Turkish Journal of Chemistry

Volume 23 | Number 2 Article 4

1-1-1999

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Turk J Chem
23 (1999) , 131 – 137.

Synthesis and Properties of the Phthalocyanines Containing Eugenol (4-Allyl-2-Methoxyphenol)

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Received 12.10.1998

New metal-free and metallophthalocyanines (M=Cu(II), Ni(II), Co(II), Zn(II) and Fe(II)) substituted with eugenol (4-allyl-2-methoxyphenol) from 1,2-dicyano-4-nitrobenzen are described. Cyclotetramerization of the substituted phthalonitrile leads to a product very soluble in common organic solvents. The characterization of the compounds was accomplished by elemental analysis, ^{1}H NMR, ^{13}C NMR, IR and UV-VIS spectral data.

Key words: Eugenol, phthalocyanines.

Introduction

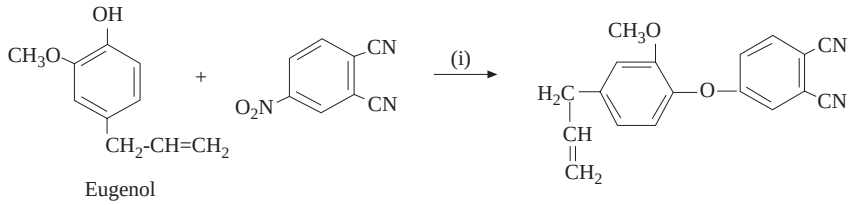
Eugenol (4-allyl-2-methoxyphenol) occurs in the essential oil of various plants[1], some of which are used in folk medicine. Eugenol is reported to show antiseptic and analgesic properties[2,3], local anesthetic[4] and spasmolitic activities[5], parasympathetic effects and direct peripheral vasodilation[6].

The importance of phthalocyanines in many fields, including chemical sensors, electrochromism, batteries, photodynamic therapy, semiconductive materials and liquid crystals is increasing rapidly as a result of newly synthesized compounds[7]. One of the important aims of research in the chemistry of phthalocyanines (Pc) is to enhance their solubility in various solvents.

Bulky substituents on the periphery enhance the solubility and the donor groups of the substituents are capable of binding to additional metal ions[8,9]. Introducion of sulfonyl[10], carboxy[11] or amino[12] groups gives water-soluble products.

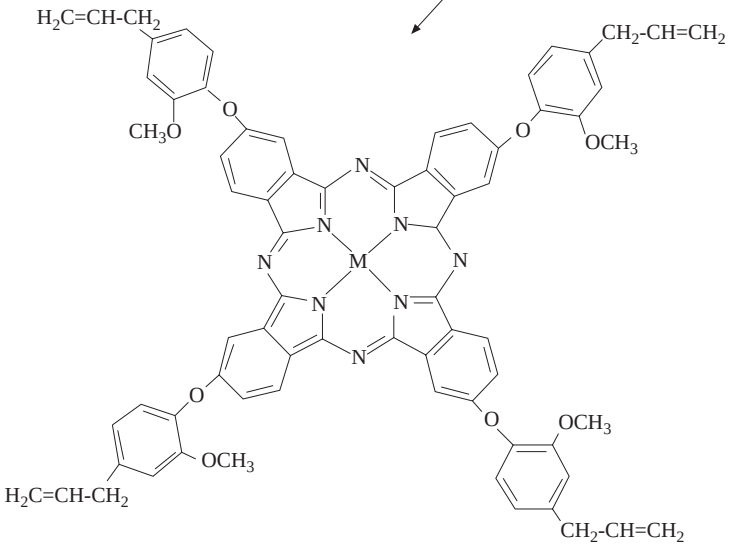
Our previous contributions describing a series of phthalocyanines with aza[13,16] and/or oxa-thia[17,19] macrocycles reported enhanced solubility of products with these bulky macrocycles on the periphery. An additional advantage of using an aza macrocycle substituent was the solubility in water obtained by quaternization of the aza function[13,14]. Phthalocyanines substituted with 12-membered tetraaza-macrocycles provided donor sites for binding transition-metal ions, leading to nonanuclear complexes[13].

In this study, phthalocyanines with four peripheral eugenol substituents were prepared and their complexes with the same metal ions were investigated.



Eugenol
(4-Allyl-2-Methoxyphenol)

(i) DMSO, K_2CO_3, room temperature



Complex	M
II	2H
1	Cu
2	Ni
3	Co
4	Zn
5	Fe

Synthesis of the Ligand and Complexes

Scheme

Results and Discussion

The first step in the synthetic procedure was to obtain phthalonitrile (1,2-dicyanobenzene) derivatives containing eugenoxy group (4-allyl-2-methoxyphenoxy). This was accomplished by a base catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile with eugenol[20]. This reaction was carried out at room temperature in dimethylsulfoxide with K_2CO_3 as the base and the yield was moderate. Cyclotetramerization of phthalonitrile in the presence of metal salts gave the metal phthalocyanines 1-5. The solvents used for these reactions were quinoline for Ni(II) (2) and Zn(II) (4), and ethylene glycol for Co(II) (3) and Fe(II) (5).

The metal-free derivative (H_2Pc) was obtained directly by the reaction of phthalonitrile **I** in the hydroquinone as a uniphase fused melt; here, the two electrons required in addition to the 16 π electrons of 8 nitriles to yield the 18 π electron system of the phthalocyanine core were supplied by the oxidation of

hydroquinone[20]. In the case of CuPc, cyclotetramerization was carried out in urea in the presence of a Cu(I) salt. The yields of these phthalocyanines **II-5** were rather low and depended upon the metal ion. The most obvious common feature of these phthalocyanines is their extensive solubility in polar solvents, such as ethyl acetate, dichloro methane, chloroform DMSO and DMF. The soluble products were obtained in sufficient purity solubility in chloroform as determined spectrophotometrically to be 10^{-4} mol dm^{-3} which is higher those of crown ether[21], azamacrocycles[13,15] and thioether-substituted phthalocyanines[17,19,22].

These products were obtained in sufficient purity after successive washing with different solvents.

Characterization of the products involved a combination of methods including IR ^{1}H and ^{13}C-NMR, elemental analysis (Table 1) and UV-VIS (Table 2).

Table 1. Analytical Data for the Starting Materials and the Phthalocyanines.

		Calc.%			Found %		
Compound	Formula	C	H	N	C	H	N
I	$C_{18}H_{14}N_2O_2$	74.48	4.83	9.65	74.44	4.80	9.62
II	$C_{72}H_{58}N_8O_8$	74.35	4.99	9.64	74.26	4.91	9.58
1	$C_{72}H_{56}N_8O_8Cu$	70.61	4.57	9.15	70.53	4.48	9.07
2	$C_{72}H_{56}N_8O_8Ni$	70.89	4.59	9.19	70.80	4.50	9.09
3	$C_{72}H_{56}N_8O_8Co$	70.88	4.59	9.19	70.79	4.49	9.11
4	$C_{72}H_{56}N_8O_8Zn$	70.51	4.57	9.14	70.44	4.47	9.07
5	$C_{72}H_{56}N_8O_8Fe$	71.06	4.60	9.21	70.93	4.51	9.16

Table 2. Electronic spectra data for the phthalocyanines in chloroform.

Compound	λ_{max}/nm($10^{-4}\varepsilon$/dm^3 mol^{-1} cm^{-1})
II	705(7.39), 670(7.56), 609(2.37)^{sh}, 395(3.45), 339(6.94), 285(8.19)
1	683(19.98), 617(5.32)^{sh}, 389(3.94), 341(9.71), 281(9.04)
2	677(24.39), 608(5.73)^{sh}, 383(4.34), 332(7.62), 284(1.18)
3	674(12.23), 608(3.50)^{sh}, 326(8.14), 281(9.36)
4	683(2.45), 614(0.96)^{sh}, 338(2.29), 278(3.30)
5	710(4.86), 605(1.70)^{sh}, 368(4.36), 287(6.98).

sh: Shoulder

Comparison of the IR spectra data clearly indicated the formation of compound **I** by the disappearance of the band OH of eugenol at 3500 cm^{-1}, and the appearance of a new absorption at 2220 cm^{-1} (C≡N). Cyclotetramerization of the dinitriles was confirmed by the disappearance of the sharp C≡N vibration at 2220 cm^{-1} of reagent **I**. The spectra of the metal-free phtahalocyanine **II** and the metal complexes **1-5** were very similar, with the exception of **II** showing NH stretching bands at 3300 and 1010 cm^{-1} due to the inner core[23]. These bands were absent from the specra of the complexes. The M-N vibrations were expected to appear at 400-100 cm^1 but they were not observed in KBr pellets[24].

In the ^{1}H-NMR spectrum of **I**, the singlet at 3.71 ppm, the edoublets at 3.44-3.41, 5.19-5.11 ppm and multiplets at 7.70-6.82 and 6.09-5.89 correspond to methoxy, allyl (-CH_2), allyl (=CH_2), aromatic and allyl (=CH) protons respectively. The ^{1}H-NMR spectrum of **II** indicates aromatic protons at 8.20-6.83, allyl (=CH, =CH_2 and -CH_2) protons at 6.12-5.18, 5.21-5.11 and 3.54-3.29 and methoxy (OCH_3) protons at 3.89 ppm respectively. A common feature of this spectra of metal-free phthalocyanines is he broad absorptions probably caused by the aggregation of phthalocyanine. Also the NH protons of this compound (II) could not be observed due to this phenomenon. Because of the distinct ring current of the

18π electron system of the inner phthalocyanine core, the protons are characteristically of **2** and **4**, the chemical shifts belonging to aromatic, olefinic and allyl (=CH, $=CH_2$ and -CH_2) and methoxy at 7.23-6.54, 7.78-6.81, 6.05-5.91, 6.06-5.98, 5.24-5.17, 5.19-5.11, 3.52-3.37, 3.44-3.30, 3.69 and 3.76 ppm were observed after the cyclotetramerization, respectively. Broad NMR absorptions were observed for Ni(II) and Zn(II) phthalocyanines possibly due to aggregation[7,19,25].

The best indications for a phthalocyanine system are given by their UV-VIS specra in solution. The UV-VIS absorption spectra of these phthalocyanines exhibit Q and B bands, which are the characteristic bands for the phthalocyanines[7]. The UV-VIS data of the phthalocyanines in chloroform are given in Table 2. There is a shoulder on the slightly higher energy side for all phthalocyanines. These phthalocyanines are also similar to those of crown ether[21], alkyl chain[26], alkylsulfanyl[27], aza[13,15], oxa-thia[17] and oxa-thia-azamacrocycles-substituted[19] phthalocyanines. Although the symmetry of the phthalocyanines is lowered by the heteroatom substituent on each benzene group, **II** still show Q-band absorptions of D_{2h} symmetry in organic solvents. In the spectra of these complexes an intense absorption at 710 nm and a second band of lower intensity at 605 nm were observed. The thermal decomposition temperatures of these complexes are higher than 200 °C.

Experimental

Routine IR spectra were recorded on a Mattson 1000 Fourier transform spectrometer as KBr pellets, 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 TÜBİTAK Marmara Research Center. 1,2-dicyano-4-nitrobenzen was synthesized according to the reported procedure[28] and eugenol (4-allyl-2-methoxyphenol) was purchased from the Merck Chemical Company. This material was used as received.

4-(4-Allyl-2-methoxyphenoxy)-1,2-dicyano benzene (I):

Eugenol (6.24 g, 38.0 mmol) was dissolved in dry dimethylsulphoxide (100 ml) under nitrogen and 4-nitrophthalonitrile (6.0 g, 34.68 mmol) was added. After stirring for 15 minutes, finely ground anhydrous K_2CO_3 (7.15 g, 51.81 mmol) was added portionwise over 2h with efficient stirring. The reaction mixture was stirred under N_2 at room temperature for 48h. Water was then added and the product filtered off, washed with water until the filtrate became neutral, and then washed with methanol. The white precipitate was crystallized from ethanol. Yield: 7.5 g (68%). This compound is soluble in ethyl acetate, chloroform, dichloromethane, DMF and DMSO, mp: 101-102 °C. IR ν_{max}/cm^{-1}: 3083-2860 (ArH and CH_2), 2220 (CN), 1640 (C=C, allyl), 1605, 1597, 1507, 1496, 1474, 1430, 1320, 1298, 1254, 1210, 1156, 1123, 1035, 958, 925, 904, 848, 826, 760, 727, 661. ^{1}H-NMR ($CDCl_3$): δ 7.70-6.82 (6H, m, Ar), 6.09-5.89 (1H, m, =CH), 5.19-5.11 (2H,d,=CH_2), 3.71 (3H, s, OCH_3) and 3.44-3.41 (2H, d, -CH_2). ^{13}C-NMR ($CDCl_3$): δ 161.97, 151.08, 140.03, 136.65, 135.13, 134.99, 122.61, 121.52, 120.70, 120.53, 120.12, 117.35, 116.60, 115.19, 113.31, 108.26, 55.77 and 40.08 ppm.

Metal-free phthalocyanine (II)

A mixture of compound**I** (2.0 g, 6,90 mmol) and hydroquinone (0.76 g, 3.40 mmol) (purified by sublimation) was gently heated under N_2 and then cooled. This mixture was heated to 200 °C under a nitrogen atmosphere and held at this temperature for 3h. After cooling to room temperature the reaction mixture was treated

with hot water to precipitate the product and then filtered. The green product was washed with hot water, hot ethanol (3X25 ml) and ethyl acetate. The green product was extracted with chloroform and filtered to remove unreacted organic materials. The filtrate was then evaporated and the green product was washed with diethyl ether and dried. Yield: 0.6 g, (30 %). This compound is soluble in chloroform, dichloromethane, DMF and DMSO. IR ν_{max}/cm^{-1}: 3300 (NH), 3085-2840, 1635, 1600, 1500, 1460, 1410, 1270, 1210, 1150, 1120, 1090, 1010, 915, 820, 745, 640. ^{1}H-NMR ($CDCl_3$): δ 8.20-6.83 (24H, m, Ar), 6.12-5.81 (4H, m, =CH), 5.21-5.11 (8H, s, $=CH_2$), 3.89 (12H, s, OCH_3) and 3.54-3.29 (8H, d, $-CH_2$). ^{13}C-NMR ($CDCl_3$): δ 159.72, 151.39, 144.54, 143.36, 138.44, 135.60, 131.82, 127.99, 122.71, 121.97, 120.71, 119.21, 113.14, 53.91 and 40.70 ppm.

Copper(II) phthalocyaninate (1):

A mixture of compound **1** (2.0 g, 6.90 mmol), anhydrous CuCl (0.17 g, 1.61 mmol) and urea (0.42 g, 7.0 mmol) was heated at 180-190°C for 3h under N_2. After cooling to room temperature, the mixture was diluted with ethanol and refluxed for 2h and filtered off. The green product was washed with NH_4OH (24 %, 3X50 ml) and then with water until the filtrate became neutral. The green product was refluxed with ethanol and filtered and washed with diethyl ether and dried. Yield: 0.6 g (28.5 %). This compound is soluble in ethyl acetate, chloroform, dichloromethane, DMF and DMSO. IR ν_{max}/cm^{-1}: 3070-2820, 1630, 1600, 1495, 1455, 1395, 1265, 1210, 1140, 1110, 1085, 940, 900, 810, 740, 635.

Nickel(II) phthalocyaninate (2):

A mixture of compound **1** (2.0 g, 6.90 mmol), anhydrous $NiCl_2$ (0.23 g, 1.77 mmol) and dry quinoline (50 ml) was heated and stirred at 200°C for 20h under N_2. After cooling to room temperature, the green mixture was diluted with ethanol (100 ml) and the crude product precipitated. It was washed with water, hot methanol, hot ethanol, and dried. Yield: 0.8 g (38 %). This compound is soluble in ethyl acetate, chloroform, dichloromethane, DMF and DMSO. IR ν_{max}/cm^{-1}: 3080-2840, 1635, 1605, 1520, 1500, 1460, 1410, 1330, 1270, 1230, 1150, 1120, 1090, 950, 820, 750, 640. ^{1}H-NMR ($CDCl_3$): δ 7.23-6.54 (24, m, Ar), 6.05-5.91 (4H, m, =CH), 5.24-5.17 (8H, d, $=CH_2$), 3.69 (12H, s, OCH_3) and 3.52-3.37 (8H, d, $-CH_2$). ^{13}C-NMR ($CDCl_3$): δ 158.63, 151.46, 143.13, 142.91, 137.76, 136.72, 129.21, 127.75, 122.17, 121.28, 120.96, 120.69, 113.06, 55.77 and 40.15 ppm.

Cobalt(II)phthalocyaninate (3):

A mixture of compound **1** (2.0 g, 6.90 mmol), anhydrous $CoCl_2$ (0.23 g, 1.77 mmol), ammonium molybdate (0.02 g. excess) and ethylen eglycol (50 ml) was heated and stirred at 200°C for 20h under N_2. After cooling to room temperature, the reaction mixture was treated with ethanol (100 ml) to precipitate the dark green product and then filtered off. The product was washed with water, hot methanol, hot ethanol and diethyl ether and dried. Yield: 0.6 g (28.6 %). This compound is soluble in ethyl acetate, chloroform, dichloromethane, DMF and DMSO. IR ν_{max}/cm^{-1}: 3075-2840, 1630, 1600, 1500, 1455, 1405, 1325, 1260, 1220, 1145, 1110, 1085, 950, 900, 815, 745, 640.

Zinc(II)phthalocyaninate(4):

A mixture of compound **1** (2.0 g, 6.90 mmol), anhydrous zinc acetate (0.31 g, 1.69 mmol) and dry quinoline (50 ml) was heated and stirred at 190-200°C for 24h under N_2. After cooling to room temperature, the

green mixture was diluted with ethanol (100 ml) and the crude product precipitated. The dark green product was filtered off and then washed with water, hot methanol, hot ethanol, and diethyl ether and dried. Yield: 0.7 g (33.3 %). This compound is soluble in ethyl acetate, chloroform, dichloromethane, DMF and DMSO. IR $\nu_{max}\,cm^{-1}$:3080-2840, 1640, 1595, 1500, 1465, 1410, 1310, 1270, 1215, 1145, 1115, 1080, 940, 905, 820, 750, 650 ^{1}H-NMR ($CDCl_3$): δ 7.78-6.81 (24H, m, Ar), 6.06-5.98 (4H, m, =CH), 5.19-5.11 (8H, d, $=CH_2$), 3.76 (12H, s, OCH_3) and 3.44-3.30 (8H, d, $-CH_2$). ^{13}C-NMR ($CDCl_3$): δ 158.65, 152.29, 146.75, 140.72, 138.35, 135.58, 130.91, 126.90, 122.43, 121.62, 121.34, 118.37, 113.33, 52.39 and 40.09 ppm.

Iron(II)phthalocyaninate (5):

A mixture of compound **1** (1.0 g, 3.45 mmol) and ethylene glycol (50 ml) under N_2 was rapidly heated and stirred at 200°C. At this temperature $Fe(CO)_5$ (0.2 ml. excess) was added slowly by means of a syringe. It was heated at 200°C for 3h. After cooling to room temperature, the reaction mixture was diluted with ethanol (100 ml) and filtered off. The dark green product was washed with water, hot methanol, hot ethanol, and diethyl ether and dried. Yield: 0.3 g (27.7 %). It is soluble in ethyl acetate, chloroform, dichloromethane, DMF and DMSO IR ν_{max}/cm^{-1}: 3080-2840, 1635, 1605, 1500, 1460, 1395, 1330, 1270, 1220, 1145, 1120, 1080, 945, 910, 815, 740, 645.

References

1. H. Friederich, **Lloydia, 39,** 1 (1976).
2. E. C. Dobbs "Pharmacology and Orral Therapeutics" 12 th ed., p.448, The C. V. Mosby Co., St. Louis, (1961).
3. L. M. Kay Drugs ın Dentistry. In: "Dental Practitioner Handbook Series", P. 156. D. D. Derrich, ed., Wright, Bristol, (1972).
4. K. D . Siemonest, H. F. Zipf and E. Ch. Dittmann, Arch, **Int. Pharmacodyn, 30,** 164, (1966).
5. K. Jurcic and H. Wagner, "Proceedings of the First Int. Congr. on Medicinal Plant Research," University of Munich, Germany, (Sept. 6-10), (1976).
6. F. D. Stitch and R. M. Smith, **J. Dent. Res., 50,** 1531 (1971).
7. C. C. Leznoff and A. B. P. Lever (eds.), "Phthalocyanines, Properties and Applications" (VCH, Weinheim), Vol.1, (1989), Vol.2, (1993).
8. V. Ahsen, E. Yılmazer, A. Gürek, A. Gül and Ö. Bekaroğlu, **Helv. Chim. Acta, 71,** 1616 (1988).
9. E. Musluoğlu, V. Ahsen, A. Gül and Ö. Bekaroğlu, **Chem. Ber., 124,** 2531 (1991).
10. J. H. Weber and D. H. Bursch, Inorg. Chem., 469 (1965).
11. N. Kobayaski, H. Shirai and N. Hojo, **J. Chem. Soc. Dalton Trans.,** 2107 (1984).
12. V. M. Deskacheau, N. J. Bundina, N. G. Meekhryakova, O. L. Kaliya, T. Y. Gulinat and E. A. Lukyanets, **Russian J. Inorg. Chem., English Edit., 26,** 911 (1981).
13. E. Ağar, B. Batı, E. Erdem and M. Özdemir, **J. Chem. Res., (S),** 16 (1995).
14. E. Ağar, S. Şaşmaz, B. Batı and M. Özdemir, **Synth. React. Inorg. Metal-Org. Chem., 25,**1165 (1995).
15. E. Ağar, S. Şaşmaz, İ. E. Gümrükçüoğlu and M. Özdemir, **Synth. React. Inorg. Metal-Org. Chem., 26,** 1243 (1996).
16. E. Ağar, S. Şaşmaz, İ. Keskin and N. Akdemir, **Dyes and Pigments, 36,** 249 (1998).

17. S. Şaşmaz, E. Ağar, N. Akdemir and İ. Keskin, **Dyes and Pigments, 37,** 223 (1998).
18. E. Ağar, S. Şaşmaz, İ. Keskin and B. Karabulut, **Dyes and Pigments, 35,** 269 (1997).
19. E. Ağar, S. Şaşmaz, N. Akdemir and İ. Keskin, **J. Chem. Soc. Dalton Trans.,** 2087 (1977).
20. A. W. Snow and J. R. Griffith, **Macromolecules, 17,** 1614 (1984).
21. A. R. Koray, V. Ahsen and Ö. Bekaroğlu, **J. Chem. Soc., Chem. Commun.,** 932 (1986).
22. E. Ağar, S. Şaşmaz, N. Akdemir and İ. Keskin, **Synth. React. Inorg. Met. Org. Chem.,** accepted.
23. H. F. Shurvell and L. Lunzuti, **Can. J. Chem. 44,** 125 (1966).
24. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", J. Willey, New York, (1970).
25. G. Gümüş, Z. Z. Öztürk, V. Ahsen, A. Gül and Ö. Bekaroğlu, **J. Chem. Soc. Dalton Trans.,** 2528 (1992).
26. M. Hanack, A. Gül, A. Hirsch, B. K. Mandal, L. R. Subramonian and E. Witke, **Mol. Cryst. Liq. Cryst., 187,** 365 (1990).
27. A. Gürek and Ö. Bekaroğlu, **J. Chem. Soc., Dalton Trans.,** 1419 (1994).
28. J. G. Young, and W. Onyebuagu, **J. Org. Chem., 55,** 2155 (1990).