of the interplanar distance (3.86 Å). For comparison, we may note that the conductivity of $NiPcI_{1.0}$ is 0.7 $\Omega^{-1}cm^{-1}$ for a distance between the molecules of 3.24 Å.[87]

Table 4. The electrical conductivities of polycrystalline $\{[Al(Pc)F]I_x\}_n$ and $\{[Ga(Pc)F]I_x\}_n$ specimens at 295 K.[85,86]

I/Al	σ, Ω⁻¹ cm⁻¹	I/Ga	σ, Ω⁻¹ cm⁻¹
0.00	$1.5\cdot10^{-4}$	0.00	10^{-6}
0.21	$1.8\cdot10^{-2}$	0.17	$1.9\cdot10^{-4}$
0.29	$1.5\cdot10^{-2}$	0.62	$1.7\cdot10^{-2}$
0.38	$2.0\cdot10^{-2}$	0.77	$4.4\cdot10^{-2}$
0.87	0.70	0.97	$7.2\cdot10^{-2}$
1.0	0.13	0.98	$8.6\cdot10^{-2}$
1.5	0.19	2.3	0.15
2.4	0.63	—	—
3.3	5.0	—	—

Among the partly oxidised quasi-one-dimensional complexes Al(Pc)Y and Ga(Pc)Y, where Y = F, Cl, or OH, we may note materials doped with $[BF_4]^-$, $[PF_6]^-$, and $[SbF_6]^-$. Owing to the presence of residual water in the initial phthalocyanine, the exact composition of the product of the oxidation of Al(Pc)OH by $NO[PF_6]$ is not known.[51] The reaction of Al(Pc)F and Ga(Pc)F with $NO(BF_4)$ and $NO(PF_6)$ proceeds rapidly in dry CH_3NO_2 or CH_2Cl_2 with formation of complexes having the composition $[M(Pc)F]Y_x$, where M = Al, Y = $[PF_6]$, and x_{max} = 0.9 or M = Ga, Y = $[PF_6]$, and x_{max} = 0.9. These compounds are thermally stable up to 110 °C; in a stream of dry nitrogen the decomposition begins at 125 °C.

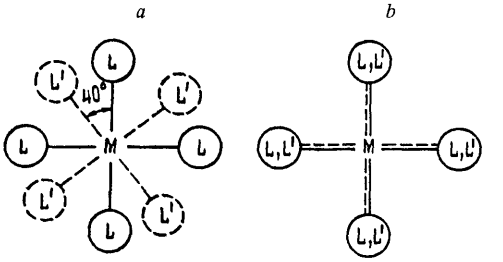


Figure 10. The arrangement of the ligands in the stack: *a*) 40° displacement; *b*) 0° displacement.

A characteristic feature of these compounds is their stability on prolonged exposure to atmospheric oxygen. Thus the conductivity of the complex $\{[Al(Pc)F][PF_6]_{0.59}\}_n$ diminished by 0.1 Ω^{-1} cm^{-1} after it had been kept in air for a month, while that of the complex $\{[Al(Pc)F][BF_4]_{0.44}\}_n$ remained unchanged at 3×10^{-2} Ω^{-1} cm^{-1} after it had been kept for a year in the air. This feature is the opposite of the behaviour of the complexes $[M(Pc)F]_n$ oxidised by iodine,[88] which lose iodine with time. Thus, although the conductivity

of polyfluorometallophthalocyanines oxidised with $NO[BF_4]$ or $NO[PF_6]$ is ten times lower than that of $\{[M(Pc)F]I_x\}_n$, they are of considerable interest in view of their high stability.[89]

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The partial oxidation of metallophthalocyanines and porphyrins is an important chemical method for the preparation of new synthetic metals. Elemental iodine, which has a large number of reduced forms, is used as a convenient reductant more frequently than others.

The ligands play the main role in the electrical conduction in iodinated metallophthalocyanines and metalloporphyrins. The metal ion in such a complex influences the properties of the ligands but is not involved directly in charge transfer. An exception is $Ni(TBP)I_{1.0}$, in which charge transfer takes place via both the ligands and the metal [in contrast to $Ni(OMTBP)I_x$, $M(TMP)I_{1.0}$, and $NiPcI_{1.0}$, where the charge is transferred only via the organic ligand]. Thus slight changes in the structure of the ligands exert a significant influence on the electrical properties of the system. It is of interest to note that in certain cases homogeneous complex catalysts incorporating a transition metal ion and a ligand with an extensive system of conjugated bonds also transfer an electron to the substrate via the ligand (the so-called peripheral mechanism).[90-92]

It has been shown in relation to the complexes $Ni(OMTBP)I_x$ that a change in the oxidation state does not affect the qualitative character of the dependence of σ on T and influences only the absolute magnitude of the conductivity. One may claim that the interplanar distances in the stacks and the steric disposition of the molecules in the latter play an important role in the conduction process. In other words, by changing these parameters, it is possible to regulate the conductivities of phthalocyanine and porphyrin systems.

In the mid 1970's it was suggested that in the future the importance of phthalocyanines may be extremely significant in fields such as those of one-dimensional conductors and superconductors.[93] There is no doubt that this prediction has come true as regards metallic conductivity. Whether or not superconductors will be obtained on the basis of phthalocyanines remains a problem for further research.

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Division of the Institute of
Chemical Physics, USSR
Academy of Sciences,
Chernogolovka