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Template Synthesis and Optical Spectra of Zinc-2,3-Naphthalocyanine

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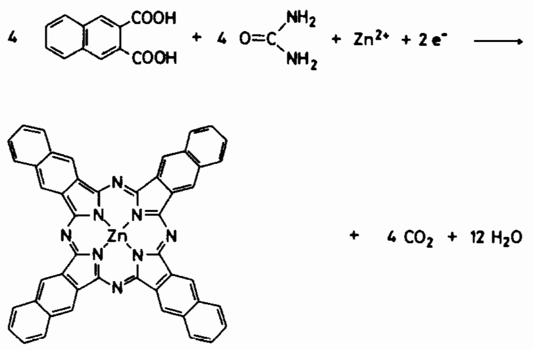
Although the first preparation of metal naphthalocyanines (NPC) was reported by Bradbrook and Linstead in 1936 [1] not much is known about the chemical and physical properties of these compounds. This is in contrast to the wealth of information on the phthalocyanines [2]. NPC should be of considerable interest because the extension of the π-electron system, compared to phthalocyanines, may effectively modify the optical spectra and other electronic properties such as redox potentials, electrical conductivity, photoconductivity and catalytic activity which have been extensively investigated for the phthalocyanines [2].

For the first preparation of NPC, 1,2- and 2,3-dicyanonaphthalines were used as starting materials. Although the synthesis of 2,3-NPC has been mentioned, a detailed description has been given only for 1,2-NPC which was obtained as a mixture of up to four isomers [1]. These isomers may be difficult to separate and characterize. The optical spectra of the isomers should depend on their symmetry [3]. To avoid any difficulties associated with this isomerism we confined our attention to 2,3-NPC. Zn–2,3-NPC was obtained by heating commercially available (Aldrich) naphthalin-2,3-dicarboxylic acid (8 g) with urea (12 g), and Zn acetate (4 g) to 310 °C for 40 min. The stoichiometry of this synthesis can be described by the equation



The two electrons which are required for the reduction may come from zinc acetate. Purification of the crude product was achieved first by sublimation of volatile impurities and then by extraction with pyridine for several days. Analytically pure Zn–2,3-NPC was obtained (1.3 g, 18% yield) as a green microcrystalline powder. The color is not as dark as that of phthalocyanines because the main absorption bands do not occur in the visible[*] (Fig. 1). The energy gap between the Soret or B-band (332 nm, ϵ = 42000) and the α- or Q-band (767 nm, ϵ = 160000) is considerably larger than for phthalocyanines [3]. The small halfwidth of the α-band (22 nm) is remarkable. Upon excitation with light of the wavelength 333 nm a strong fluorescence occurs in the near infra-

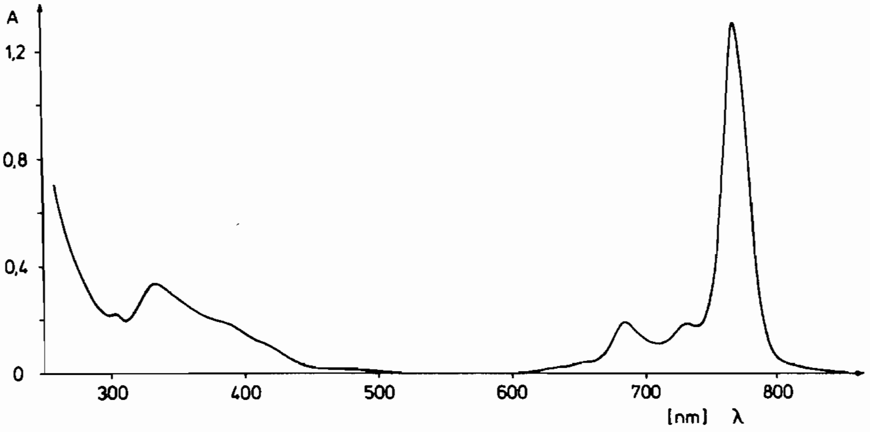


Fig. 1. Absorption spectrum of 8.12 × 10^{-6} *M* Zn–2,3-NPC in DMSO; 1 cm cell.

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[*] An absorption spectrum of NPC (probably 1,2-) has been reported for a β isomer of the free base and an α isomer of the Cu salt [4]. The identity of these isomers does not seem to be known [1]. The energy gap between Soret and α-band lies within the usual range of phthalocyanines. Some spectral data on 1,2-NPC of other metals are given in ref. 5.

red at 770 nm. A phosphorescence was not observed but may be outside of the detection range of a conventional emission spectrometer.

Acknowledgements

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