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Structural formula of phthalocyanine labeled (I)

Figure 1: Structural formula of phthalocyanine labeled (I)

Abstract

Full Text

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On the Synthesis and Properties of Osmium Phthalocyanine

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It is known that phthalocyanine, having the skeletal formula (I), is a universal addend. It forms complex compounds with metals of all groups of the periodic system.

Linstead, who discovered this exceptionally interesting and important group of pigments, together with co-workers synthesized phthalocyanines of 25 different metals (^1). Phthalocyanines of iron and tin were obtained by them in lower and higher valence states. Later phthalocyanines of Ga^3+ and In^3+ (^2), Co^3+ (^3), Mn^4+ (^4), and copper in the zero oxidation state (^5) were synthesized. An important event in the chemistry of complex compounds was the synthesis of phthalocyanines in which Ge^IV (^6) and As^III (^7), elements with clearly pronounced metalloid properties, act as the central ions. Unfortunately, the properties of the newly obtained phthalocyanines have practically not been studied.

(I)

Of greatest interest among the newly obtained phthalocyanines are stable phthalocyanines, since they are readily isolated in a chemically pure state. Further synthesis of stable phthalocyanines is to be expected. Analysis of the literature data (^1), as well as study of the kinetics of dissociation of phthalocyanines in acidic media (^8, ^9), show that among the factors determining the stability of phthalocyanines, the possibility of planar (dsp^2) or octahedral (d^2sp^3) arrangement of bonds and the size of the excited central ion are of primary importance. The charge is significant only when its change leads to a noticeable decrease in radius. Thus, for example, Al^3+ ($r = 0.57$ Å) gives an extremely strong phthalocyanine, whereas Mg^2+ ($r = 0.78$ Å) forms a very unstable compound. Phthalocyanine Sn^IV ($r = 0.74$ Å) is stable, whereas Sn^II ($r = 1.04$) is labile. The complexes Ag^+ ($r = 1.13$) and Hg^2+ ($r = 1.12$) (^10) are only slightly stable, especially the latter. This is apparently due to the impossibility of placing the sp^3d bonds of the excited ions in the limited space provided by phthalocyanine (formula I) to the central ion. From this point of view, one may expect the synthesis of new stable phthalocyanines for those cations which have a small radius, about 0.8 Å or less, and which have vacant *d*-orbitals in the ground or lower excited state. A special position is occupied by the elements of the platinum group, which, despite their large size, owing to their exceptional complex-forming ability form extremely strong phthalocyanines (^11).

One may expect the synthesis of strong phthalocyanines formed by Sc^3+, Ti^IV, Ru^III, Rh^III, Ir^III, and Os^IV, which have not yet been described in the literature. It is impossible

to obtain stable complexes of Cu^+, Tl^{3+}, Y^{3+}, La^{3+} and the lanthanides, Zr , V^{2+}, Cr^{2+}, Ga^{2+}. Indeed, our attempt to obtain the phthalocyanines of Nd^{3+} and Cd^{3+} was not successful. However, we have obtained osmium phthalocyanine, which is formed in theoretical yield when OsO_4 is introduced into an excess of molten phthalonitrile and this mixture is heated in a flask with a reflux condenser for four hours. The osmium phthalocyanine obtained from the melt, after removal of organic impurities with benzene and acetone and twofold reprecipitation from oleum, consists of very fine dark-blue crystals.

The compound contains the ion ${SO_4}^{2-}$ and corresponds to the formula $(SO_4)OsPc$. For this compound the calculated values are: Os 23.84%, found 24.34%; 24.90%; SO_4 calculated–12.02%, found 11.70%; 11.63%.

Thus, in the reaction of OsO_4 with phthalonitrile, osmium is reduced to the tetravalent state. Apparently, in the solid state in this complex osmium has coordination number 6 and an alternation of ions

$$-OSO_2O - Os - OSO_2O - Os - OSO_2O - Os - \ldots$$

The remaining four valencies of osmium are saturated by the phthalocyanine residue (Pc^{2-}).

Osmium phthalocyanine differs from all other stable phthalocyanines in a number of physical and physicochemical properties. In $(SO_4)OsPc$ six σ-bonds of the d^2sp^3-configuration are formed. In this case the $dx^2 - y^2$- and dz^2-orbitals are occupied. On the remaining, probably energetically equivalent, orbitals dxy, dxz and dyz are placed four *d*-electrons of Os(IV). They should correspond to a spin component of the magnetic moment with $\mu_{\text{eff}} = 2.83\,\mu_{\text{B}}$. However, measurement of the magnetic susceptibility by the Gouy method (magnetic field 10,000 oersted) showed that the compound $(SO_4)OsPc$ is diamagnetic. Apparently, the diamagnetism is due to participation of the dxz- and dyz-orbitals in strong π-bonds. There are indications in the literature ([13]) that osmium compounds are distinguished by minimal paramagnetism in comparison with other elements of the platinum group, and this is associated with the high degree of participation of osmium *d*-electrons in the formation of covalent σ- and π-bonds of high strength. Indeed, osmium phthalocyanine proved to be the most stable of all known metallophthalocyanines. Table 1 gives kinetic data on the dissociation of osmium phthalocyanine in sulfuric acid solution:

Table 1

Rate constants for the dissociation of some metallophthalocyanines in H_2SO_4 solutions

Central ion	Temp., °C	Conc. H_2SO_4, mol/l	Rate constants in equation (2) (K_{op}, $h^{-1} \cdot 1000$)
Os(IV)	155	16.20	181\$±14||*Os*(*IV*)|120|16.20|12.0±1.0||*Os*(*IV*)|120

$$(\mathrm{SO_4})\mathrm{OsPc}_{(\mathrm{s})} + 2\mathrm{H}^+ \rightleftarrows \mathrm{H_2PcH}^+ + (\mathrm{SO_4})\mathrm{Os}^{2+}. \tag{1}$$

It was noted earlier (^{9}, ^{14}) that the dissociation of stable phthalocyanines obeys a first-order kinetic equation:

$$\frac{dC_{\mathrm{MPcH}^+}}{dt} = K_{\mathrm{op}} \cdot C_{\mathrm{MPcH}^+}. \tag{2}$$

The quantity K_{op} depends on the nature of the metal and on the concentration of hydrogen ions:

$$K_{\mathrm{op}} = K \cdot C^2_{\mathrm{H_3O}^+}. \tag{3}$$

Under comparable conditions, the value of K_{op} characterizes the kinetic stability of complex phthalocyanines, which for complexes of the same type, to a first approximation, varies in parallel with the thermodynamic stability (^{15}–^{17}). The data in Table 1 show that the kinetic stability

of osmium phthalocyanine is much higher than that of the analogs with Pd and Pt, which until now have been considered the most stable in this respect.

The conclusions following from the study of the magnetic properties and kinetic data are confirmed by data on the solubility of $(\mathrm{SO_4})\mathrm{OsPc}$ in sulfuric acid. Dissolution is accompanied, probably as for other phthalocyanines (^{14}), by single protonation:

$$(\mathrm{SO_4})\mathrm{OsPc}_{(t)} + \mathrm{H_2SO_4} \rightleftarrows (\mathrm{SO_4})\mathrm{OsPcH}^+ + \mathrm{HSO_4^-}. \tag{4}$$

From Table 2, which gives the solubilities of the phthalocyanines of Os(IV), Pd(II), and Pt(II) in H_2SO_4, it is seen that the solubility of osmium phthalocyanine exceeds the solubility of the platinum and palladium compounds by tens of times. The solubility value of the phthalocyanines of divalent metals, which have approximately the same parameters and crystal-lattice energy (^{18,19}), is determined by the magnitude of the basic properties of the macrocycle, which in turn is a function of the strength of the σ- and π-bonds in the complex ([20]). Since the basic properties of the macrocycle, and consequently the solubility of the phthalocyanines, decrease with strengthening of the σ-bonds and with increasing effective charge of the cation ([12]), we expected a sharp decrease in the solubility of $(SO_4)OsPc$ in comparison with PtPc and PdPc due to an increase in the formal charge of the ion (from $+2y$Pt to $+4y$Os) and, as a consequence, strengthening of the σ-bonds.

Table 2

Solubility of osmium, platinum, and palladium phthalocyanines in H_2SO_4 at 25°C

Initial conc., mol/l	Central ion	Solubility, 10^5 mol/l	Equilibrium constant of the dissolution reaction
14.00	Os (IV)	2790	0.07
14.50	Os (IV)	5070	0.15
15.00	Os (IV)	2470	0.71
15.50	Os (IV)	5200	0.60
14.50	Pt (II)	202	1.49
15.00	Pt (II)	459	1.40
15.50	Pt (II)	567	1.57
14.00	Pd (II)	126	1.40
14.50	Pd (II)	172	1.55
15.00	Pd (II)	417	1.44
15.50	Pd (II)	680	1.49

The unexpectedly high solubility of $(SO_4)OsPc$ cannot be explained solely by the formation of very strong π-bonds of Os(IV) with the macrocycle, although the π-bond causes a noticeable increase in solubility ([11]). The principal cause of the high solubility of osmium phthalocyanine is apparently the special properties of its crystal lattice and the unusual form of the particles in sulfuric-acid solution. Owing to the high strength of the osmium-oxygen bond ([21]) and, in general, to its high complex-forming ability, as evidenced by the magnetic data ([13]), osmium phthalocyanine can exist

Table 3

Positions of the absorption bands (λ_{max}, mμ) and their intensities ($\log \varepsilon$) in the spectra of sulfuric-acid solutions of phthalocyanines at 25°C

Phthalocyanine	Conc. H_2SO_4, mol/l	I	II	III	IV	V
$(SO_4)OsPc$	18.00	805(4.11)	720(4.32)	–	280(4.74)	–
$(SO_4)OsPc$	15.00	768(4.31)	700(4.44)	415(4.47)	280(4.93)	223(5.11)
$(SO_4)OsPc$(in acetone)	–	675(diffuse)	608	301	271	–
PtPc	17.44	772(5.18)	686(4.47)	438(4.26)	271(4.93)	–
PdPc	17.44	771(5.17)	702(4.44)	441(4.29)	262(4.73)	–
CuPc	17.80	794(5.36)	700(4.56)	440(4.32)	305(4.73)	225(4.82)

in an H_2SO_4 solution in the form of a multinuclear protonated complex

$$HOSO_2O—Os(PcH^+)—OSO_2O—Os(PcH^+)—OSO_2O—Os(PcH^+)—\dots,$$

and not all phthalocyanine nuclei of this macromolecule are protonated in solution. In dilute sulfuric acid the degree of protonation is small; in concentrated H_2SO_4 it may approach unity. Molecules with a low degree of protonation may pass into solution; therefore the solubility of $(SO_4)OsPc$, especially in sulfuric acid of medium concentrations (8–14 mol/l), should greatly exceed the solubility of PtPc and other MPc, which pass into solution in the form of monomeric $MPcH^+$.

The same reasons can explain the increased solubility of Os(IV) phthalocyanine in alcohol, acetone, and other polar solvents. The considerations expressed are also confirmed by spectral data. The absorption spectra of $(SO_4)OsPc$ in sulfuric-acid solution differ noticeably from the spectra of all other phthalocyanines (Table 3) by the low intensity of the long-wavelength bands, their strong shift toward the long-wavelength region of the spectrum with increasing H_2SO_4 concentration, and a noticeable broadening of the absorption bands (Fig. 1). Protonation causes a strong bathochromic shift of the absorption bands of phthalocyanines ([22]). With increasing H_2SO_4 concentration the degree of protonation increases (since the protonating agent for MPc is only H_2SO_4 molecules). This causes a continuous bathochromic shift of the absorption bands of $(SO_4)OsPc$ with increasing H_2SO_4 concentration. The absorption bands of osmium phthalocyanine are considerably broader than the bands of other MPc (Fig. 1). They apparently arise as a result of superposition of the bands of protonated and unprotonated chromophores of phthalocyanine that are part of the multinuclear complex.

Fig. 1. Absorption spectra of osmium and platinum phthalocyanines. 1 –PtPc in 17.4 M H_2SO_4, 2 –$(SO_4)OsPc$ in 18 M H_2SO_4, 3 –$(SO_4)OsPc$ in acetone (in optical-density units).

The decrease in the intensity of the long-wavelength band is apparently associated with deformation of the chromophore skeleton by the osmium ion. A less pronounced deformation was observed earlier in the case of Pt phthalocyanine ([18]). At present we are attempting to obtain phthalocyanines with other metals of the platinum group, on which the above assumptions will be tested.

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