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Synthesis and characterization of phthalocyanines containing 4-allyl-2-methoxyphenyl moieties

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Abstract

Phthalocyanines containing a eugenol moiety have been prepared from 1,2-dieugenoxy-4,5-dicyanobenzene and the corresponding metal salts. All of these complexes are extremely soluble in polar solvents. The structures were confirmed by elemental analysis, ^{1}H NMR, UV–VIS and IR.

Keywords: Phthalocyanine; Eugenol; Complexes

1. Introduction

Eugenol (4-allyl-2-methoxyphenol) occurs in the essential oil of various plants [1], some of which are used in folk medicine. Eugenol has been reported to show antiseptic and analgesic properties [2,3], local anesthetic activity [4], spasmolitic activity [5], parasympathetic effects and direct peripheral vasodillation [6].

Phthalocyanines have recently received much attention, especially because of their synthetic [7] and structural aspects [8], spectral properties [9], electrochromic behaviour [10] and electrical conductivity [11]. Also, their use as efficent photosensitizers in obtaining singlet oxygen is becoming especially important in the photodynamic therapy of tumors [12]. A common requirement in all these applications is the enhanced solubility of the phthalocyanine core, which is known for its insolubility in most common solvents in the case of unsubstituted derivatives. In this context, solubility in aqueous media should be considered as a prerequisite in the photodynamic therapy of tumours. For the broad range of applications, the stable phthalocyanine core should be amenable to modifications, which can be accomplished either by changing the central metal ion or by adding functional groups on the periphery [13]. Our primary aim has been the synthesis of new phthalocyanines with various functional groups and/or macrocycles. Among these we may cite the N-, and S, O- and N, S, O- containing functionalities such as oxathiaethers [14], oxadithiadiaza ethers and aza macrocycles [15–19]. While phthalocyanines with N-, O- and S-donor substituents have frequently been reported, those with conjoint N, O or O, S donor moieties are rather few [20–22].

In this present paper, we report the preparation and characterization of metal and metal-free phthalocyanines containing a eugenol moiety.

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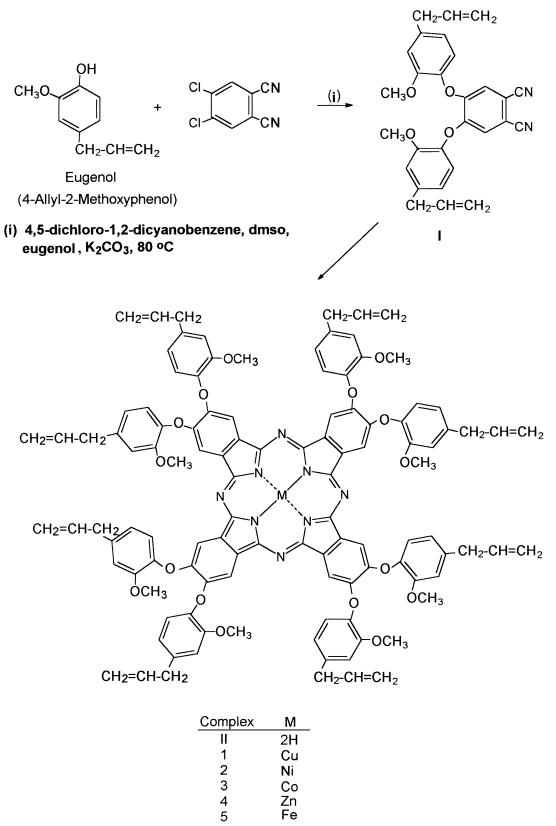
2. Results and discussion

Starting from eugenol (4-allyl-2-methoxyphenol), the general route for the synthesis of the new phthalocyanines is shown in Scheme 1. 1,2-Dichloro-4,5-dicyanobenzene has been used to prepare 4,5-disubstituted phthalonitrile derivatives through base-catalysed nucleophilic aromatic displacement [23–25]. The same route was applied to prepare 1,2-dieugenyl-4,5-dicyanobenzene **I** from eugenol and 1,2-dichloro-4,5-dicyanobenzene. The reaction was carried out in dimethylsulphoxide at 80°C and gave moderate yield (49.78%). The metal-free phthalocyanine **II** was synthesized by heating a mixture of the dicyano compound **I** with freshly sublimed hydroquinone in the absence of solvent [26]. The metallo phthalocyanines were prepared from the dicyano derivative and the corresponding metal salts in high-boiling anhydrous solvents (e.g. quinoline or ethylene glycol). The yields were satisfactory, and depended upon the transition metal ion.



Scheme 1. Synthesis of the ligand and complexes.

The most evident feature of metal-free phthalocyanine and metallophthalocyanines is their extensive solubility in common organic solvents such as chloroform, dichloromethane, dimethylformamide and dimethylsulfoxide. The solubilities in chloroform or dichloromethane are higher than those of phthalocyanines containing S and O, or S, O and N cyclic substituents [14–19].

The elemental analytical results of the starting materials and the phthalocyanine compounds show good agreement with the calculated values. Characterization of the products involved a combination of methods including IR, elemental analysis (Table 1), UV/VIS spectroscopy (Table 2) and ^{1}H and ^{13}C NMR spectroscopy.

Comparison of the IR spectral data clearly indicated the formation of compound **I** by the disappearance of the C–Cl band of 1,2-dichloro-4,5-dicyanobenzene at 640 cm^{-1} and of the OH band of eugenol at 3500 cm^{-1}, and the appearance of a new absorption at 2225 cm^{-1} (C≡N).

In the IR spectrum of **I**, the strong absorption vibration at 2225 cm^{-1} corresponding to the C≡N groups disappear after their conversion to the metallophthalocyanines **1–5** and metal-free phthalocyanine **II**. The rest of the IR spectra are very similar to those of **I** including the characteristic vibration of allyl group ($CH=CH_2$). The IR spectrum of **I** exhibits characteristic frequencies at 3080–2840 (Ar–H and C–H), 2225 (C≡N) and 1649 (allyl C=C) cm^{-1}. In the ^{1}HNMR spectrum of **I**, the doublet at δ: 3.45–3.42 ($-CH_2$), the singlet

Table 1
Analytical data for the starting materials and the phthalocyanines

Compound	Calc. (%)			Found (%)		
	C	H	N	C	H	N
I	74.34	5.31	6.19	74.38	5.32	6.22
II	74.25	5.41	6.19	74.35	5.45	6.23
1	71.81	5.13	5.98	71.94	5.18	6.06
2	72.00	5.14	6.00	72.24	5.17	6.10
3	72.00	5.14	6.00	72.21	5.20	6.09
4	71.74	5.12	5.98	71.86	5.19	6.08
5	72.10	5.15	6.00	72.27	5.20	6.10

Table 2
Electronic spectral data for the phthalocyanines in chloroform

Compound	λ_{max}/nm (10^{-4} ε/dm^3 mol^{-1} cm^{-1})						
II	705(1.68),	669(1.50),	645(0.64)[a],	345(2.90),	315(4.35),	291(4.41),	264(4.54).
1	684(0.48),	648(0.10)[a],	339(1.20),	264(3.10).			
2	675(3.20),	642(0.97)[a],	369(1.57),	306(3.80),	282(3.91),	255(3.84).	
3	672(2.94),	640(0.93)[a],	363(0.52),	338(1.49),	309(1.98),	252(1.94).	
4	680(1.50),	630(0.60)[a],	378(1.88),	282(3.03),	250(3.37).		
5	674(1.08),	645(0.72)[a],	348(2.70),	291(4.47),	261(4.51).		

[a] Shoulder.

at δ: 3.82 (OCH_3), the doublet at δ: 5.19–5.11 ($=CH_2$), the multiplets at δ: 7.25–6.80, 6.10–5.91 ppm correspond to aromatic protons and allyl (=CH) protons. The ^{13}C-NMR spectrum of **I** in $CDCI_3$ gave signals at 151.15, 150.93, 146.20, 142.18, 136.72, 129.45, 122.29, 121.42, 119.23, 116.55 (C≡N), 113.42, 109.12, 55.87 and 40.07 ppm.

The IR spectrum of **II** is very similar to that of **I**. This spectrum indicates new NH bands at 3290 and 1015 cm^{-1}. A disagnotic feature of the phthalocyanine formation from the dicyano derivative (**I**) is the disappearance of the precursor compound. The ^{1}HNMR spectrum of **II** indicates aromatic protons at 7.26–6.83 ppm, allyl (CH_2) protons as a doublet at 3.61–3.43 ppm, methoxy (OCH_3) protons as a singlet at 3.79 ppm, allyl (=CH2) protons as a doublet at 5.21–5.10 ppm, and allyl (CH=) protons as a multiplet at 6.05–5.87 ppm. A common feature of the spectra of metal-free phthalocyanine is the broad absorption probably caused by the aggregation of phthalocyanine [7,27]. Also, the NH protons of compound **II** could not be observed due to this phenomenon. Because of the ring current of the 18π electron system of the inner phthalocyanine core, the protons are characteristically shifted to low or high field [28].

In order to obtain the metallophthalocyanines **1–5**, the dinitrile derivative **I** was directly treated with the anhydrous transition metal salts [CuCL, $NiCL_2$, $CoCL_2$, $Zn(CH_3COO)_2$ and $Fe(CO)_5$]. The intense green products were very soluble in a number of solvents such as chloroform, dichloromethane, dimethylformamide and dimethylsulfoxide.

Elemental analyses, IR, UV–VIS, ^{1}H and ^{13}CNMR spectra confirmed the proposed structures of the metallophthalocyanines. In the IR spectrum of **I**, the intense absorption vibrations at 2225 cm^{-1} corresponding to the C≡N groups, disappear after their conversion into the metallophthalocyanines (**1–5**); the rest of the IR spectra bands were very similar to those of **I**, including the characteristic vibration of allyl and aromatic groups. The M–N vibrations were expected to appear at 400–100 cm^{-1} but they were not observed in KBr pellets [29]. In the ^{1}HNMR spectra of **2** and **4**, the chemical shifts relevant to the aromatic, allyl (–CH=), allyl (=CH_2), methoxy (OCH_3) and allyl (–CH_2) groups at δ: 7.25–6.86, 7.26–6.84, 6.02–5.90, 6.16–5.90, 5.20–5.11, 5.16–5.01, 3.84, 3.79, 3.44–3.29, 3.41–3.29 ppm were observed after the cyclotetramerization, respectively. Broad NMR absorptions were observed for Ni(II) and Zn(II) phthalocyanines, possibly due to aggregation.

The phthalocyanines **1–5** showed typical electronic spectra with two strong absorption regions, one of them in the UV region at about 378 nm (B band) and the other in the visible region at 705 nm (Q band) (Table 2); these are very similar to those of azamacrocycle [16–18]-substituted phthalocyanines. Although the symmetry of the phthalocyanines is lowered by the heteroatom substituent on each phenyl group, compound **II** still shows Q-band absorptions of D_{2h} symmetry in organic solvents [7]. These complexes showed an intense absorption at 705 nm and a shoulder band of lower intensity at 648 nm. The thermal decomposition temperatures of these complexes were higher than 200°C.

The main purpose of the substitutions is to enhance the very limited solubility, and to enable the convenient preparation of a series of new phthalocyanines.

3. Experimental

IR spectra were recorded on a Mattson 1000 Fourier-transform spectrometer (KBr), UV/VIS spectra on a Unicam UV/VIS spectrometer, and ^{1}H and ^{13}C NMR spectra on a Bruker AC-200 Fourier-transform spectrometer. Elemental analysis was performed by the Instrumental Analysis Laboratory of Tübitak Gebze Research Center. 1,2-Dichloro-4,5-dicyanobenzene [25] was synthesized according to the reported procedure and eugenol (4-allyl-2-methoxyphenol) was purchased from Merck Chemical Company, and was used as purchased.

3.1. 1,2-Bis(-4-allyl-2-methoxyphenoxy)-4,5-dicyanobenzene (**I**)

Eugenol (6.57 g, 40 mmol) was dissolved in dry DMSO (150 ml) under nitrogen and 1.2-dichloro-4.5-dicyanobenzene (3.94 g, 20 mmol) was added. After stirring for 10 min at 80°C, finely ground anhyd. K_2CO_3 (5.52 g, 320 mmol) was added portionwise in 2 h with good stirring. After stirring for 8 h at 80°C, the reaction mixture was poured into ice-water (500 g). The precipitate was filtered, washed with water to remove inorganic residues; and recrystallized from ethanol. Yield 4.5 g (49.78%). The compound was soluble in hot ethanol, ethyl acetate, chloroform, dichloromethane, dimethylsulfoxide and dimethylformamide. Mp. 161–162°C. IR: r_{max}/cm^{-1}: 3080–2840 (Ar-H and CH), 2225 (C≡N), 1649 (C=C, allyl), 1610, 1595, 1511, 1477, 1420, 1408, 1295, 1215, 1146, 1124, 1044, 965, 918, 884, 827, 758, 736 and 660. ^{1}H NMR ($CDCl_3$): δ 7.25–6.80 (8 H, m, Ar), 6.10–5.91 (2 H, m, =CH), 5.19–5.11 (4 H, d, $=CH_2$), 3.82 (6 H, s, OCH_3) and 3.45–3.42 (4 H, d, $–CH_2$) ^{13}C NMR ($CDCl_3$): δ 151.15, 150.93, 146.20, 142.18, 136.72, 129.45, 122.29, 121.42, 119.23, 116.55 (C≡N), 113.42, 109.12, 55.87 and 40.07 ppm.

3.2. Metal-free phthalocyanine (**II**)

3.2.1. Method A

A mixture of compound **I** (2.0 g, 4.42 mmol) and hydroquinone (0.49 g, 2.21 mmol) was gently heated under N_2 and then cooled. The mixture was heated to 200°C under N_2 and held at this temperature for 5 h. After cooling to room temperature, the reaction mixture was treated with boiling ethanol (three times) and hot water and dried. The product was purified by column chromotography (silica gel, CH_3OH:$CHCl_3$, 1:80). Yield 0.7 g (35.0%). It was soluble in chloroform, dichloromethane, DMSO and DMF. IR: ν_{max}/cm^{-1}: 3290, 3083–2840, 1645, 1603, 1511, 1455, 1420, 1283, 1215, 1156, 1135, 1015, 965, 918, 873, 827, 747 and 656. ^{1}H NMR ($CDCl_3$): δ 7.26–6.83 (32H, m, Ar), 6.05–5.87 (8 H, m, =CH), 5.21–5.10 (16 H, d, $=CH_2$), 3.79 (24 H, s, OCH_3) and 3.61–3.43 (16 H, d, –CH2). ^{13}C NMR ($CDCl_3$): δ 158.51, 152.45, 150.77, 149.80, 137.40, 137.12, 130.71, 121.47, 121.04, 120.98, 114.09, 110.40, 56.47 and 40.65 ppm.

3.2.2. Method B

Compound **I** (2.0 g. 4.42 mmol) was refluxed for 48 h under N_2 in diethylaminoethanol (50 ml). After cooling to room temperature, the green liquor was diluted with water (100 ml) and filtered. The resultant green product was washed with boiling ethanol (three times), then with hot water, and dried. The product was purified by column chromotography (silica gel, CH_3OH: $CHCl_3$, 1:80).

3.3. Copper(**II**) *phthalocyaninate* (**1**)

3.3.1. Method A

A mixture of compound **I** (2.0 g. 4.42 mmol), CuCl (0.11 g, 1.10 mmol) and diethylaminoethanol (50 ml) was refluxed and stirred for 24 h under N_2. After cooling to room temperature, the green coloured liquor was diluted with water (100 ml) and the crude product precipitated. The mixture was filtered, washed with NH_4OH (24% w/w) to remove inorganic residues, then with water until the filtrate became neutral, and then with hot ethanol to remove unchanged organic materials, and finally dried. The product was purified by column chromotography (silica gel, CH_3OH: $CHCl_3$, 1:80). Yield 0.8 g (38.6%). The product was soluble in chloroform, dichloromethane, DMSO and DMF. IR: ν_{max}/cm^{-1}: 3056–2840,

1640, 1605, 1515, 1489, 1415, 1275, 1210, 1152, 1130, 964, 921, 877, 833, 745 and 657.

3.3.2. Method B

A mixture of compound **I** (2.0 g. 4.42 mmol), CuCl (0.11 g 1.10 mmol) and urea (0.18 g, 4.50 mmol) was heated at 180–190°C for 5 h under N_2. After cooling to room temperature, the mixture was diluted with ethanol, refluxed, and filtered. The resultant green product was washed with NH_4OH (24%, 50 ml) and then with water until the filtrate was neutral. The product was refluxed with then ethanol, the liquor filtered and the product dried. The green colored product was purified by column chromotography (silica gel, CH_3OH: $CHCl_3$, 1:80).

3.4. Nickel (II) phthalocyaninate (2)

A mixture of compound **I** (2.0 g 4.42 mmol), anhyd. $NiCl_2$ (0.145 g 1.10 mmol) and dry quinoline (50 ml) was heated and stirred at 200°C for 24 h under N_2. After cooling to room temperature, the dark green mixture was diluted with ethanol (100 ml) and the crude product precipitated. It was washed with hot ethanol, hot methanol, water, and diethyl ether and dried. The product was purified by column chromotography (silica gel, CH_3OH: $CHCl_3$, 1:80). Yield 0.5 g (24.3%). It was soluble in chloroform, dichloromethane, DMSO and DMF. IR: ν_{max}/cm^{-1}: 3060–2843, 1644, 1605, 1510, 1468, 1419, 1282, 1213, 1155, 1125, 959, 915, 861, 822, 753 and 655. ^1H NMR ($CDCl_3$): δ 7.25–6.86 (32 H, m, Ar), 6.02–5.90 (8 H, m, =CH), 5.20–5.11 (16 H, d, $=CH_2$), 3.84 (24 H, s, OCH_3) and 3.44–3.29 (16 H, d, $-CH_2$). ^{13}C NMR ($CDCl_3$): δ 156.13, 152.18, 149.13, 148.92, 136.51, 136.26, 136.20, 121.22, 120.89, 119.67, 113.30, 110.24, 55.96 and 40.02 ppm.

3.5. Cobalt(II) phthalocyaninate (3)

A mixture of compound **I** (2.0 g. 4.42 mmol), anhyd. $CoCl_2$ (0.145 g, 1.10 mmol), ammonium molybdate (0.02 g, excess) and ethylene glycol (50 ml) was heated and stirred at 200°C for 24 h. under N_2. After cooling to room temperature, the reaction mixture was treated with ethanol (100 ml) to precipitate the dark green product, and filtered. The product was washed with hot ethanol, hot methanol, water, and diethyl ether, dried, and purified by column chromotography (silica gel, CH_3OH:$CHCl_3$, 1:80). Yield 0.7 g (33.9%). It was soluble in chloroform, dichloromethane, DMSO and DMF. IR: ν_{max}/cm^{-1} : 3080–2840, 1641, 1602, 1515, 1471, 1415, 1284, 1218, 1152, 1130, 965, 910, 866, 822, 756 and 658.

3.6. Zinc(II) phthalocyaninate (4)

A mixture of compound **I** (2.0 g, 4.42 mmol), anhyd. zinc acetate (0.20 g, 1.10 mmol) and dry quinoline (50 ml) was heated and stirred at 190–200°C for 24 h under N_2. After cooling to room temperature, the dark green mixture was diluted with ethanol (100 ml) and the crude product which precipitated was filtered, washed with hot ethanol, hot methanol, water, and diethyl ether and dried. The product was purified by column chromotography (silica gel, CH_3OH:$CHCl_3$, 1:80). Yield 0.5 g (24.1%). It was soluble in chloroform, dichloromethane, DMSO and DMF. IR: r_{max}/cm^{-1} : 3081-2842, 1638, 1604, 1510, 1464, 1406, 1290, 1209, 1162, 1128, 965, 919, 895, 826, 756 and 652. ^1H NMR ($CDCl_3$): δ 7.26–6.84 (32 H, m, Ar), 6.16–5.90 (8 H, m, =CH), 5.16–5.01 (16 H, d, $=CH_2$), 3.79 (24 H, s, OCH_3) and 3.41–3.29 (16H, d, CH_2). ^{13}C NMR ($CDCl_3$): δ 157.17, 152.24, 149.76, 149.67, 136.82, 136.71, 130.54, 121.33, 119.87, 119.81, 113.90, 110.32, 56.35 and 40.58 ppm.

3.7. Iron(II) phthalocyaninate (5)

A mixture of compound **I** (2.0 g, 4.42 mmol) and ethylene glycol (50 ml) was rapidly heated and stirred at 200°C under N_2. At this temperature [$Fe(CO)_5$] (0.145 ml, 1.10 mmol) was added slowly by means of a syringe, and heating was continued at 200°C for 6 h. After cooling, the reaction mixture was diluted with ethanol (100 ml) and filtered. The resultant dark green product was washed with hot ethanol, hot methanol, water, and diethyl ether and dried. Yield 0.8 g (38.8%). It was soluble in chloroform, dichloromethane, DMSO and DMF. IR: ν_{max}/cm^{-1}: 3083–2834, 1642, 1608,

1515, 1457, 1410, 1283, 1213, 1155, 1132, 970, 910, 900, 866, 831, 749 and 645.

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