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## Examples of UV-Vis profiles use as tool for evidence of the Metallophthalocyanines transformation

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#### Highlights

The oxidation of M(II)Pc to M(IV)Pc(acac)<sub>2</sub> is occurred in acetylacetone (Hacac).

The *acac*<sup>-</sup> ligand of MPc(acac)<sub>2</sub> is substituted by *Cl*<sup>-</sup> in reaction with HCl.

The *I* ligand of MPcs is replaced by *Cl* in benzene during reaction with HCl.

Reaction of MPcs with HCl may lead to demetalation.

#### Abstract

The UV-Vis spectra for a set of MPcs (M- metal, Pc = phthalocyanine ligand), *i.e.*: In(III)PcI (1), Hf(IV)PcI<sub>2</sub>Pht (Pht = phthalonitrile) (2), Sn(II)Pc (3), Sn(IV)PcI<sub>2</sub> (4), and Ge(IV)PcI<sub>2</sub> (5) have been examined in two solvents, O-donative acetylacetone, and non-coordinative benzene. The UV-Vis spectra in Hacac solution of 1,2 and 4,5 shows that the axially ligated iodine atoms are replaced by (*acac*)<sup>-</sup> anions of the solvent, whereas in 3 the oxygen donors of the solvent causing the auto-oxidation of Sn(II) to Sn(IV) ions and as a result the Sn(II)Pc is transformed into the Sn(IV)Pc(acac)<sub>2</sub>. The chloride complexes of the 1-5 compounds are formed at Hacac solution after acidification by hydrochloric acid, however each compound solution behaviors specifically. The UV-Vis spectra collected for the studied compounds at benzene solvent both before and after the solution acidization clearly indicate that the respective Q band character (besides 3) remains practically unchanged. The presence of the Cl<sup>-</sup> ions at the Sn(II)Pc solution in benzene results in the formation of Sn(IV)PcCl<sub>2</sub>.

## **Graphical abstract**



**Keywords:** Metallophthalocyanines, spectrum UV-Vis, hydrochloric acid, transformation, demetalation, autooxidation

#### 1. Introduction

The intense colour of the metallophtalocyanines (MPcs) besides their high thermal and chemical stability, is one of the key factors for their usage as colourants for almost a century [1]. These features are also essential for the increasing use of MPcs as sensors, catalysts and active species in photo-electrochemical processes and devices [2]. The UV-Vis examination of the MPc in the solution is a popular and very accurate method which characterizes the MPcs molecules optical properties. It is well known that such MPc spectrum shows sharp and intense absorption levels, Q band, as approximately somewhere in the 650-700 nm region. Therefore, the Pc(2-) chromophore Q band registration could be used to detect and to monitor the behaviour of the MPc compound in the environment of the solvent molecules [3-6]. It is well examined that the Q band position may be shifted by the choice of solvent, although usually by several nm only [7]. On the other side the Q band shape should be dependent on the symmetry and the MPc molecule and be single and sharp due to its  $D_{4h}$  symmetry and more or less split due to its  $C_{4v}$  or lower symmetry [8].

A classic experiment provides examples which accordingly represent the M(II)Pc homologues spectra and H<sub>2</sub>Pc spectra [9,10]. However, besides H<sub>2</sub>Pc, other MPcs whose molecules do not exhibit the D<sub>4h</sub> symmetry show far less significant splitting of the Q band [11] or even contrary to expectations, the absence of it [12]. Therefore, in order to have more inside factors influencing the specificity of Q band, we decided to measure the same and selected solvents from the UV-Vis spectra for a set of MPcs previously synthesized and characterized by us, and therefore well recognized and easily accessible. As regards the solvents, one potentially coordinative, i.e. bidendately O-donative acetylacetone, and one non-coordinative, i.e. benzene was chosen. The MPcs compounds selected are: In(III)PcI (1) [13], Hf(IV)PcI<sub>2</sub>Pht (Pht = phthalonitrile) (2) [14], Sn(II)Pc (3) [15,16], Sn(IV)PcI<sub>2</sub> (4) [17,18], and Ge(IV)PcI<sub>2</sub> (5) [19,20]. In the compounds 1, 2, 3 the central atom is out-of-plane of the phthalocyanine ring [13-16], whereas in the compounds 4 and 5 the central atom lies in the plane of macrocycle [17-20]. It should be noticed here that the UV-Vis spectra for the selected metallophthalocyanines during reaction with HCl have been recorded for the first time and the characteristic  $\lambda_{max}$  value of the Q band for Sn(IV)PcI\_2 and for Ge(IV)PcI\_2 compounds were not previously reported.

It is generally accepted that under acidic conditions the phthalocyanine core undergoes protonation of azomethine nitrogen atoms [21-32], but in certain cases it suggests the

existence of adducts: phthalocyanines - HCl [33]. The reaction of phthalocyanines with trifluoroacetic acid (TFA) or other acceptor species (*e.g.* HCl) in homogenous solutions can be monitored by electronic absorption spectra measurements [31,32] and as it is well known, the spectra consist of shifting the Q band to red. The protonation of MPc containing axial ligands proceeds by the loss of the axial ligands as judged by a small blue shift of Q band to that of non-ligated MPc [32].

## 2. Materials and methods

The solvents *i.e.* acetylacetone (Hacac) and benzene as well as the hydrochloric acid (~24.5%) were purchased from a commercial supplier and used as obtained. The solutions of the **1-5** compounds were prepared in the same way, *i.e.* the crystal/s of the selected compound was/were weighed and then dissolved at the appropriate volume level of solvent (~10 mL), corresponding to the MPc concentration of  $10^{-6} - 10^{-5}$  mol/L. After this each solution had its UV-Vis spectrum registered, it was acidized with the MPc equivalent quantity/ies of HCl and soon after it was measured again. However, in the case of compound **3**, which at the selected compounds set is the only one non-axially substituted by iodine, the additional measurement at specially changed time conditions were also performed. The registration of the UV-Vis spectra of the compounds examined solutions was carried out using Carry-Varian 2300 spectrometer.

# **3.** Specification and characterization of compounds 1-10 transformations in the selected solutions

The inspections and comparison of the characteristic features of the UV-Vis absorption traces presented in Fig.1-10 means that the results can be interpreted as follows:

Spectra of InPcI (1) at net and acidized Hacac, Fig.1



*Fig.1. UV-Vis spectra of* 1 *solution at Hacac:* a – *net solution, b, c, d* – *solution acidized with one, two and three HCl.* 

Solution of 1 at net Hacac (a) shows splitting of the Q band, where  $\lambda_{max}$  for  $Q_1 = 679$  and  $\lambda_{max}$  for  $Q_2 = 687$  nm. Acidization of the solution with HCl leads to remarkable changes of its spectrum in the Q band area: after the first HCl portion (b) the splitting of Q band vanishes and only a component at  $\lambda$  corresponding to  $Q_2$  remains. After the next acidization steps (c, d), the peak at  $Q_2$  position also vanishes and two new, finally nearly equally intense and well separated peaks at 655 and at 691 nm are seen which indicates that free phthalocyanine was formed [9]. Similar observations were reported for MgPc when DMF was used as solvent and TFA as acid [31].

We ascribe the spectra to the following InPcI compound successive transformations and states: (a) The molecular anions  $(acac)^{-}$  present in the solvent repels the I<sup>-</sup> from its coordinative site at InPcI molecule. (b) The first acidization with HCl causes the next substitution *i.e.*  $(acac)^{-}$  by *Cl*<sup>-</sup> and finally after succeeding acidizations (c, d) the indium

phthalocyanine has gone through demetalation. The such deduced processes may be written in the short form:

Scheme 1.

- (a)  $InPcI + Hacac \xrightarrow{Hacac} InPc(acac) + HI$
- (b)  $InPc(acac) + HCl \xrightarrow{Hacac} InPcCl + Hacac$
- (c-d) InPcCl+HCl  $\longrightarrow$  InCl<sub>3</sub>+H<sub>2</sub>Pc

## Spectra of HfPcI<sub>2</sub>Pht (2) at net and acidized Hacac, Fig.2



Fig.2. UV-Vis spectra of 2 solution in Hacac: a – net solution, b, c – solution acidized with one and two HCl

Solution of **2** at net Hacac (a) shows splitting of the Q band, whereas  $\lambda_{max} Q_1$  is 685 and  $\lambda_{max} Q_2$  is 690 nm. After the first acidization with HCl (b) only  $Q_2$  is observed, but apart from that a quite new and well-separated  $Q_3$ ,  $\lambda = 722$  nm, band appears. The next acidization causes a decrease in  $Q_2$  and an increase in  $Q_3$  intensity (c). We interpret the traces (a-c) registered as follows:

Scheme 2.

- (a)  $HfPcI_2Pht + 2Hacac \xrightarrow{Hacac} HfPc(acac)_2 + 2HI + Pht$
- (b-c)  $HfPc(acac)_2 + 2HCl \xrightarrow{Hacac} [HfPc]^{2+} 2Cl^{-} + 2Hacac$

Spectra of Sn(II)Pc (3) at net and acidized Hacac, Fig.3



Fig.3. UV-Vis spectra of 3 solution in Hacac: a - 10 minutes; net solution, b – solution acidized with HCl, c - 1 day net solution, d - 1 day solution acidized with HCl

Ten minutes solution of **3** in net Hacac shows a relatively wide Q band at 695 nm and a shoulder on the longer  $\lambda$  site (a). After acidization with HCl the Q band becomes sharp and the  $\lambda_{max}$  is 693 nm (b). A one day solution of **3** at net Hacac shows a broad Q band at 695-698 nm (c) indicating two but not well resolved components. After acidization with HCl the Q band becomes sharp and the  $\lambda_{max}$  is 693 nm. The measurements in net Hacac indicate that in that solvent the process of auto-oxidation of Sn(II) took place, which at the 10 minutes solution is not complete and therefore that solution contains Sn(II)Pc and Sn(IV)Pc chromophore (a). That process may be written in short form:

Scheme 3.



Fig.4. UV-Vis spectra of 4 solution in Hacac: a – net solution, b – solution acidized with two HCl

Traces registered for solution of **4** at net and acidized Hacac shows the same absorbance maxima positions and shapes as that registered for a 1 day solution of **3**. In analogy to **3**, the process deduced for **4** may be written:

## Scheme 4.

- (a)  $Sn(IV)PcI_2 + 2Hacac \xrightarrow{Hacac} Sn(IV)Pc(acac)_2 + 2HI$
- (b)  $Sn(IV)Pc(acac)_2 + 2HCl \xrightarrow{Hacac} Sn(IV)PcCl_2 + 2Hacac$

Spectra of  $GePcI_2(5)$  at net and acidized Hacac, Fig.5



Fig.5. UV-Vis spectra of 5 solution in Hacac: a – net solution, b – solution acidized with two HCl

The solution of **5** at net Hacac shows a well-developed Q band with maximum at  $\lambda$ =680 nm (a). After acidization with HCl, the Q band becomes only a little sharper but it is spectacularly

shifted batochromically by roughly 10 nm (b). The deduced corresponding process in short form is:

Scheme 5.

- (a)  $Ge(IV)PcI_2 + 2Hacac \xrightarrow{Hacac} Ge(IV)Pc(acac)_2 + 2HI$
- (b)  $Ge(IV)Pc(acac)_2 + 2HCl \xrightarrow{Hacac} Ge(IV)PcCl_2 + 2Hacac$

Spectra of InPcI (1) at net and acidized benzene, Fig.6,



Fig.6. UV-Vis spectra of InPcI at benzene: a – net solution, b – solution acidized with one HCl

The solution of **1** at net benzene (a) shows a strong and sharp Q band with maximum at 688 nm. After acidization the Q band is only insignificantly batochromically shifted (b),  $\lambda_{max}$ = 690 nm. This change corresponds at least to the exchange reaction:

Scheme 6.

 $InPcI + HCl \xrightarrow{benzene/HCl} InPcCl + HI$ 

Spectra of HfPcI<sub>2</sub>Pht (2) at net and acidized benzene, Fig. 7



Fig.7. UV-Vis spectra of 2 at benzene: a - net solution, b - solution acidized with HCl

Solution of 2 at net as well as at HCl acidized benzene shows the same spectrum traces with sharp Q band with a maximum at 686 nm. The results indicate the relative stability of 2 in benzene.

Spectra of Sn(II)Pc (3) at net and acidized benzene, Fig.8



Fig.8. UV-Vis spectra of 3 at benzene: a - net solution, b - solution acidized with two HCl, c - acidized solution measured after one day.

Solution of **3** at net benzene shows a well-developed Q band with  $\lambda_{max}$  at 695 nm (a). After acidization, the early measurement (b) shows the Q band maximum in a slightly longer  $\lambda$  position, 696 nm, but the final measurement performed after 1 day (c) shows the reverse Q band shift and a maximum at 693 nm. The deduced chemical process undergoing in the acidized solution is:

Scheme 7.

 $Sn(II)Pc + 2HCl \xrightarrow{benzene/HCl} Sn(IV)PcCl_2 + H_2 \uparrow$ 

Spectra of  $Sn(IV)PcI_2$  (4)at net and acidized benzene, Fig. 9.



Fig.9. UV-Vis spectra of 4 at benzene: a – net solution, b – solution acidized with two HCl

Traces registered for the solution of 4 at net (a) and acidized benzene (b) shows a little sharpening of Q band with maximum at 693 nm after acidization. It may correspond to the halogen exchange reaction:

Scheme 8.

 $Sn(IV)PcI_2 + 2HCl \xrightarrow{\text{benzene/HCl}} Sn(IV)PcCl_2 + 2HI$ 

Spectra  $Ge(IV)PcI_2(5)$  at net and acidized benzene, Fig.10



Fig.10. UV-Vis spectra of 5 at benzene: a – net solution, b – solution acidized with two HCl

Traces registered for the solution of 5 at net (a) and acidized benzene (b) show nearly the same Q band position, at 692 nm, and are almost identical. Therefore, we suppose that in acidized solution of 5 the exchange reaction took place:

Scheme 9.

 $Ge(IV)PcI_2 + 2HCl \xrightarrow{benzene/HCl} Sn(IV)PcCl_2 + 2HI$ 

#### **IV Discussion**

When comparing the UV-Vis traces recorded for the **1-5** compounds solution at net Hacac (Fig.1-5, traces a) the following is evident: after the molecules composing of the crystals of **1-5** compounds undergo a disassembling and are dissolved by Hacac, in case of **1**, **2** and **4**, **5** compounds their axially ligated iodine atoms are replaced by  $(acac)^{-}$  anions present in the solvent due to  $Hacac \Leftrightarrow H^{+} + acac^{-}$  balance, which finally occupy the respective coordinative axial sites. The solvation of compound **3** however at Hacac is controlled by yet another mechanism. In this case the hard oxygen donors of the solvent are capable of causing the auto-oxidation of Sn(II) to Sn(IV) ions and as a result the Sn(II)Pc molecules are transformed to Sn(IV)Pc(acac)<sub>2</sub> molecules, whereas the hydrogen molecules are expulsed.

The acidized effect of the **1-5** compounds solution at Hacac (Fig. 1-5, traces b, c) are very clearly seen on UV-Vis traces. Obviously acidization causes changes not only of the dissolved species state but also the solvent molecules balance. Upon acidization of the Hacac solvent its ionized form vanishes, (see scheme 10), and at such a state the solvent is coordinately less effective.

#### Scheme 10.

## $H^+ + (acac)^- \xrightarrow{HCl} Hacac$

Consequently in the cases of all **1-5** compounds after acidization, of the corresponding acetylacetone solution the chloride complex is formed, whereas each compound solution behaviors specifically. In the case of **1** the easy demetalation of indium phthalocyanine seems quite particular. In case of **2** the exceptional absorbance changes and strong batochromically Q band shifts should be noted: initially, at net Hacac, Q band is splitted disappears after acidization and only its component on the longer wavelength site, the showing a decrease in the intensity with the acidization increase and simultaneously the new shifted band intensity increase is seen. The latter we ascribe to the cationic form of the chromophore which correspondingly involved the shrinking of a negatively charged Pc ring. In the case of both tin phthalocyanines (**3,4**) and germanium phthalocyanine (**5**) solution, the spectacularly

respectively hipsochromic and batochromic Q band position shifts after the acidization of those solutions, are registered. Besides, it is noteworthy, as documented here, that the Q bands of the  $(acac)^{-}$  ligated complexes are more or less wider than that of the halogen ligated ones. Therefore, we postulate that the tautomerizm of  $(acac)^{-}$  and the state of the balance, graphically shown as:

Scheme 11.



at the complex may be the main factor decisive for the Q band wideness or even splitting. When comparing the UV-Vis traces reordered for **1-5** compounds at benzene as well as before as upon the solution acidization (Figs. 6-10) it is evident that the respective Q band character, with exception of **3**, remains practically unchanged. The Sn(II)Pc represents a very interesting case. As proved (Fig. 8) this compound at benzene shows the Q band maximum at 695 nm. However, upon acidization the Q band immediately moves to 696 nm and next slowly moves back and after a day it reaches the stable position at 693 nm. This value is found as characteristic for Sn(IV)Pc chromophore. Therefore, we conclude that the presence of the CI ions at the Sn(II)Pc solution in benzene firstly provokes the Sn(II) ion into greatly protruding from the Pc plane and next the transformation of Sn(II)Pc to Sn(IV)PcCl<sub>2</sub> took place. Moreover as the Sn(IV) is still a relatively big ion (for comparison radius for Sn(IV) is 0.71 Å but for Ge(IV) is 0.53 Å [17]), it must be squeezed to the Pc plane and in the effect, the Pc ring undergoes expanding, which is manifested by the fact that the Q band  $\lambda_{max}$  of Sn(II)Pc is greater than the Sn(IV)Pc complex.

#### **V** Conclusions

In conclusion we have shown in this work that the UV-Vis spectra in Hacac solution of In(III)PcI, Hf(IV)PcI<sub>2</sub>Pht, Sn(IV)PcI<sub>2</sub> and Ge(IV)PcI<sub>2</sub> shows that the axially ligated iodine atoms are replaced by (*acac*)<sup>-</sup> anions of the solvent, whereas in Sn(II)Pc the oxygen donors of the solvent causing the auto-oxidation of Sn(II) to Sn(IV) ions and as a result the Sn(II)Pc is transformed into the Sn(IV)Pc(acac)<sub>2</sub>. In all studied compounds the acidized effect in solution at Hacac clearly shows the chloride complex is formed. The observed UV-Vis spectra for the Sn(II)Pc at benzene with HCl results oxidation of Sn(II) to Sn(IV) and the Sn(IV)PcCl<sub>2</sub> is formed. Whereas for the remained studied compounds at benzene solvent both before and after the solution acidization there are no noticeable changes of the Q band. Finally, we want

to add that for the examined set of phthalocyanines no experimental evidence for the Q band profile character dependence on the MPc complexes molecules  $C_{4v}$  or  $D_{4h}$  symmetry class has been found. The examples examined here lead us however to a conclusion that when the  $N_4$  square core of the Pc ring undergoes expansion, then the Q band  $\lambda_{max}$  position lowers and when it undergoes shrinking the Q  $\lambda_{max}$  moves to longer wavelengths.

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## Highlights

The oxidation of M(II)Pc to M(IV)Pc(acac)<sub>2</sub> is occurred in acetylacetone (Hacac).

The *acac*<sup>-</sup> ligand of MPc(acac)<sub>2</sub> is substituted by *Cl*<sup>-</sup> in reaction with HCl.

The I ligand of MPcs is replaced by Cl in benzene during reaction with HCl.

Reaction of MPcs with HCl may lead to demetalation.