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Synthesis and characterization of phthalocyanines containing phenothiazine moieties

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Abstract

New phthalocyanines (M = 2H, Cu, Ni, Co or Zn) substituted with four phenothiazine moieties are described. All of these complexes are very soluble in common organic solvents. The characterization of the compounds was accomplished by elemental analysis, ^{1}H, ^{13}C NMR, IR and UV–VIS spectral data. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

For many years, phthalocyanines have continuously attracted great interest in various research fields such as chemical sensors, electrochromism, batteries, photodynamic therapy, semiconductive materials, liquid crystals and nonlinear optics [1–3]. The exceptionally high thermal and chemical stability of the phthalocyanine core results in a versatile chemical system. An infinite number of variations is possible by varying the central metal ion or peripheral substituents. Bulky substituents on the periphery enhance the solubility, and the donor substituents groups are capable of binding to additional metal ions [4,5]. The introduction of sulfonyl [6], carboxy [7] or amino groups [8] gives water-soluble products. Phthalocyanines with thia-substituents tend to exhibit stronger absorption bonds at longer wavelengths in the near-IR region with respect to their unsubstituted or O-substituted analogues [9,10]. This is important in applications utilizing semiconductor lasers [11].

We have previously synthesized novel phthalocyanines carrying macrocyclic substituents (e.g aza [12–15], oxathia [16,17], oxadithiadiaza-macrocycles [18]) which are capable of binding to transition metal cations. While phthalocyanines with N–, O–and S– donor substituents have frequently been described, those with N–O, O–S or N–S donor moieties together have not been to extensively described [19–21]. An additional advantage of using an aza macrocycle substituent was the solubility in water obtained by quaternization of the aza function [12,13]. Phthalocyanines substituted with 12-membered tetraaza-macrocycles provided donor sites for binding transition-metal ions, leading to nonanuclear complexes [12].

The present paper reports the synthesis of metal-free and metal-complexed phthalocyanines containing four azathia-cyclic moieties in the molecule.

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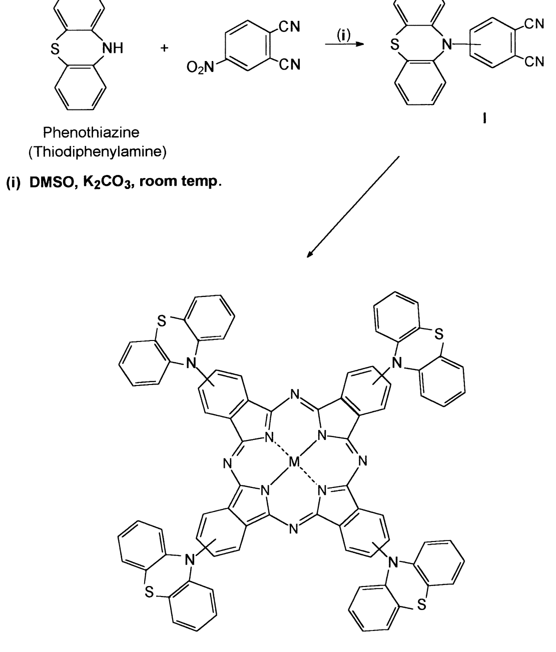
2. Results and discussion

1,2-Dicyano-4-nitrophthalonitrile has been recently used to prepare 1,2-disubstituted phthalonitrile derivatives through base catalysed aromatic displacement [19]. The same route was applied to prepare *N*-(3,4-dicyanophenyl)phenothiazine **I** from the corresponding phenothiazine and 1,2-dicyano-4-nitrobenzene (Scheme 1). This reaction was carried out at room temperature in dimethylsulfoxide with K_2CO_3 as the base and the yield was moderate. The metal-free phthalocyanine was obtained by treating a mixture of the dicyano derivative with hydroquinone in a sealed tube [22]. The metallophthalocyanines were prepared from the dicyano derivative and the corresponding metal salts in high-boiling anhydrous solvents (e.g. quinoline and ethylene glycol). The yields were satisfactory and depended upon the transition metal ion. The most apparent feature of the metal-free 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 similar complexes containing crown ether [23], aza macrocycles [12–14], thia [24], oxa-thia [16,17], aza-thia [25], or oxa-thia-aza macrocycle substituents [18]. The unusual solubilities of these compounds are due to the substitution by bulky groups.



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

Scheme 1. Synthesis of the ligand and complexes.

Elemental analyses (Table 1), IR, ^1H and ^{13}C NMR and UV–VIS spectra (Table 2) confirm the proposed structures of the compounds. These products were obtained in sufficient purity after successive washing with different solvents. Comparison of the IR spectral data clearly indicated the formation of compound **I**, by the disappearance of the NH band of the phenothiazine moiety at 3353 cm^{-1}, and the appearance of a new absorption at 2220 cm^{-1} ($C{\equiv}N$). This spectrum exhibits characteristic frequencies at 3080–3000 (Ar–H) cm^{-1}. In the ^1H NMR spectrum of **I**, the multiplets at δ: 7.57–7.12 ppm are for the aromatic protons. The ^{13}C NMR spectral data given below are also in accord with the excepted structure. The carbon resonances of the aromatic groups appear at δ: 149.78, 139.21, 135.42, 134.35, 129.59, 128.82, 127.98, 127.59, 127.32, 127.25, 127.19 and 127.15 ppm; the other chemical shifts belonging to nitrile carbons, appear at δ: 117.35, 116.68 and 116.53 ppm.

The metal-free derivative (H_2Pc) **II** was synthesized by heating a mixture of the dicyano derivatives **I** with hydroquinone in a shlenk system. The metal-free phthalocyanine **II** was obtained 35% yield. The IR spectra of **II** is very similar to that of **I**. A diagnostic feature of the phthalocyanine formation from dicyano derivative **I** is the disappearance of the $C{\equiv}N$ stretching vibration at 2220 cm^{-1} of the precursor compound. Another difference is the presence of NH stretching and bending vibrations assigned to bands at 3290 and 1010 cm^{-1}, respectively [19]. The ^1H NMR spectrum of **II** shows aromatic protons at 7.23–6.84 ppm. A common feature of the spectra of the metal-free phthalocyanines is the broad absorptions probably caused by aggregation of phthalocyanine. The NH protons of

Table 1
Analytical data for the starting materials and the phthalocyanines

Compound	Formula	Calc. (%)				Found (%)			
		C	H	N	S	C	H	N	S
I	$C_{20}H_{11}N_3S$	73.78	3.38	12.91	9.84	73.74	3.35	12.88	9.76
II	$C_{80}H_{46}N_{12}S_4$	73.73	3.53	12.89	9.84	73.64	3.47	12.84	9.77
1	$C_{80}H_{44}N_{12}S_4Cu$	70.41	3.22	12.31	9.39	70.31	3.17	12.26	9.28
2	$C_{80}H_{44}N_{12}S_4Ni$	70.66	3.23	12.35	9.43	70.56	3.19	12.29	9.36
3	$C_{80}H_{44}N_{12}S_4Co$	70.64	3.24	12.35	9.43	70.57	3.19	12.30	9.37
4	$C_{80}H_{44}N_{12}S_4Zn$	70.31	3.22	12.29	9.38	70.23	3.17	12.24	9.31

Table 2
Electronic spectral data for the phthalocyanines in chloroform

Compound	λ_{max}/nm (10^{-4} ε/dm^3 mol^{-1} cm^{-1})
II	704(20.09), 665(11.17),[a] 338(16.72), 257(29.31)
1	686(11.94), 620(3.74),[a] 341(9.90), 260(13.69)
2	674(11.52), 608(3.48),[a] 335(9.78), 296(10.49), 257(21.15)
3	680(2.28), 614(1.14),[a] 380(2.35), 302(6.57), 233(21.97)
4	680(17.56), 617(3.68),[a] 350(8.40), 254(19.25)

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 shifted to low or high field [26,27].

In the case of copper phthalocyanine **1**, the dinitrile derivative **I** was directly treated with urea and anhydrous Cu(1) salt. The other metallophthalocyanines **1–4** were treated with the anhydrous transition metal salts, $NiCl_2$, $CoCl_2$ and $Zn(O_2CMe)_2$. The yields obtained were satisfactory, although the workup was cumbersome. The metallo phthalocyanine 1 was obtained in 38.0% yield, and the other compounds **2–4** were obtained in 33.5, 28.7 and 33.3% yield. The intense green products were very soluble in solvents such as chloroform, dichloromethane, dimethylformamide and dimethyl sulfoxide.

In the IR spectrum of **I**, the intense absorptions at 2220 cm^{-1} corresponding to the C≡N groups disappear after the conversion to the metallophthalocyanines **1–4**. The rest of the IR spectra are very similar to those of **I**, including the characteristic vibrations of aromatic groups. These bands are absent from the spectra of the complexes. The M–N vibrations were expected to appear at 400–100 cm^{-1}, but they were not observed in KBr pellets [28]. In the ^{1}H NMR spectra of **2** and **4**, the chemical shifts for the aromatic systems at 7.30–6.71 and 7.80–6.92 ppm were observed after the cyclotetramerization, respectively. ^{1}H NMR measurements were precluded, owing to the paramagnetic nature of the copper phthalocyanine **1** and the cobalt phthalocyanine **3** [2].

The UV–VIS absorption spectra of the metal-free and metal phthalocyanine complexes exhibited characteristic Q and B bands [1,2]. Phthalocyanine containing the phenothiazine moiety **II-4** show typical electronic spectra with two strong absorption regions, one in the visible region at 600–700 nm (Q band) attributed to the $\pi \rightarrow \tau^*$ transition from the HOMO to the LUMO of the Pc^{-2} ring, and the other in the UV region at 300–350 nm (B band) arising from the deeper π levels→LUMO transition [2] (Table 2). In extremely dilute solution (ca. 10^{-6} mol dm^{-3}), the molecules are present as monomers in chloroform. An increase in the concentration leads to aggregation, which is easily monitored by the position of the Q band, which is shifted to shorter wavelengths, and to a decrease in the molar absorbtion coefficient.

3. Experimental

IR spectra were recorded on a Mattson 1000 Fourier-transform spectrometer (KBr), UV–VIS spectra on a Unican UV–VIS spectrometer, and

^1H and ^{13}C NMR spectra on a Bruker AC-200 Fourier-transform spectrometer. Elemental analysis was performed by the Instrumental Analysis Laboratory of Tübıtak Gebze Research Center. 1,2–dicyano-4-nitrobenzene was synthesized according to the reported procedure [29] and phenothiazine was purchased from Merck Chem. Co.; This material was used as received.

3.1. N-(3,4-Dicyanophenyl)phenothiazine (**I**)

Phenothiazine (11.95 g, 60.0 mmol) was dissolved in dry dimethylsulphoxide (200 ml) under nitrogen and 4-nitrophthalonitrile (10.38 g, 60.0 mmol) was added. After stirring for 15 min, finely ground anhyd. K_2CO_3 (12.42 g, 90.0 mmol) was added portionwise over 2 h with stirring. The reaction mixture was stirred under N_2 at room temperature for 24 h. Water was then added and the product filtered off, washed with water until the filtrate became neutral, and then washed with cold ethanol and diethyl ether. The yellow precipitate was crystallized from ethanol. Yield: 11.0 g (56.38%). This compound was soluble in hot ethanol, hot methanol, ethyl acetate, chloroform, dichloromethane, benzene, pyridine, acetone, CS_2, DMF and DMSO, mp: 199–200°C. IR ν_{max}/cm^{-1}: 3080–3000 (Ar, H), 2220 (C≡N), 1590, 1485, 1465, 1440, 1400, 1330, 1265, 1130, 1100, 1040, 760 and 650. ^1H NMR ($CDCl_3$): δ 7.57–7.12 (11 H, m, Ar–H). ^{13}C NMR ($CDCl_3$): δ 149.78, 139.21, 135.42, 134.35, 129.59, 128.82, 127.98, 127.59, 127.32, 127.25, 127.19, 127.15, 117.35, 116.68 and 116.53.

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

A mixture of compound **I** (2.0 g, 6.15 mmol) and hydroquinone (0.69 g, 3.08 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 3 h. After cooling to room temperature the reaction mixture was digested with ethanol (2×100 ml) and then ethyl acetate (2×100 ml). The product was extracted with chloroform and filtered to remove unreacted organic materials. The filtrate was then evaporated and the green product was washed with hot ethanol, hot ethyl acetate, diethyl ether and then dried. Yield: 0.7 g, (35%). This compound was soluble in chloroform, dichloromethane, DMF and DMSO. IR ν_{max}/cm^{-1}: 3290 (NH), 3070–3000, 1600, 1580, 1500, 1490, 1470, 1440, 1390, 1300, 1250, 1110, 1090, 1050, 1010, 740, 660. ^1H NMR ($CDCl_3$): δ 7.23–6.84 (46 H, m, Ar). ^{13}C NMR ($CDCl_3$): δ 144.23, 143.16, 142.94, 127.66, 127.55, 127.49, 127.41, 127.30, 127.18, 127.01, 126.62, 124.96, 124.13 and 123.40.

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

A mixture of compound **I** (2.0 g, 6.15 mmol), anhyd. CuCl (0.17 g, 1.61 mmol) and urea (0.38 g, 6.33 mmol) was heated at 180–190°C for 3 h under N_2. After cooling to room temperature, the mixture was diluted with ethanol, refluxed and then filtered. The resultant green product was washed with NH_4OH (24%, 3×50 ml) and then with water until the filtrate became neutral. The product was extracted with chloroform and filtered off. The filtrate was then evaporated and the product was digested with ethanol (2×100 ml) and ethyl acetate (2×100 ml), and finally filtered. The green product was washed with hot ethanol, hot methanol, ethyl acetate and diethyl ether and dried. Yield: 0.8 g (38.0%). This compound was soluble in chloroform, dichloromethane, DMF and DMSO. IR ν_{max}/cm^{-1}: 3080–3005, 1605, 1580, 1500, 1480, 1460, 1445, 1400, 1310, 1250, 1120, 1090, 1050, 745 and 665.

3.4. Nickel (**II**) phthalocyaninate (**2**)

A mixture of compound **I** (2.0 g, 6.15 mmol), anhyd. $NiCl_2$ (0.20 g, 1.58 mmol) and dry quinoline (50 ml) was heated and stirred at 200°C for 20 h. under N_2. After cooling to room temperature, the green coloured mixture was diluted with ethanol (100 ml) and the crude product precipitated and filtered. The product was refluxed with ethanol (2×100 ml) and with then ethyl acetate (2×100 ml), and filtered off. The resultant green product was washed with hot ethanol, hot methanol, hot ethyl acetate and diethyl ether and dried. Yield: 0.7 g (33.5%). This compound was soluble in chloroform, dichloromethane, DMF and DMSO. IR ν_{max}/cm^{-1}: 3075–3000, 1600, 1580, 1505, 1480, 1460, 1440, 1305, 1245, 1115, 1090, 1045, 745 and 665. ^{1}IH NMR ($CDCl_3$): δ 7.30–6.71 (44, m, Ar) ^{13}C-NMR ($CDCl_3$): δ 144.10, 143.54, 142.53, 140.18, 136.51, 128.28, 127.97, 127.83, 127.64, 127.30, 127.23, 127.00, 123.82 and 123.07.

3.5. *Cobalt* (**II**) *phthalocyaninate* (**3**)

A mixture of compound **I** (2.0 g, 6.15 mmol), anhyd. $CoCl_2$ (0.20 g, 1.58 mmol), ammonium molybdate (0.02 g excess) and ethylene glycol (50 ml) was heated and stirred at 200°C for 20 h under N_2. After cooling to room temperature, the reaction mixture was treated with ethanol (100 ml) to precipitate the dark green product, which was then filtered off. The product was extracted with chloroform and filtered to remove unreacted organic materials. The filtrate was evaporated and the resultant green product was refluxed with ethanol (2×100 ml), then ethyl acetate (2×100 ml), and filtered off. The product was washed with hot ethanol, hot methanol, hot ethyl acetate and diethyl ether and dried. Yield: 0.6 g (28.7%). This compound was soluble in chloroform, dichloromethane, DMF and DMSO. IR $\nu_{\max/\mathrm{cm}^{-1}}$: 3080–3000, 1600, 1580, 1495, 1480, 1465, 1440, 1400, 1305, 1250, 1115, 1090, 1050, 740 and 660.

3.6. *Zinc* (**II**) *phthalocyaninate* (**4**)

A mixture of compound **I** (2.0 g, 6.15 mmol), anhyd. zinc acetate (0.29 g, 1.58 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 solution was evaporated. The precipitate was refluxed with ethanol (2×100 ml) and then ethyl acetate (2×100 ml) and filtered off. The green product was washed with hot ethanol, hot methanol, hot ethyl acetate and diethyl ether and dried. Yield: 0.7 g (33.3%). This compound was soluble in chloroform, dichloromethane, DMF and DMSO. IR $\nu_{\max}/\mathrm{cm}^{-1}$: 3080–3000, 1605, 1580, 1480, 1455, 1440, 1390, 1305, 1240, 1120, 1085, 1040, 740 and 660 ^{1}H NMR ($CDCl_3$): δ 7.80–6.92 (44 H, m, Ar) ^{13}C NMR ($CDCl_3$): δ 144.21, 143.23, 142.55, 140.68, 128.70, 128.31, 127.76, 127.67, 127.51, 127.12, 127.02, 126.28, 125.84 and 122.96.

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References

[1] Moser FH, Thomas AL. The phthalocyanines, vols. I and II. Boca Raton (FL): CRC Press, 1983.
[2] Leznoff CC, Lever ABP, editors. Phthalocyanines, properties and applications, vols. I–III. Weinheim, New York: VCH 1989–1993.
[3] Schultz H, Lehmann H, Rein M, Hanack M. Struct Bonding (Berlin) 1990;41:74.
[4] Ahsen V, Yılmazer E, Gürek A, Gül A, Bekaroğlu Ö. Helv Chim Acta 1988;71:1616.
[5] Musluoğlu E, Ahsen V, Gül A, Bekaroğlu Ö. Chem Berichte 1991;124:2531.
[6] Weber JH, Bursch DH. Inorg Chem 1965;469.
[7] Kobayaski N, Shirai H, Hojo N. Dalton Trans 1984;2107.
[8] Deskacheau VM, Bundina NJ, Mekhryakova NG, Kaliya Ol, Gulinat TY, Lukyanets EA. Russian J Inorg Chem, English Edn 1981;26:911.
[9] Wöhrle D, Eskes M, Shigehara K, Yamada A. Synthesis 1993; 194.
[10] Suda Y, Shigehara K, Yamada A, Matsuda H, Okada S, Masaki A, Nakanishi H. Proc SPIE Int Soc Opt Eng 1991;75:1560.
[11] Hayashida S, Hayashi N. Chem Lett 1990;2137.
[12] Ağar E, Batı B, Erdem E, Özdemir M. J Chem Res 1995;S:16.
[13] Ağar E, Şaşmaz S, Batı B, Özdemir M. Synthetic Reactions. In: Inorg and Metal–Organic Chem 1995;24:1165.
[14] Ağar E, Şaşmaz S, Gümrükcüoğlu İE, Özdemir M. Synthetic Reactions. In: Inorg and Metal-Organic Chem 1996;26:1243.
[15] Ağar E, Şaşmaz S, Gümrükcüoğlu İE, Özdemir Ö. Dyes and Pigments 1998;36:407
[16] Şaşmaz S, Ağar E, Akdemir N, Keskin, I. Dyes and Pigments 1998;37:223
[17] Ağar E, Şaşmaz S, Keskin ı, Karabulut B. Dyes and Pigments 1997;3:269.
[18] Ağar E, Şaşmaz S, Akdemir N, Keskin I. J Chem Soc Dalton Trans 1997;2087.
[19] Snow AW, Griffith JR. Macromolecules 1984;17:1614.
[20] Wöhrle D, Schnurfell G, Knothe G. Dyes and Pigments 1992;18:71.
[21] Ahsen V, Gürek A, Musluoğlu E, Bekaroğlu Ö. Chem Berichte 1989;122:1073.
[22] Snow AW, Jarvis NL. J Am Chem Soc 1984;106:4706.
[23] Koray AR, Ahsen V, Bekaroğlu Ö. J Chem Soc Chem Commun 1986;932.
[24] Gürek A, Bekaroğlu Ö. J of Porphyrins and Phthalocyanines 1997;1:67.
[25] Yılmaz ı, Bekaroğlu Ö. Chem Berichte 1996;129:967.

[26] Gümüş G, Öztürk ZZ, Ahsen V, Gül A, Bekaroğlu Ö. J. Chem Soc Dalton Trans 1992;2585.

[27] Hirsch A, Hanack M. Chem Berichte 1991;124:833.

[28] Nakamoto K. Infrared spectra of inorganic and coordination compounds. New York: J. Wiley, 1970.

[29] Young JG, Onyebuagu W. J of Org Chem 1990;55:2155.