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Abstract

Full Text

Chemistry

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SYNTHESIS AND PROPERTIES OF RHODIUM PHTHALOCYANINE

(Presented by Academician A. N. Terenin, February 15, 1963)

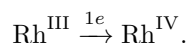
On the basis of an analysis of the available experimental data on the synthesis and properties of phthalocyanine complexes, we previously proposed ⁽¹⁾ considerations concerning the possibility of synthesizing new phthalocyanines stable in an acidic medium (stable phthalocyanines). Among the expected, but previously not obtained, stable complexes, in addition to osmium phthalocyanine ⁽¹⁾, we have synthesized phthalocyanine of trivalent rhodium (Rh^{III}). Rhodium phthalocyanine is obtained in fairly good yield (60-80%) by heating anhydrous RhCl₃ with a fivefold excess of phthalonitrile in a flask with a reflux condenser for 4 hours. Purified of organic impurities by repeated treatment with warm acetone and by twofold reprecipitation from 96% H₂SO₄, it consists of dark-blue crystals which, unlike most phthalocyanines, are readily soluble in acetone and absolute alcohol. Solutions in acetone are dark green, and in alcohol dark blue. The compound obtained in this way corresponds to the formula (HSO₄)RhPc. Analysis for Rh and SO₄ gave average values of 17.93% and 13.20%, respectively; calculated: 17.00% Rh and 12.86% SO₄.

Table 1

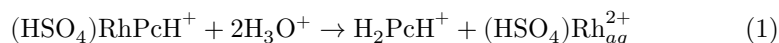
Rate constants for the dissociation of certain phthalocyanine complexes

Central ion	Temp., °C	Rate constants of equation (2) $k_V \cdot 10^3$, hour ⁻¹ · l ² · mol ⁻²
Rh ^{III}	120	0.253 ± 0.030
Rh ^{III}	138	1.02 ± 0.10
Os ^{IV}	120	0.136 ± 0.012
Pt ^{II}	120	0.452 ± 0.023
Pd ^{II}	120	0.450 ± 0.030
Cu ^{II}	120	10.2 ± 1.2
Cu ^{II}	136	61.0 ± 5.0
Al ^{III}	120	1.10 ± 0.07

The oxidation state of Rh in this compound, in addition to the initial data on the synthesis, was confirmed by a recently proposed method ⁽²⁾, based on the number of gram-equivalents of oxygen consumed in the oxidation of a known weighed portion of (HSO₄)RhPc by dichromate in a sulfuric-acid medium. It was found that the oxidation of a molecule of rhodium phthalocyanine consumes three electrons, two of which go to the oxidation of the free phthalocyanine ⁽³⁾, while one is consumed in the reaction



Thus, the oxidation state of Rh in the compound (HSO₄)RhPc is equal to three. Unlike Os^{IV}, rhodium(III) has no vacant *d*-orbitals; therefore the formation of rhodium phthalocyanine is associated with pairing of all its electrons. The expenditure of energy for electron pairing ⁽⁴⁾, as well as the smaller formal charge of Rh^{III} in comparison with Os^{IV}, gives grounds to expect a lower stability of (HSO₄)RhPc in comparison with the osmium complex, and higher rates of its dissociation in acidic media. Table 1 gives the rate constants for the dissociation of rhodium phthalocyanine in sulfuric acid solution, proceeding according to the reaction



The dissociation obeys a third-order kinetic equation:

$$-\frac{dC_{\text{MPcH}^+}}{dt} = k_V \cdot C_{\text{MPcH}^+} \cdot C_{\text{H}_3\text{O}^+}^2 \quad (2)$$

and follows the trimolecular mechanism as the most probable. The rate constants (k_V) reliably characterize the rate of dissociation of phthalocyanine in 14–18.8 *M* H₂SO₄ solutions, in which the activity coefficients of MPcH⁺ and H₃O⁺ remain practically constant ⁽⁵⁾. From the data in Table 1 it is seen that, in stability in an acidic medium, rhodium phthalocyanine is inferior only to the osmium complex, but leaves far behind the complexes of Cu^{II}, Al^{III}, and even Pt^{II} and Pd^{II}.

We believe that the value of k_V qualitatively characterizes the strength of the chemical bond of the metal with the phthalocyanine macrocycle. The strength of the chemical bond is determined to a considerable extent by the degree of overlap of the electron clouds of the central ion and the ligand and, in a series of similar complexes, should be related to the magnitude of the effective charge of the central ion.

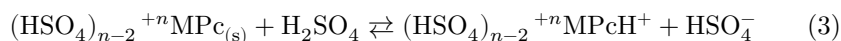
Table 2

Values of the effective charges of the central ion in complexes of Os, Pt, Pd

Complex	Effective charge	Complex	Effective charge
K ₂ OsCl ₆	+0.8	K ₂ PtCl ₆	+0.64
K ₂ OsCl ₅ (NO)	+0.7	K ₂ PdCl ₆	+0.58
K ₂ OsO ₄	+0.8	K ₂ PtBr ₆	+0.28
KOsO ₃ N	+1.0	K ₂ PdBr ₆	+0.22
OsO ₂	+0.0	K ₂ PtBr ₆	+0.28

Table 2 gives data available in the literature ^(6,7) on the effective charges of platinum metals in complexes. They give grounds to assume that the degree of filling of the orbitals of Pt and Pd ions by ligand electrons (and therefore also the strength of the covalent σ -bond) is the same, since the values of the effective charges coincide within the limits of experimental error. For Os^{IV}, despite the extremely high strength of the complexes (1), the degree of filling of the orbitals, as is seen from the values of the effective charges (Table 2), is somewhat smaller than for Pt^{IV} and Pd^{IV}. Most likely, this is connected with the appearance in the osmium ion of very strong dative bonds. The formation of dative π -bonds decreases the degree of filling of the orbitals of the central ion, while simultaneously increasing the strength of the compound. These considerations help to understand the identical values of the dissociation rate constant (k_V) of Pt and Pd phthalocyanines and its considerably smaller value for Os phthalocyanine. It should be recalled ⁽⁶⁾ that, in the formation of covalent complexes, the magnitude of the effective charge not only does not increase with increasing oxidation state of the central ion, but may even decrease. Hence, in phthalocyanines of Pt^{II}, Pd^{II}, Rh^{III}, Os^{IV}, one may expect approximately the same effective charge of the central ion, and, consequently, an increase in the degree of filling of vacant orbitals and an increase in bond covalency in the series Pt^{II}, Pd^{II} > Rh^{III} > Os^{IV}. If the value of k_V depends qualitatively on the strength of the metal-ligand bond, then it is understandable that k_V of the Rh complex exceeds its value for Pt^{III} and Pd^{II} and is less than for Os^{IV}.

It is of interest to compare the basicity of the nitrogen atoms of the macrocycle in (HSO₄)RhPc with the analogous property of phthalocyanines of other platinum metals. It was shown earlier ^(8,9) that the solubility of phthalocyanines of di-, tri-, and tetravalent metals in sulfuric acid, conveniently expressed by the magnitude of the dissolution reaction constant:



is a quantitative measure of the basicity of the macrocycle. However, as shown in the study of the solubility of Os^{IV} phthalocyanine [1], in the series of polyvalent platinum metals, the formation of chains of polynuclear complexes of the type $-\text{X}-\text{MPC}-\text{X}-\text{MPC}-\text{X}-\text{MPC}-$ is apparently possible; these may exist not only in the crystalline complex but also in sulfuric acid solution, complicating the picture of the dissolution process. In solution, SO₄²⁻ acts as the bridging particle

X. The number of links and the degree of protonation of the chains in solution may vary depending on the nature of the central ion and the concentration of H_2SO_4 . The formation of such chains leads to the unusually high solubility of Os^{IV} phthalocyanine in H_2SO_4 and po

polar organic solvents. The increase in the solubility of polymeric phthalocyanines in polar organic solvents, as has recently been shown ⁽¹⁰⁾, also occurs in parallel with an increase in the degree of polymerization. Table 3 gives the solubility values and the values of the exponent of the equilibrium constant of the dissolution reaction (pK) of Rh^{III} phthalocyanine:



and of several other phthalocyanines in sulfuric acid.

The solubility of $(\text{HSO}_4)\text{RhPc}$ proves to be unusually high. Under comparable conditions it is three times higher than that of the Pt and Pd compounds, and five times higher than that of CuPc .

Table 3

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

Phthalocyanines	Initial conc. H_2SO_4 , mol/l	Solubility, $S \cdot 10^5$, mol/l	pK of reaction (3)
$(\text{HSO}_4)\text{RhPc}$	14.00	697	0.69
$(\text{HSO}_4)\text{RhPc}$	14.50	670	1.03
$(\text{HSO}_4)\text{RhPc}$	15.00	1310	1.00
$(\text{HSO}_4)\text{RhPc}$	15.50	1915	1.06
$(\text{HSO}_4)\text{RhPc}$	15.50	2390	0.99
$(\text{HSO}_4)\text{RhPc}$	16.00	4500	0.90
$(\text{HSO}_4)\text{RhPc}$	16.00	3150	1.05
$(\text{HSO}_4)\text{RhPc}$	16.50	5480	1.03
$(\text{HSO}_4)\text{RhPc}$			Average 1.01 ± 0.04
PtPc	15.50	567	1.57
PdPc	15.50	680	1.49
$(\text{SO}_4)_2\text{OsPc}$	15.50	5200	0.60
$(\text{HSO}_4)_2\text{SnPc}$	16.00	8.1	3.59
$(\text{HSO}_4)\text{AlPc}$	16.00	85.5	2.60
CuPc	16.00	721	1.68

It is characteristic that in the case of base metals, which give multiply charged ions and have little tendency toward complex formation (Al, Sn), the phthalocyanines have extremely low solubility (Table 3). In the formation of stable

phthalocyanines of Al and Sn^{IV} , the outer d -orbitals are filled, which is apparently associated with a smaller decrease in the formal charge than in the formation of complexes with filling of the inner d -orbitals (platinum metals).

The presence of a larger effective charge on Al and Sn in their phthalocyanines leads to a decrease in the basic properties of the macrocycle, to a sharp decrease in solubility, and to a dependence of the pK of reaction (3) on the concentration of H_2SO_4 . These facts were discussed by us earlier⁽⁹⁾. Chains of polynuclear complexes for these phthalocyanines may exist in the crystal, but on passing into a solution of H_2SO_4 they will readily be destroyed because of the low tendency of Al and Sn toward complex formation with SO_4^{2-} .

Table 4

Positions of absorption bands (λ_{max} , $m\mu$), and their intensity ($\lg \varepsilon$) in the spectra of sulfuric-acid solutions of phthalocyanines

Phthalocyanine	Conc. H_2SO_4 , mol/l						
		I	II	III	IV	V	VI
$(\text{HSO}_4)\text{RhPc}$	8.00	768(4.56)	692(4.28)	437(4.07)	312(4.55)	269(4.55)	224(4.66)
$(\text{HSO}_4)\text{RhPc}$	6.00	768(4.57)	698(4.28)	439(4.07)	308(4.50)	269(4.57)	224(4.72)
$(\text{SO}_4)\text{OsPc}$	15.00	768(4.31)	700(4.44)	415(4.47)	—	280(4.93)	223(5.11)
PdPc	17.5	771(5.17)	702(4.44)	441(4.29)	—	262(4.73)	225(4.85)
PtPc	17.5	772(5.18)	686(4.47)	438(4.26)	—	271(4.93)	225(4.86)
CuPc	17.8	794(5.36)	700(4.56)	440(4.32)	305(4.73)	—	225(4.82)

The extremely high solubility of rhodium phthalocyanine (in comparison with $\text{HSO}_4 \cdot \text{AlPc}$), which has a formal charge as in Al, indicates that the effective charge on Rh in the phthalocyanine is small and approaches the charge on Os^{IV} in its complex. The absence of a dependence of the pK of rhodium phthalocyanine on the concentration of H_2SO_4 , if the latter is above 14 molar, indicates, in all probability, not the absence but the lower stability of the complex $\text{HSO}_4 \cdot \text{RhPc} \cdot \text{SO}_4 \cdot \text{RhPc}$ in comparison with the osmium complex⁽¹⁾. Such a rhodium complex must exist only in the crystal and in less concentrated solutions of H_2SO_4 (below 14.5 molar), in which the concentration of strongly protonating H_2SO_4 molecules is low and hydrated ions predominate.

H_3O^+ . Thus, the difference between the phthalocyanines of Rh^{III} and Os^{IV} consists in the lower strength of the bond of Rh^{III} with oxygen-containing ions of the type SO_4^{2-} , which leads to a simple picture of the solubility of $(\text{HSO}_4)\text{RhPc}$, the same as for phthalocyanines of divalent metals. We believe, moreover, that Rh^{III} forms stronger π -bonds with phthalocyanine than do Pt and Pd. Their formation can explain the significantly greater solubility⁽⁸⁾, i.e., the greater basicity of the macrocycle $(\text{HSO}_4)\text{RhPc}$. However, these bonds are apparently less strong than in $(\text{SO}_4)\text{OsPc}$, which has twice the solubility

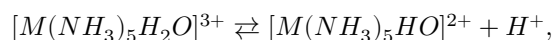
Fig. 1. Absorption spectra of phthalocyanines in solution. 1-(HSO₄)RhPc in 18 M; 2-(HSO₄)RhPc in 16 M; 3-(HSO₄)₂OsPc in 15 M; 4-PdPs in 18 M H₂SO₄.

Figure 1: Fig. 1. Absorption spectra of phthalocyanines in solution. 1-(HSO₄)RhPc in 18 M; 2-(HSO₄)RhPc in 16 M; 3-(HSO₄)₂OsPc in 15 M; 4-PdPs in 18 M H₂SO₄.

in 15 and 15.5 M H₂SO₄, in which, as we believe, owing to the presence of a considerable amount of undissociated H₂SO₄ molecules, the solubility will depend not so much on the degree of protonation of the chains SO₄ · MPc · SO₄ · MP, as on the character of the chemical bonds M—N.

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The greater tendency of Os to form π-bonds in comparison with Rh is not unexpected. The tendency to form π-bonds in the eighth group increases from top to bottom. In support of this one may cite the following generally known fact. In the series Co^{III}—Rh^{III}—Ir^{III}, with increasing nuclear charge there is a successive weakening of the dissociation⁽¹⁾ of the ion:



which is explained by strengthening of the chemical bonds M—N and by a decrease in the effective charge of the ion from Co to Ir. The decrease in effective charge promotes the formation of dative π-bonds⁽¹¹⁾. Their formation apparently explains the increase in the strength of the M—Cl bond in the ions [M(NH₃)₅Cl]²⁺ in the series Co, Rh, Ir⁽¹⁰⁾.

The absorption spectra of Rh^{III} phthalocyanine (Fig. 1 and Table 4) are closer to the spectra of Pt^{II} and Pd^{II} phthalocyanines than to Os^{IV}. This circumstance, as well as the identity of the spectra of the rhodium complex in 16 M and 18 M H₂SO₄, indicates an unchanged composition of the protonated Rh^{III} phthalocyanine particles upon variation of the H₂SO₄ concentration and the absence, under these conditions, of multinuclear chains in solution.

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

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