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Synthesis of mono- and bisphthalocyanine complexes using microwave irradiation

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Starting with phthalic and 4-*tert*-butylphthalic acid derivatives, the bisphthalocyanines of rare earth elements and hafnium and zirconium were prepared using microwave irradiation.

Phthalocyanines are of interest not only as model compounds for biologically important porphyrins but also because of their outstanding physical properties, including semiconductive, liquid crystalline and non-linear optical behaviour.[1–4]

Generally, the published methods of phthalocyanine synthesis, rely on the interaction of phthalogens (anhydrides of phthalic acids or phthalodinitriles) with metals or their salts at high temperatures.[5–8] These methods require long-term heating (for 2.5–5 h) of a reaction mixture in a melt (fusion) or high-boiling solvent. In more recent publications,[9,10] it was proposed to use alcohols as solvents and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the base in order to decrease the temperature of the synthesis. However, the synthesis takes 12–14 h, and the range of phthalogens is limited to phthalodinitrile.

Recently, the synthesis of metal-containing (Cu, Co, Ni and Fe) phthalocyanines has been reported using microwave irradiation,[11] which simplified the synthesis in the absence of solvents and shortened its duration from several hours to few minutes. However, Shaabani[11] restricted his studies to complex formation from phthalic anhydride in the presence of urea.

We investigated the synthesis of phthalocyanine complexes using microwave irradiation with different phthalogens: phthalodinitrile **1a**, phthalimide **1b**, phthalic anhydride **1c**, and phthalic acid **1d**. *tert*-Butyl-substituted phthalocyanines were synthesised from 4-*tert*-butyl phthalodinitrile **2a** or 4-*tert*-butyl phthalimide **2b**.

The reaction mixtures were irradiated in a microwave oven (Samsung, model 1714R) for 5–10 min at 450–850 W. Following these experiments, we were able to select optimal conditions for the production of planar and sandwich-like complexes, depending on the nature of starting reagents and their ratio.

The interaction of phthalodinitrile or 4-*tert*-butyl phthalodinitrile with lithium methylate (taken in a 2:1 ratio of nitrile to lithium methylate) for 3–5 min at the irradiation power 700 W resulted in the formation of di-lithium complexes of the corresponding phthalocyanines in yields of as high as 70%. Treating the reaction mass with a 3% HCl solution gave the quantitative yields of free phthalocyanines, since the complexes of alkali metals are unstable and lithium is rapidly removed from complexes even with trace water.[12] The other phthalogens used for the synthesis of lithium phthalocyanines and free phthalocyanine were found to be less active in the complex formation reactions.

When we carried out the synthesis of divalent metal (Co, Zn, Cu and Ni) phthalocyanines, we observed that the activity of phthalogens increased in the order phthalic acid < phthalic anhydride < phthalimide < phthalodinitrile; *tert*-butyl phthalocyanines were produced in better yields than unsubstituted phthalocyanines. The highest yield (70–80%) was attained with the use of 4-*tert*-butyl phthalodinitrile as the initial reagent under microwave irradiation at 650–700 W for 6–10 min.

To synthesise manganese and chromium phthalocyanines, $MnCl_2$ or $Mn(OAc)_2$ and chromium hexacarbonyl $Cr(CO)_6$ served as the initial reagents. Unsubstituted Mn- and Cr-containing phthalocyanines were produced from precursors **1a**–**b**. As in the case of divalent metals, the yield of phthalocyanines was lowest after synthesis from phthalic acid, while the use the other phthalogens ensured similarly good production of metal-containing phthalocyanines. Therewith, phthalimide and phthalodinitrile have some advantages for the synthesis of Cr and Mn phthalocyanines, respectively.

As the described for the divalent metals studied, *tert*-substituted phthalocyanines of Cr and Mn were produced in greater yield (52% and 30%, respectively) than their unsubstituted analogues after 6–10 min exposure to microwave irradiation (650–700 W).

Of particular interest was the synthesis of the phthalocyanines of rare-earth elements, which are capable of forming both planar and sandwich-like complexes.[13] In our work, rare-earth elements phthalocyanines were produced from tetrahydrated Tb, Dy and Lu acetates and different phthalogens.

Inasmuch as we found previously[14] that the formation of bisphthalocyanines proceeds *via* planar phthalocyanines, our attempts were focused on the production of individual mono- and bisphthalocyanines by varying the phthalogen : salt ratio (4:1, 8:1, 12:1) and the time of synthesis. Indeed, with increasing time of synthesis, the proportion between mono- and bisphthalocyanine yields was shifted toward the bisphthalocyanine.

The activity of **1b**–**d** as phthalogens slightly increased in the order: phthalic acid < phthalic anhydride < phthalimide, but the main final product was mono-phthalocyanine even if the reagents were taken in the ratio optimal for bisphthalocyanine synthesis. However, the reaction with **1a** as a precursor gave bisphthalocyanine as the main final product, which was formed even at the phthalodinitrile : salt ratio equal to 4:1. Thus, depending upon the nature of the phthalogen, its proportion to the metal salt, and the duration of microwave irradiation, it was possible to control the yield of final products. Unexpectedly, the yield of the *tert*-butyl-substituted phthalocyanines of rare earth elements under microwave irradiation was much smaller than that of unsubstituted phthalocyanine analogues. Thus, the yield of unsubstituted bisphthalocyanines synthesised from rare-earth acetates was 7–10 times higher than that of *tert*-butyl phthalocyanines and accounted for more than 70%.

Earlier, we found that the heating of the reaction mixture consisting of phthalodinitrile and hafnium and zirconium salts at 250–280 °C for several hours was necessary for the formation of sandwich-like complexes of these metals.[15] In this work, this reaction was accomplished over a few minutes under exposure to 650–700 W microwave irradiation and the amount of side products was lower, which make final purification simpler. Thus, a single purification procedure with the use of column chromatography gives the individual compounds with a high degree of purity, as is evident from TLC, elemental analysis and the UV and visible spectra.

Hence, the proposed method of phthalocyanine synthesis allows one to avoid lengthy heating of the reaction mass at high temperatures, which is undesirable for some of phthalodinitriles in view of their possible destruction.

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