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Note to titanium (III) and (IV) phthalocyanines synthesis in modified microwave oven.

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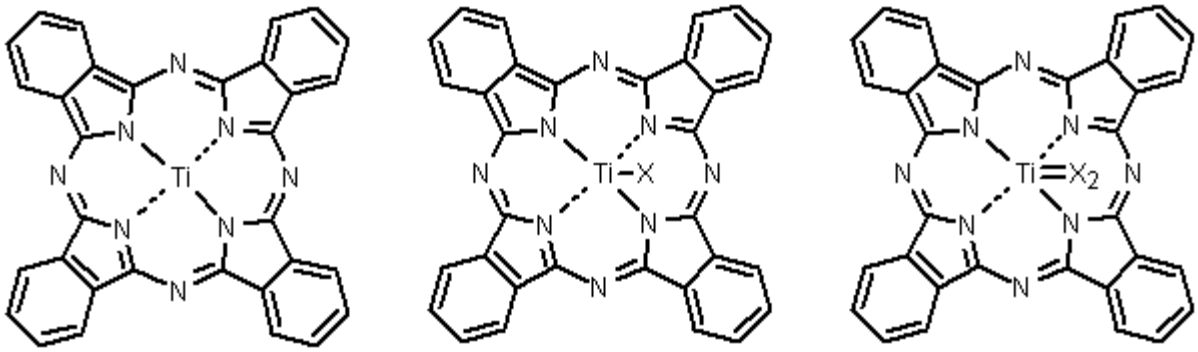
Abstract: Microwave irradiation of 1,2-dicyanobenzene (phthalodinitrile) and reducing agent (hydrogen donor) or 1,3-diiminoisoindoline in organic solvents with titanium (III) or titanium (IV) chlorides after treating with water leads to titaniumoxo (IV) phthalocyanine. The formation of titaniumchloro (III) phthalocyanine in solvent-free conditions and in solvents under microwave irradiation is discussed.

There are known three types of phthalocyaninatotitanium complexes in which titanium possesses valence II, III, and IV.

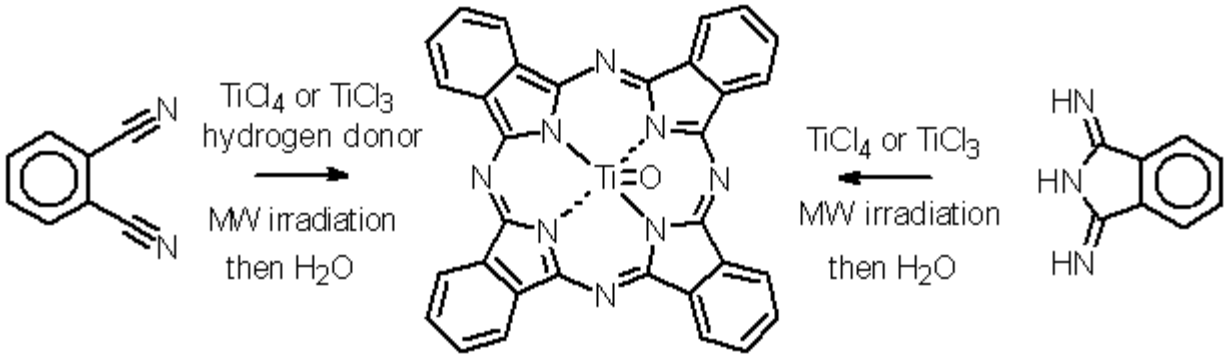


I **II** **III**

While the complexes of **I** and **II** types are relatively rare compounds, the complexes of type **III** now are widely used in industry and widely described in literature. The most widely used is titaniumoxo (IV) phthalocyanine (**III**, X_2 = O, (**IV**)). It is used as photoconductive pigment in light-sensitive elements for laser printers, xerographic apparatuses, light diodes, photovoltaic cells, solar cells, etc. In our best knowledge, the quantity of publications covered by Chemical Abstracts, in which compound **IV** was described, to present time is more than 1800. Almost all of them are papers and patents. Most of conference posters are not covered in Chemical Abstracts, and so, overall quantity of printed works concerning **IV** is much more. At present, every three days appears a new publication concerning **IV**. Only one of these publications was dealed with microwaves: dispersions of **IV** in organic solvents were purified in special apparatus by combined action of microwaves and ultrasound with magnetic stirrer [1].

The first synthesis of titanium phtalocyanine complex in microwave oven was described in [2]. Reaction of 1,2-dicyanobenzene (**V**) and titanium (III) chloride hydrate without solvent after washings with water, acetone, and dichloromethane gives **II** (X=Cl, **VI**); UV-vis and IR were given, microanalytical data (C, H) was satisfactory (not given).

In our hands in modified microwave oven reaction of **V** with titanium (III) chloride in the presence of hydrogen donor (reducing agent) in organic solvent after water treatment gaves mainly **IV**. In MALDI TOF mass-spectrum of crude **IV** peaks at 575.7(100%) and 576.6 (60%), $C_{32}H_{16}N_8TiO$ are main, peaks at 594.6 (10%, $C_{32}H_{16}N_8TiCl$) and 1135.8 (5%, $(C_{32}H_{16}N_8Ti)_2O$, dimeric phthalocyanine) are minoric. The reaction of **V** with titanium (IV) chloride in the presence of reducing agent in organic solvent after water treatment gaves **IV**, too. The reaction of 1,3-diiminoisoindoline (**VII**) with both $TiCl_3$ and $TiCl_4$ after water treatment leads also to **IV** [3].



V **IV** **VII**

The first synthesis of **VI** by reaction of $C_{32}H_{16}N_8Li_2$ with $TiCl_3$ in boiling quinoline was carried out in absence of moisture and O_2 (C, H, N, Cl, Ti microanalytical data were given). Then by oxidation of **VI** with air in boiling quinoline **IV** was obtained (C, H, N, Ti were given) [4].

The reaction of titanium (III) chloride with **V** proceeds as follows [5]:

$$4\ C_6H_4(CN)_2 + 2TiCl_3 = C_{32}H_{16}N_8TiCl_2 + TiCl_4$$

Titanium (IV) chloride formed can to react with **V** in the presence of hydrogen donor (for example, hydroquinone):

$$8\ C_6H_4(CN)_2 + 2\ TiCl_4 + C_6H_4(OH)_2 = 2\ C_{32}H_{16}N_8TiCl_2 + 8\ HCl + C_6H_4O_2$$

In absence of hydrogen donor second stage proceeds with tarry impurities formation.

Titanium dichloro (IV) phtalocyanine **III** (X = Cl, (**VIII**)) is readily hydrolysable. As we have observed, even in wet air few hours is enought to complete transformation of **VIII** to **IV**:

$$C_{32}H_{16}N_8TiCl_2 + H_2O = C_{32}H_{16}N_8TiO + 2HCl$$

According to above equations formation of **IV** from titanium (III) chloride can to be explain.

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