



Research paper

Solvothermal modification of magnesium phthalocyanine

Jan Janczak

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland

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ABSTRACT

Reactivity of magnesium phthalocyanine (MgPc) in the dry 3,4-lutidine (3,4-lut), in the 3,4-lut/DMSO, in DMSO and in 3,4-lut/acetylacetone (acacH) systems has been investigated. Reaction of MgPc with dry 3,4-lut leads to formation of MgPc(3,4-lut) compound (**1**), in which the Mg atom is characterised by rarely encountering in magnesium phthalocyanines 4 + 1 N-type of coordination. In presence of the water tracer, depending on the reaction conditions and the 3,4-lut quantity in the MgPc/3,4-lut/DMSO system the solvothermal reaction leads to formation of three complexes in the crystalline form: MgPc(H₂O)₂(3,4-lut) – (**2**), [MgPc(3,4-lut)][MgPc(H₂O)₂(3,4-lut)]·½(3,4-lut) – (**3**) and [MgPc(H₂O)₂(3,4-lut)][MgPc(DMSO)]·½(DMSO) – (**4**). Reaction of MgPc with DMSO yields crystalline MgPc(DMSO) complex (**5**). In these complexes in the solid-state the central Mg atom of MgPc exhibits 4 + 1 coordination. The reaction of MgPc in the case of 3,4-lut/acacH system leads to demetallation of MgPc and formation of crystalline Mg(acac)₂(H₂O)₂ compound (**6**) that after several days at ambient air in the mother liquor transforms into organic crystalline compound of C₁₀H₁₂O₂ (**7**). The structure of **1–7** has been determined by X-ray single crystal diffraction. All MgPc-derivatives (**1–5**) were characterised by thermogravimetric analysis. Partial MO energy diagrams and the calculated absorption spectra of the MgPc-derivatives were compared with the experimental electronic absorption spectra in 3,4-lutidine and DMSO solutions. These results point that the axial ligation of MgPc by O- and N-donor ligands do not change significantly the energy gap of the HOMO–LUMO levels which is compared with that of the parent MgPc pigment.

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1. Introduction

Ever since Linstead's report in 1934 [1] phthalocyanine and its metal complexes are used as industrial dyes and pigments. Nevertheless, novel application of these macrocycles, which structurally consist of four isoindole units connected by azamethine bridges to form an 18- π electron aromatic macrocycles, are extensively studied. They are intensively studied as multiply functional materials useful for modern technology [2–5]. They can be useful as organic materials for electronic, optoelectronic and photoelectronic devices like as recordable disks (CD), active matrix liquid crystals displays, photoconductors in laser printers and solar cells [6–10]. Moreover, metallophthalocyanines have been applied as photosensitizers for photodynamic therapy, both in their free form as well as after incorporation into liposomes [11–17]. PDT is a cancer treatment that necessitates the activation of a photosensitizer in the cancer cell with the appropriate wave-length of light [12].

Our interest in magnesium phthalocyanine and its 4 + 1 and 4 + 2 coordinated derivatives (MgPcL and MgPcL₂, where L is

N- or O-donating ligands) arises from their similarity and relationships to the chlorophyll that provides the possibility to them to be used as synthetic model [18]. MgPc, similar to other metal(II) phthalocyanines, crystallises in two polymorphic forms α and β . However, the X-ray single crystal structure has been determined only for its β modification [19]. Additionally, it has been stated that the crystals of MgPc are unstable in ambient atmosphere forming complexes with the compositions of (MgPc)₂-O₂ and (MgPc)₂N₂ [20]. The formation of the oxygenated magnesium phthalocyanine complex has been confirmed by the X-ray single crystal analysis [21]. In the solid state MgPc exhibits an intense absorption band in the near-IR spectral region due to its non-planar nature that arises from the interaction of electropositively polarised Mg center of one molecule with the electronegatively polarised N-azamethine atom of a neighbouring MgPc molecule along the stacking arrangement [19,22].

A wide application of metallophthalocyanines including the MgPc for technological purposes is limited by their relatively low solubility in most organic solvents. The well-known way to tune the application properties of metal(II) phthalocyanine complexes is modify the phthalocyaninato(2–) macroring by the aryl,

E-mail address: j.janczak@int.pan.wroc.pl

alkyl and other substituents [23–29] or by additive metal center complexation [30–33]. Some of axially ligated magnesium phthalocyanine derivatives MgPc(L) with different ligands like as F, Cl, Br and triphenylphosphine oxide crystallise as solvate and their molecular structures were determined by the Homborg group [34,35]. The role of the peripheral substituents in the chemistry of phthalocyanines and their optical properties was the subject of some reviews [36–38]. Both methods improve the solubility of the M(II)Pc-complexes due to the steric hindrance of axial ligands or substituents of hydrogen atoms on phthalocyaninate(2–) macrocycle that lowers the π - π interactions as well as the aggregation in solutions [39–41]. Correspondingly it has been well experienced that the feature of MPC's may be tuned by their annealing in various solvents. The MPC's in such processes undergo not only the recrystallization or purification, but they may interact with the solvent molecules forming MPC-derivatives [42–47]. The interaction of some MPC's with solvent molecules resulting in their decomposition was found in the indium monophthalocyanine [48]. Another examples of the active role of the solvents are interactions of the hafnium monophthalocyanine and hafnium diphthalocyanine complexes with acetylacetone, benzonitrile and 4-methylpyridine yielding to formation of novel hafnium phthalocyaninate complexes [49], as well as the formation of the holmium open phthalocyanine (oPc) complex that has been isolated during investigation of the reactivity of iodine doped holmium diphthalocyanine (HoPc₂I) in the acetylacetone-water system [50]. The active role of MgPc in the catalytic transformation of the cyano group in the organic cyano compounds has been confirmed [51].

Quite recently, solvothermal reaction of MgPc in dry 3,5-lutidine, in 3,5-lutidine/DMSO and in 3,5-lutidine/acetylacetone systems resulting in the formation of new complexes in the crystalline form has been performed [52]. In the present work, the investigation of the interaction of the MgPc with the solvent molecules, i.e. in dry 3,4-lutidine, in 3,4-lutidine/DMSO, in DMSO and in 3,4-lutidine/acetylacetone systems, is the aim of this work. The solvothermal reaction of the MgPc in such systems lead to formation of the new products in the crystalline form. Additionally, other behaviour of the 3,4-lutidine in relation to 3,5-lutidine in these systems will be discussed.

2. Experimental

2.1. Materials and methods

Crystalline form of MgPc was obtained as described previously [19]. 3,4-lutidine, DMSO and acetylacetone were obtained from Aldrich. The composition of the obtained crystals was checked with a Perkin-Elmer 2400 elemental analyser and with energy dispersive spectroscopy (EDS). EDS spectra were acquired and analysed using an EDAX Pegasus XM4 spectrometer with SDD Apollo 4D detector mounted on a FEI Nova NanoSEM 230 microscope. In addition the elemental analysis was carried out also with a Perkin-Elmer 240 elemental analyzer. Measurements of the UV-Vis spectra were carried out at room temperature using a Cary-Varian 2300 spectrometer. The UV-Vis spectra were recorded in 3,4-lutidine or DMSO solution ($c = 10^{-6}$ mol/l). Thermal analysis was carried out on a Linseis L81 thermobalance apparatus with Pt crucibles. The initial sample mass was about 25 mg. Powder Al₂O₃ was used as a reference. The measurements were performed under static air on heating from room temperature to 300 °C at the heating rate of 5 °C min⁻¹. The rest of the samples after TG analyses were checked on a PANanalytical X'Pert diffractometer equipped with a Cu-K α radiation source ($\lambda = 1.54182$ Å) at room temperature.

2.2. Preparation procedure

2.2.1. Synthesis of MgPc(3,4-lut) complex (1)

Freshly obtained crystalline MgPc (0.15 g) was added to the dry 3,4-lut (10 mL). The suspension of MgPc in 3,4-lut was degassed and sealed under reduced pressure in a glass ampoule. Next the ampoule was heated at 160 °C for two days and then it was cooled to the room temperature. After such processing several well-developed single crystals of **1** were obtained. The crystals of **1** were separated by filtration and dried in air. Yield: 0.152 g (85%). Analysis: found: Mg, 3.81; C, 72.67; N, 19.64 and H, 3.88%. Calculated for C₃₉H₂₅N₉Mg: Mg, 3.77; C, 72.74; N, 19.58 and H, 3.91%.

2.2.2. Synthesis of MgPc(H₂O)·2(3,4-lut) complex (2)

MgPc (0.2 g) was added to a mixture of 3,4-lut (10 mL) with DMSO (1 mL). The MgPc in the 3,4-lut/DMSO (10:1) system was degassed and sealed under reduced pressure in a glass ampoule, and it was thermally processed at 130 °C during two days and then it was cooled to the room temperature. After such processing blue-violet well-developed single crystals of **2** were obtained. The crystals of **2** were separated by filtration washed with diethyl ether and dried in air. Yield: 0.235 g (82%). Analysis: found: Mg, 3.15; C, 71.72; N, 18.15; O, 2.18 and H, 4.80%. Calculated for C₄₆H₃₆N₁₀OMg: Mg, 3.16; C, 71.83; N, 18.11; O, 2.28 and H, 4.62%.

2.2.3. Synthesis of [MgPc(3,4-lut)] [MgPc(H₂O)·2(3,4-lut)]·½(3,4-lut) – (3)

MgPc (0.2 g) was added to a mixture of 3,4-lut (10 mL) with DMSO (2 mL). The suspension of MgPc in 3,4-lut/DMSO (5:1) was degassed and sealed under reduced pressure in a glass ampoule. Solvothermal processing was identical as used for the crystals **2**. The obtained crystals **3** were separated by filtration and dried in air. Yield: 0.152 g (56%). Analysis: found: Mg, 3.39; C, 72.04; N, 18.55; O, 1.18 and H, 4.48%. Calculated for C_{88.5}H_{65.5}N_{19.5}OMg₂: Mg, 2.62; C, 72.98; N, 17.32; O, 1.72 and H, 5.36%.

2.2.4. Synthesis of [MgPc(H₂O)·(3,4-lut)] [MgPc(DMSO)]·½(DMSO) – (4)

MgPc (0.2 g) was added to a mixture of 3,4-lut (8 mL) with DMSO (8 mL). The suspension of MgPc in 3,4-lut/DMSO was degassed and sealed under reduced pressure in a glass ampoule. The ampoule with the suspension was thermally processed at 130 °C during two days and then it was cooled to the room temperature. After such processing blue-violet well-developed single crystals of **4** were obtained. The crystals of **4** were separated by filtration washed with diethyl ether and dried in air. Yield: 0.192 g (78%). Analysis: found: Mg, 3.65; C, 67.58; N, 18.16; O, 3.11, S, 3.58 and H, 3.92%. Calculated for C₇₄H₅₂N₁₇O_{2.5}S_{1.5}Mg₂: Mg, 3.69; C, 67.44; N, 18.09; O, 3.14, S, 3.66 and H, 3.98%.

2.2.5. Synthesis of MgPc(DMSO) complex – (5)

Freshly obtained crystalline MgPc (0.15 g) was added to the DMSO (15 mL). The suspension of MgPc in DMSO was degassed and sealed under reduced pressure in a glass ampoule. Next the ampoule was heated at 170 °C for one day and then it was cooled to the room temperature. After such processing several well-developed blue-violet single crystals of **5** were obtained. The crystals of **5** were separated by filtration. The crystals of **5** were separated by filtration washed with diethyl ether and dried in air. Yield: 0.155 g (90%). Analysis: found: Mg, 3.98; C, 66.54; N, 18.12; O, 2.72; S, 5.11 and H, 3.53%. Calculated for C₃₂H₂₂N₈OSMg: Mg, 3.95; C, 66.41; N, 18.22, O, 2.60; S, 5.21 and H, 3.61%.

2.2.6. Synthesis of Mg(acac)₂(H₂O)₂ – (6) and C₁₀H₁₂O₂ – (7)

MgPc (0.15 g) was added to a mixture of 3,4-lut (6 mL) with acacH (6.0 mL). The MgPc in the 3,4-lut/acacH system was

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