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New Complex Compounds of Phthalocyanine with Ruthenium and Iridium

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The complex compounds of phthalocyanine with Os(IV) and Rh(III) obtained earlier ([1,2]) have certain special features in comparison with other stable phthalocyanines (Cu^{2+}, Al^{3+}). They also differ from Pt(II) and Pd(II) phthalocyanines by the high value of their solubility in sulfuric acid and by broad and less intense absorption bands in the electronic spectra.

At the same time, they possess extremely high kinetic stability in acidic media. We continued the search for possibilities of obtaining new phthalocyanines of metals of the platinum group. By refluxing a fivefold excess of dry, chemically pure phthalonitrile with $RuCl_3$ and $IrCl_3$ in a flask with a reflux condenser for 4 h, Ru(III) and Ir(III) phthalocyanines were obtained in 80% yield. Dark-blue ClRuPcCl* with a slight greenish tint and dark-green ClIrPcCl dissolve well in acetone, somewhat less readily in benzene and alcohol. Purified by extraction of impurities with boiling benzene and ethanol, and then by double reprecipitation from 96% H_2SO_4, the phthalocyanines corresponded to the formulas $(HSO_4) \cdot RuPcCl$ (found 13.45% Ru and 9.79% SO_3, calculated 13.60% Ru and 10.73% SO_3), and $(HSO_4) \cdot IrPcCl$ (found 23.74% Ir and 10.77% SO_3, calculated 23.11% Ir and 9.56% SO_3).

The acid-base properties, absorption spectra, and kinetic stability of the new phthalocyanine complexes were studied. In Table 1 are pre—

Table 1

Solubility in H_2SO_4 and pK values of phthalocyanines at 25°C

Phthalocyanine	Initial conc., mol/g	Solubility $S \cdot 10^5$, mol/l	pK of reaction (1)
$HSO_4 \cdot IrPc$	17.00	4120	1.38
$HSO_4 \cdot IrPc$	16.50	2890	1.31
$HSO_4 \cdot IrPc$	16.00	1490	1.35
$HSO_4 \cdot IrPc$	15.50	1040	1.33
$HSO_4 \cdot IrPc$	15.00	1060	1.07

Phthalocyanine	Initial conc., mol/g	Solubility $S \cdot 10^5$, mol/l	pK of reaction (1)
$HSO_4 \cdot IrPc$	14.50	640	1.01
$HSO_4 \cdot IrPc$	14.00	455	0.87
$HSO_4 \cdot RuPc$	17.50	16700	1.01
$HSO_4 \cdot RuPc$	17.00	11100	0.94
$HSO_4 \cdot RuPc$	17.00	11300	0.94
$HSO_4 \cdot RuPc$	16.50	7800	0.88
$HSO_4 \cdot RuPc$	16.00	3840	0.95
$HSO_4 \cdot RuPc$	15.50	2620	0.93
$HSO_4 \cdot RuPc$	15.00	1410	0.97
$HSO_4 \cdot RuPc$	14.00	1178	0.46

Table 2

Rate constants for the dissociation of phthalocyanines according to equation (2), k_V, $h^{-1} \cdot l^2 \cdot mol^{-2}$

Phthalocyanine	T-ra, °C	Conc. H_2SO_4, mol/l	$k_V \times 10^4$, $h^{-1} \cdot l^2$ $mol^{-2}
HSO_4IrPc	119	17.58	2.97 ±0.3
HSO_4IrPc	135	15.50	5.76 ±0.72
HSO_4IrPc	155	17.58	11.7 ±0.5
HSO_4RuPc	135	17.07	4.80 ±0.2
HSO_4RuPc	135	16.70	5.05 ±0.11
HSO_4RuPc	135	16.63	4.83 ±0.45
HSO_4RuPc	135	16.20	4.75 ±0.1
HSO_4RuPc	155	17.58	18.2 ±0.9
HSO_4RuPc	155	16.20	20.6 ±2.0
HSO_4RuPc	155	16.20	20.5 ±2.0

* Pc –phthalocyanine residue.

the values of the equilibrium constants of the dissolution reaction are introduced

$$HSO_4 \cdot MPc^*_{(s)} + H_2SO_4 \rightleftharpoons HSO_4 \cdot MPcH^+ + HSO_4^-. \tag{1}$$

Table 2 gives the values of the dissociation rate constants of these compounds for the reaction:

$$HSO_4 \cdot MPcH^+ + 2H_3O^+ \to H_2PcH^+\{+\}HSO_4 \cdot M^{2+}_{aq}. \tag{2}$$

As can be seen from the tabulated data, the values of $pK = -\lg K$ of reaction (1) in the Brand region (15–18.8 M –H_2SO_4) remain constant and indicate the increased basic properties of $HSO_4 \cdot IrPc$ and $HSO_4 \cdot RuPc$ (Table 3). The free energy of the dissolution reaction of phthalocyanines in sulfuric acid, $\Delta F_s = RT \ln K$, changes in parallel with the free energy of their protonation, ΔF_{H+} (^{3}), and, as a consequence, is a measure of the participation of the lone electron pairs of the outer N atoms of the macroring in conjugation with the π-cloud.

Table 3

Values of pK for reaction (1) of phthalocyanines of metals of the eighth group

Phthalocyanine	pK	Phthalocyanine	pK
$HSO_4 \cdot RuPc$	0.94 ± 0.03	CoPc	2.07 ± 0.04
$HSO_4 \cdot RhPc$	1.01 ± 0.04	NiPc	1.46 ± 0.03
$HSO_4 \cdot IrPc$	1.34 ± 0.02	PdPc	1.52 ± 0.05
$(HSO_4)_2OsPc$	0.04 ± 1.29	PtPc	1.50 ± 0.06

The extent of their participation in conjugation in free phthalocyanine, according to approximate calculations (^{4}), is about 50%. In the process of complex formation with a metal (M^{n+}), the extent of their participation in conjugation changes under the influence of the formation of σ- and π-bonds M^{n+}–N, owing to the inductive effect of the M^{n+} field, and also owing to possible distortion of the framework of the macroring. Formation of σ-bonds and the field effect increase ΔF_s (in comparison with ΔF_s of free phthalocyanine), i.e., they enhance the participation of the electron pairs of the outer N atoms in conjugation by excluding from conjugation the pairs of the inner N atoms. Formation of π-bonds and the geometric factor, on the contrary, decrease ΔF_s as a result of partial removal of the electron pairs of the N atoms from conjugation.

An especially strong influence may be expected from distortion of the π-framework of the macroring [5]. The extent of participation of the electron pairs in conjugation, judging from the magnitude of ΔF_s, increases in the series of phthalocyanines formed by metals: Os(IV) > Ru(III), Rh(III) > Ir(III) > Ni(II), Pt(II), Pd(II) > Co(II). The position of individual cations in this series has been discussed previously (^{1,2}).

Table 4

(Kinetic characteristics of the dissociation reaction (2) of phthalocyanines)

Phthalocyanine	Rate constant kV, $h^{-1} \cdot l^2 \cdot mol^{-2}$, 120°	Rate constant kV, $h^{-1} \cdot l^2 \cdot mol^{-2}$, 25°	Activation energy E, cal/mol	Activation entropy, $\Delta S^{\ddagger}$, e.u.
Rh (III)	$2.9 \cdot 10^{-4}$	$3.2 \cdot 10^{-8}$	22 400	−34.0
Ir (III)	$3.3 \cdot 10^{-4}$	$2.0 \cdot 10^{-6}$	12 500	−59.0
Co (II)	$4.9 \cdot 10^{-3}$	$8.0 \cdot 10^{-7}$	21 400	−31.0
Ru (III)	$1.54 \cdot 10^{-4}$	$7.7 \cdot 10^{-9}$	24 300	−30.0
Os (IV)	$1.36 \cdot 10^{-4}$	$1.9 \cdot 10^{-8}$	21 800	−37.0
Ni (II)	$1.5 \cdot 10^{-3}$	$6.6 \cdot 10^{-7}$	32 100	−40
Pt (II)	$4.5 \cdot 10^{-4}$	$9.4 \cdot 10^{-10}$	19 000	−8.5

It is apparently determined by the strength of the σ- and π-bonds, since the field effect can be neglected owing to the small values of the effective charge of the central ion (2) and its approximate constancy in the platinum-metal series. On the basis of this series it may be concluded that either Ru(III) forms stronger π-bonds than Ir(III), or the σ-bond Ir—N is stronger than the σ-bond Ru—N. The answer to this question follows from comparison of the kinetic data on the dissociation of phthalocyanines in a solution of H_2SO_4 (Table 4). It was shown by the author (6) that in series of related porphyrin and phthalocyanine complexes the kinetic stability (measured—value $h\nu$) and thermodynamic stability vary symbatically. From Table 4 it is seen that Ru(III) forms a more strongly bound phthalocyanine than Ir(III). However, owing to the sharp difference in the activation energies of the dissociation reaction, already at 150° the Ir(III) phthalocyanine proves to be kinetically more stable than Ru(III).

The extremely high strength of $HSO_4 \cdot IrPc$ and $HSO_4 \cdot RuPc$ is not unexpected (1). In the low-lying excited states Ir^{3+} ($5d^6$) and Ru^{3+} ($4d^5$) have vacant $d_{x^2-y^2}$ and d_{z^2} orbitals suitable for the formation of σ-bonds and filled d_{xy}- and d_{xz}-orbitals capable of participating in the formation of dative π-bonds. High ionization potentials and medium values of the covalent radii (7), not exceeding 1.26—1.28 Å, promote the formation of strong covalent complexes with phthalocyanine.

Comparison of the electronic absorption spectra of metal phthalocyanines in sulfuric-acid solutions (Fig. 1, Table 5) makes it possible to put forward certain considerations concerning changes in the structure of the macrocycle upon coordination of the metal. According to the absorption spectra, MPc can be divided into two groups: some have a high-intensity long-wavelength absorption band (complexes of Zn, Cu, Pt, Al, Ga, Co, Pd, V, Sn with $\log \varepsilon$ from 5.3 to 5.0), while others possess a first band of reduced intensity (Ru, Rh, Ir, Os, Ni with $\log \varepsilon$ 4.6—4.0).

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* The Cl atom in the benzene ring is omitted.

Fig. 1. Absorption spectra in H_2SO_4 of phthalocyanines of Ir^{3+} (1 –16 M, 2 –17.6 M), Ru (3 –15.0 M, 4 –17.6 M) and Pt (5 –17.6 M)

We suppose that cations of the first group, when coordinating with phthalocyanine, do not alter the conditions of conjugation of the π-electrons of the phthalocyanine macrocycle, and do not appreciably change either the planar configuration of the chromophore or the valence angles in it. These ideal conjugation conditions without distortion of the σ-framework upon coordination are preserved, as we see, in all cases where the cation has either vacant $(n-1)d$-orbitals and a sufficiently large–

Table 5

Position of the bands (λ_{max}, mμ) and their intensity ($\lg\varepsilon$) in the absorption spectra of sulfuric-acid solutions of MPc

Phthalocyanine	Conc. H_2SO_4, mol/l	I	II	III	IV	V	VI
Ru (III)	17.60	788(4.60)	702(3.99)	–	307(4.39)	–	277(5.04)
Ru (III)	15.00	784	700	–	291	–	226
Rh (III)	17.60	768(4.56)	692(4.28)	437(4.07)	312(4.55)	269(4.55)	224(4.66)
Ir (III)	17.60	762(3.90)	710(6.68)	–	344(4.02)	–	228(4.74)
Ir (III)	16.00	770(4.01)	705(3.78)	400(3.85)	–	280(4.39)	225(4.80)
Os (IV)	15.00	768(4.31)	700(4.44)	415(4.47)	–	280(4.93)	223(5.11)
Pt (II)	17.60	772(5.18)	686(4.47)	438(4.26)	–	271(4.93)	225(4.86)
Ni (II)	17.50	778(4.57)	690(4.18)	–	302(4.61)	–	226(4.77)
Cu (II)	17.8	494(5.36)	700(4.56)	440(4.32)	305(4.73)	–	225(4.82)

covalent radius (Pd, Pt), or accessible nd-orbitals and not too large a covalent radius ((Zn, Al, Ga, Sn, Cu). V also falls into this group owing to the moderate strength of the V—N bonds.

In the second group of phthalocyanines, the decrease in the intensity of the absorption bands in sulfuric-acid solutions and the considerable hypsochromic shift of λ_{max} of the first band in comparison with CuPc are apparently due to some distortion of the π-skeleton of phthalocyanine. Such a distortion may occur as a result of filling the inner $(n-1)d$-orbitals with σ-electrons of the ligand.

With covalent radii smaller than the radius of the phthalocyanine cavity and a high electron affinity (Ni^{2+} and the M^{3+} and M^{4+} ions of the platinum metals), the formation of σ-bonds will lead to attraction of the N atoms of phthalocyanine toward the center of the cavity and to deterioration of the conditions for conjugation in the macrocycle. As X-ray structural investigation of NiPc has shown (^{8,9}), the diameter of the phthalocyanine cavity indeed decreases by 0.18 Å in comparison with H_2Pc. The cause of this phenomenon was the attraction of N atoms upon filling the $(n-1)d$-orbitals of the small-sized Ni^{2+}. The coordinating ability of the M^{3+} and M^{4+} platinum metals is higher than that of Ni^{2+}, and therefore an analogous distortion effect may be expected to be greater.

It is of interest to compare our results on the synthesis of Ru phthalocyanine with the data of Krueger and Kenney (^{10}), who started from $RuCl_3$ and *o*-cyanobenzamide and obtained, as they believe, the phthalocyanine of divalent ruthenium, RuPc. The synthesis conditions (^{10}) in essence did not differ in any way from those described in our work. The presence of one HSO_4^- in the composition of our complex leaves no doubt as to the trivalence of Ru. We are inclined to believe that in work (^{10}) a complex of trivalent ruthenium, $CH_3CO_2 \cdot RuPcCl$, was obtained, and not RuPc. Confirmation of this is the absence of reducing agents in the synthesis process, the instability of Ru^2 compounds and, most essentially, the inability of the Ru phthalocyanine obtained in (^{10}) to sublime, which is not characteristic of M^{2+} phthalocyanines but is characteristic of M^{3+}.

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Note: Figure translations are in progress. See original paper for figures.