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Syntheses and thermal characterization of the magnesium phthalocyanine complexes with 2-methoxy- and with 2-ethoxyethanol. X-ray structure of (2-ethoxyethanol)magnesium phthalocyanine

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Abstract

The syntheses of the magnesium phthalocyanine complexes with dry 2-methoxy-ethanol and 2-ethoxyethanol have been performed by recrystallization method using both anhydrous MgPc and aquated magnesium phthalocyanine, $MgPcH_2O$, as a starting material. It has turned out that in the temperature range below ca. 140 °C, the bi-axially ligated complexes are formed, i.e., MgPc(2-methoxyethanol)$_2$ and MgPc(2-ethoxyethanol)$_2$ with 4 + 2 coordination of Mg, whereas at higher temperatures, up to about 200 °C, the mono-axially ligated complexes are stable, i.e., MgPc(2-methoxyethanol) and MgPc(2-ethoxyethanol) with 4 + 1 coordination of Mg.The single crystal structure of MgPc(2-ethoxyethanol) complex has been determined. The central Mg atom is displaced towards the hydroxyl group of the ligand by about 0.37 Å from the (*N*-isoindole)$_4$ plane of the Pc ring. Hydrogen bonds of the type O–H···N between the hydroxyl groups of 2-ethoxyethanol and one of the azamethine N-atoms of the Pc ring link the molecules related by a centre of symmetry. Such a packing arrangement in the crystal leads to a dimerization with the ligand-to-Pc connections. The syntheses, thermogravimetric results and structure characteristics are compared with the known MgPc complexes with O- and N-donating molecules.

Keywords: Magnesium phthalocyanine; Complexes; Crystal structure; Thermogravimetry

1. Introduction

Metallophthalocyanines are industrially important class of compounds [1]. They are of particular interest both for versatile basic and applied researches [2,3]. One of the ways to obtain new, metallophthalocyanine based compounds is the additive complexation of the metallocyanine metal core with organic ligands. Such type of complexes of the magnesium phthalocyanine, PcMg, where Pc = $C_{32}H_{16}N_8^{2-}$, are of special interest because they can be regarded as synthetic analogue of chlorophyll. The processes observed by the PcMg complexation and transformation appeared to be similar to those involved in biological processes. In particular, a single crystal of magnesium phthalocyanine, bi-axially ligated with pyridine (4 + 2 coordination of Mg), has been obtained in order to show that when PcMg(py)$_2$ is in contact with water molecules, the latter repell the pyridine molecules from their coordinative sites in the complex [4]. The process leads to a transformation of the bi-axial PcMg(py)$_2$ into the mono-axially ligated complex $PcMgH_2O(py)_2$ with 4 + 1 coordination of Mg described in [4,5] and which is shown in Scheme 1.

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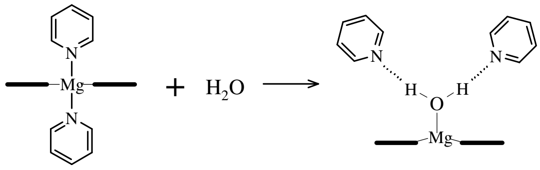

Scheme 1.

Recently, our attention was drawn by two novel, biaxially ligated magnesium phthalocyanine complexes reported in [6], i.e., di-aqua-magnesium phthalocyanine (N-methyl-2-pyrrolidone) solvate (**1**) and bis(2-methoxyethanol-O-)magnesium phthalo-cyanine (**2**). As mentioned in [6], the single crystals of (**1**) and (**2**) were obtained by a recrystallization method, but the details of the processing have been missed. Assuming that the two compounds were grown in similar external conditions and from the same magnesium phthalocyanine as a common substrate, an obvious question may be raised: where does the water molecule in (**1**) originate from and thus, why only the complex (**1**) is aquated, while (**2**) is water free.

To broaden the experimental basis and trying to clarify this issue, we have performed recrystallization of MgPc and separately $MgPcH_2O$ from 2-methoxyethanol and 2-ethoxyethanol. The results and their relation to the findings of the reference [6] will be described below.

2. Experimental

2.1. Materials

The powder of magnesium phthalocyanine MgPc (dye content 90%), 2-methoxyethanol, 2-ME (anhydrous, b.p. 124–125 °C) and 2-ethoxyethanol, 2-EE (water < 0.08%, bp 135 °C) were purchased from Sigma Aldrich Co. The magnesium phthalocyanine powder was purified and converted into the polycrystalline β-form [7] by zone refining before use. The aqua-magnesium phthalocyanine was obtained from purified magnesium phthalocyanine by grinding under water as described elsewhere [8]. All the crystalline products obtained in the preparative work were controlled by X-ray powder (STOE Stadi -2 with PSD detector) and/or single crystal diffraction (KM-4 with CCD detector) methods.

2.2. Syntheses

2.2.1. $PcMg(2\text{-}ME)_2$

(a) 1 g of PcMg compound was inserted into a glass tube and covered with 10 ml of 2-ME. The tube was degassed and the ampoule with the suspended MgPc was sealed off. As MgPc became partly dissolved in methoxyethanol, the suspension was non-transparent. The temperature of the suspension was gradually raised up to the boiling point and then kept constant by a day, to ensure the complete conversion. Next, the suspension was slowly cooled (1°/h) to room temperature and the solid part was removed from the mother liquor by filtration. As a result the red–violet, parallelepiped crystals up to 1 mm in edge were obtained. *Anal* Calc. for $C_{38}H_{32}N_8O_4Mg$: Mg, 3.53; C, 66.24; H, 4.68; N, 16.26. Found: Mg, 3.5; C, 66.4; H, 4.8; N, 16.2%.

(b) The suspension of 1 g $PcMgH_2O$ and 10 ml 2-ME was prepared as in (a). In the early stage of reaction, the colour of the suspension was not as intense as in (a), but on prolonged heating it became non-transparent. Cooling to room temperature yielded the crystals, identical in shape and colour with those in (a).

Individual crystals selected from (a) and (b) samples examined with KM-4/CCD showed the same crystal lattices, consistent with those published in [6].

2.2.2. $PcMg(2\text{-}EE)_2$

(c) The suspension of 1 g PcMg and 10 ml 2-EE was processed as in (a). The violet solid species that filtered off were mostly microcrystalline, but several, red-violet crystals with well-developed edges have also been seen under optical microscope. One of such crystals was taken for the X-ray intensity data collection and identified as PcMg(2-EE). *Anal.* Calc. for $C_{40}H_{36}N_8O_4Mg$: Mg, 3.39; C, 67.00; H, 5.06; N, 15.63. Found: Mg, 3.4; C, 67.4; H, 5.2; N, 15.4%.

(d) The suspension of 1 g $PcMgH_2O$ and 10 ml of 2-EE was processed as in (a). After cooling the reactants to room temperature, besides the microcrystalline $PcMg(2\text{-}EE)_2$, some colourless needle-shaped, but heavily intergrown species were present. They were separated from the filtrate but not analyzed here.

It should be added that the X-ray powder diffraction patterns taken from samples (c) and (d) were mutually consistent.

2.3. Thermal measurements

The thermogravimetric (TG) and differential thermal analyses (DTA) were carried out with a Linseis-81 thermobalance. The powdered Al_2O_3 was used as a standard. The measurements were performed using platinum crucibles in a static air atmosphere on heating from room temperature to 300 °C, with a heating rate of 5°/min.

2.4. X-ray diffraction

The crystal of PcMg(2-EE) of dimensions $0.23 \times 0.16 \times 0.10$ mm was chosen for the X-ray diffraction measurements on a four-circle KM-4/CCD diffractometer (Kuma Diffraction). The intensity data were collected using graphite monochromated Mo Kα radia-