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## Abstract

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# SYNTHESIS AND PROPERTIES OF RHODIUM PHTHALOCYANINE

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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 $RhCl_3$ 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% $H_2SO_4$, 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 $(HSO_4)RhPc$. Analysis for Rh and $SO_4$ gave average values of 17.93% and 13.20%, respectively; calculated: 17.00% Rh and 12.86% $SO_4$.

**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$^{-1} \cdot$ l$^2 \cdot$ mol$^{-2}$ |
|---|---:|---:|
| $Rh^{III}$ | 120 | $0.253 \pm 0.030$ |
| $Rh^{III}$ | 138 | $1.02 \pm 0.10$ |
| $Os^{IV}$ | 120 | $0.136 \pm 0.012$ |
| $Pt^{II}$ | 120 | $0.452 \pm 0.023$ |
| $Pd^{II}$ | 120 | $0.450 \pm 0.030$ |
| $Cu^{II}$ | 120 | $10.2 \pm 1.2$ |
| $Cu^{II}$ | 136 | $61.0 \pm 5.0$ |
| $Al^{III}$ | 120 | $1.10 \pm 0.07$ |

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 $(HSO_4)RhPc$ 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

$$\mathrm{Rh}^{\mathrm{III}} \xrightarrow{1e} \mathrm{Rh}^{\mathrm{IV}}.$$

Thus, the oxidation state of Rh in the compound $(HSO_4)RhPc$ is equal to three. Unlike $\mathrm{Os}^{\mathrm{IV}}$, 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 $\mathrm{Rh}^{\mathrm{III}}$ in comparison with $\mathrm{Os}^{\mathrm{IV}}$, gives grounds to expect a lower stability of $(HSO_4)RhPc$ 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

$$(\mathrm{HSO_4})\mathrm{RhPcH}^+ + 2\mathrm{H_3O}^+ \rightarrow \mathrm{H_2PcH}^+ + (\mathrm{HSO_4})\mathrm{Rh}^{2+}_{aq} \qquad (1)$$

The dissociation obeys a third-order kinetic equation:

$$-\frac{dC_{\mathrm{MPcH}^+}}{dt} = k_V \cdot C_{\mathrm{MPcH}^+} \cdot C^2_{\mathrm{H_3O}^+} \qquad (2)$$

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 $M$ $H_2SO_4$ solutions, in which the activity coefficients of $\mathrm{MPcH}^+$ and $H_3O^+$ 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 $\mathrm{Cu}^{\mathrm{II}}$, $\mathrm{Al}^{\mathrm{III}}$, and even $\mathrm{Pt}^{\mathrm{II}}$ and $\mathrm{Pd}^{\mathrm{II}}$.

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 |
|---|---:|---|---:|
| $K_2OsCl_6$ | +0.8 | $K_2PtCl_6$ | +0.64 |
| $K_2OsCl_5(NO)$ | +0.7 | $K_2PdCl_6$ | +0.58 |
| $K_2OsO_4$ | +0.8 | $K_2PtBr_6$ | +0.28 |
| $KOsO_3N$ | +1.0 | $K_2PdBr_6$ | +0.22 |
| $OsO_2$ | +0.0 | $K_2PtBr_6$ | +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 $\sigma$-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 $\pi$-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 $(HSO_4)RhPc$ 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:

$$(HSO_4)_{n-2}{}^{+n}MPc_{(s)} + H_2SO_4 \rightleftarrows (HSO_4)_{n-2}{}^{+n}MPcH^+ + HSO_4^- \tag{3}$$

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 –X–MPc–X–MPc–X–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, $SO_4^{2-}$ 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:

$$(HSO_4)RhPc_{(s)} + H_2SO_4 \rightleftarrows (HSO_4)MPcH^+ + HSO_4^- \qquad (4)$$

and of several other phthalocyanines in sulfuric acid.

The solubility of $(HSO_4)RhPc$ 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) |
|---|---|---|---|
| $(HSO_4)RhPc$ | 14.00 | 697 | 0.69 |
| $(HSO_4)RhPc$ | 14.50 | 670 | 1.03 |
| $(HSO_4)RhPc$ | 15.00 | 1310 | 1.00 |
| $(HSO_4)RhPc$ | 15.50 | 1915 | 1.06 |
| $(HSO_4)RhPc$ | 15.50 | 2390 | 0.99 |
| $(HSO_4)RhPc$ | 16.00 | 4500 | 0.90 |
| $(HSO_4)RhPc$ | 16.00 | 3150 | 1.05 |
| $(HSO_4)RhPc$ | 16.50 | 5480 | 1.03 |
| $(HSO_4)RhPc$ | | | Average $1.01 \pm 0.04$ |
| PtPc | 15.50 | 567 | 1.57 |
| PdPc | 15.50 | 680 | 1.49 |
| $(SO_4)_2OsPc$ | 15.50 | 5200 | 0.60 |
| $(HSO_4)_2SnPc$ | 16.00 | 8.1 | 3.59 |
| $(HSO_4)AlPc$ | 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 ($\lambda_{max}$, 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 |
|---|---|---|---|---|---|---|---|
| $(HSO_4)RhPc$ | 18.00 | 768(4.56) | 692(4.28) | 437(4.07) | 312(4.55) | 269(4.55) | 224(4.66) |
| $(HSO_4)RhPc$ | 16.00 | 768(4.57) | 698(4.28) | 439(4.07) | 308(4.50) | 269(4.57) | 224(4.72) |
| $(SO_4)OsPc$ | 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 $HSO_4 \cdot AlPc$), 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 $HSO_4 \cdot RhPc \cdot SO_4 \cdot RhPc$ 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 $(HSO_4)RhPc$, the same as for phthalocyanines of divalent metals. We believe, moreover, that $Rh^{III}$ forms stronger $\pi$-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 $(HSO_4)RhPc$. However, these bonds are apparently less strong than in $(SO_4)OsPc$, 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 $M$ $H_2SO_4$, in which, as we believe, owing to the presence of a considerable amount of undissociated $H_2SO_4$ molecules, the solubility will depend not so much on the degree of protonation of the chains $SO_4 \cdot MPc \cdot SO_4 \cdot MP$, as on the character of the chemical bonds $M$—$N$.

Fig. 1. Absorption spectra of phthalocyanines in solution. 1—($HSO_4$)RhPc in 18 $M$; 2—($HSO_4$)RhPc in 16 $M$; 3—($HSO_4$)$_2$OsPc in 15 $M$; 4—PdPs in 18 $M$ $H_2SO_4$.

The greater tendency of Os to form $\pi$-bonds in comparison with Rh is not unexpected. The tendency to form $\pi$-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:

$$[M(NH_3)_5H_2O]^{3+} \rightleftarrows [M(NH_3)_5HO]^{2+} + H^+,$$

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 $\pi$-bonds$^{(11)}$. Their formation apparently explains the increase in the strength of the $M$—$Cl$ bond in the ions $[M(NH_3)_5Cl]^{2+}$ 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 $M$ $H_2SO_4$, indicates an unchanged composition of the protonated $Rh^{III}$ phthalocyanine particles upon variation of the $H_2SO_4$ 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.*