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Synthesis and characterization of novel phthalocyanines containing four 15-membered oxadithiadiaza mixed-donor macrocycles

Erbil Ağar, Selami Şaşmaz, Nesuhi Akdemir and Ibrahim Keskin

Department of Chemistry, Ondokuz Mayis University, Samsun, Turkey

Symmetrically tetrasubstituted metal-free and metal phthalocyanines (M = 2H, Cu, Ni, Co, Zn or Fe) with four 15-membered heteroatom (N, O, S)-containing donor sites attached have been synthesized and characterized by elemental analysis, IR, NMR, UV/VIS spectroscopy and thermogravimetric analysis.

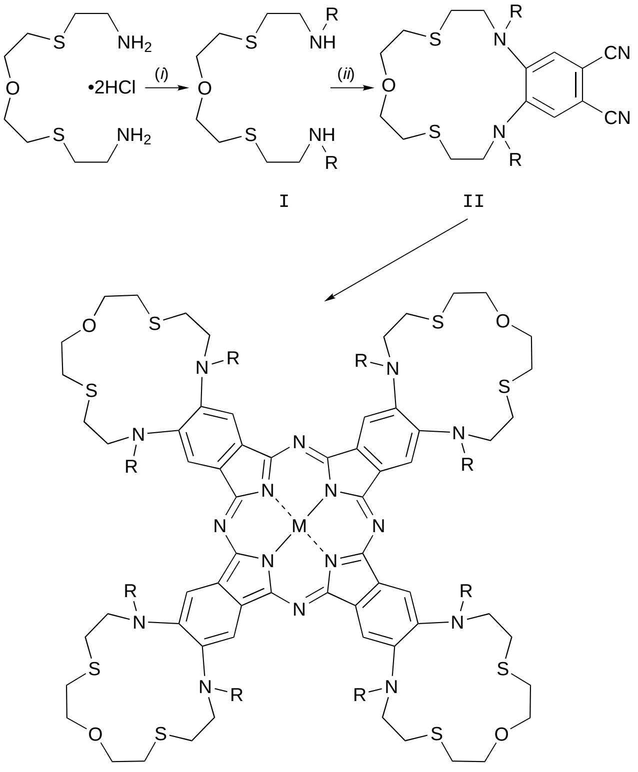
Phthalocyanines comprise a remarkably robust and versatile class of chemical compounds. They are of enormous technological importance for the manufacture of blue and green pigments. Other areas of current interest include applications in colours, catalysis, chemical sensors, electrochromism, batteries, photodynamic therapy, semiconductive materials, liquid crystals and modified supports for gas–solid chromatography as a result of newly synthesized compounds.[1]

Tetrasubstituted phthalocyanines are generally obtained from monosubstituted phthalonitrile, phthalic acid, phthalic anhydride or isoindoline. 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.[2] 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-containing functionalities such as oxothioethers[3] and azamacrocycles.[4–7] An additional advantage of using an azamacrocycle substituent is the solubility in water obtained by quaternization of the aza function. Phthalocyanine substituted with 12-membered tetraazamacrocycles provided donor sites for binding transition-metal ions, leading to nonanuclear complexes.[5] While phthalocyanines with N-, O- and S-donor substituents have frequently been encountered, those with N, O or O, S donor moieties together are rather few.[8–10]

In the present paper, we report a straightforward synthetic approach to oxadithiadiaza-substituted phthalocyanines and their metal complexes which can be used as intermediates to obtain symmetrical phthalocyanines.

Results and Discussion

As a first step, the benzo-substituted oxadithiadiaza macrocycle was prepared (Scheme 1). Compound **I** [*N*,*N*′-di(*p*-tolylsulfonyl)-6-oxa-3,9-dithiaundecane-1,11-diamine] was prepared from 6-oxa-3,9-dithiaundecane-1,11-diamine dihydrochloride with toluene-*p*-sulfonyl chloride in dichloromethane containing sodium hydroxide as the base. 1,2-Dichloro-4,5-dicyanobenzene was used recently to prepare 4,5-disubstituted phthalonitrile derivatives through base-catalysed nucleophilic aromatic displacement.[11–13] The same route was applied to prepare 15,16-dicyano-1,13-di(*p*-tolylsulfonyl)-2,3,5,6,8,9,11,12-octahydro-1,4,13,7,10-benzooxadithiadiazacyclopentadecene **II** from *N*,*N*′-di(*p*-tolylsulfonyl)-6-oxa-3,9-dithiaundecane-1,11-diamine and 1,2-dichloro-4,5-dicyanobenzene (Scheme 1). The reaction was carried out in dimethylformamide (dmf) at 50 °C and gave moderate yields (63%). The metal-free phthalocyanine **III** was obtained directly from the reaction of the phthalonitrile derivative **II** with freshly sublimed hydroquinone in the absence of solvent.[14] The reaction of the dinitrile derivative in high-boiling anhydrous solvents (*e.g.* quinoline or ethylene glycol) with the appropriate metal salt gave the metal phthalocyaninates **1**–**5** (M = Cu$^{\mathrm{II}}$, Ni$^{\mathrm{II}}$, Co$^{\mathrm{II}}$, Zn$^{\mathrm{II}}$ or Fe$^{\mathrm{II}}$). The yields were rather low and depended upon the metal ion. The insoluble products were obtained in sufficient purity after successive washings with different solvents.



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

Scheme 1 R = *p*-$\mathrm{MeC_6H_4SO_2}$. (*i*) *p*-$\mathrm{MeC_6H_4SO_2Cl}$, $\mathrm{CH_2Cl_2}$, NaOH, water; (*ii*) 1,2-dichloro-4,5-dicyanobenzene, dmf, $\mathrm{K_2CO_3}$, 50 °C

The intense green products are soluble in hot dmf and hot dimethyl sulfoxide (dmso). The solubility in dmso as determined spectrophotometrically was 10^{-4} mol dm^{-3} which is lower than those of crown ether[15] and azamacrocycles[4–7] but higher than those of thioether-substituted phthalocyanines.[16] The elemental analytical results of the starting materials and phthalocyanine compounds show good agreement with the calculated values. Characterization of the products involved a combination of methods including IR spectroscopy, elemental analysis (Table 1), UV/VIS spectroscopy (Table 2) and thermal analysis (Table 3).

Comparison of the IR spectral data clearly indicated the formation of compound **II** by the disappearance of the C−Cl band of 1,2-dichloro-4,5-dicyanobenzene at 640 cm^{-1} and of the NH band of compound **I** at 3300 cm^{-1}, and the appearance of a new absorption at 2225 cm^{-1} (CN). The spectrum of **II** also indicates the presence of alkyl, CN and SO_2 groups by the intense stretching bands at 3090–2820 (C−H), 2225 (C≡N) and 1340, 1160 cm^{-1} (SO_2). The CN absorptions disappear after phthalocyanine formation. The spectra of the free phthalocyanine **III** and the metal complexes **1**–**5** are very similar, with the exception of **III** showing NH stretching bands at 3300 and 1010 cm^{-1} due to the inner core.[17] 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.[18]

A common feature of the ^1H NMR spectra of phthalocyanines and their metal complexes (M = Ni^{II} or Zn^{II}) is a broad absorption probably caused by the aggregation of phthalocyanines which is frequently encountered at the concentrations used for NMR measurements.[1,19,20] Also the NH protons of the phthalocyanine **III** could not be observed due to this phenomenon. Owing to the distinct ring current of the 18π-electron system of the inner phthalocyanine core, the protons are characteristically shifted to low or high field.[21] However the shifts are rather small for the protons sufficiently far away from the ring current (*e.g.* CH_2O, CH_2S, CH_2N).

The ^1H NMR spectrum of compound **I** revealed the protons of the NH, aromatic rings, OCH_2, NCH_2, SCH_2 and *p*-Me. The ^{13}C NMR spectrum in $(CD_3)_2SO$ gave signals at δ 21.24 (*p*-Me), 35.44 and 36.14 (CSC), 50.82 (NC), 66.78 (COC), 145.52, 143.18, 136.84 and 129.70 (aryl). While the ^1H NMR spectra of **I** and **II** are similar, the proton-coupled ^{13}C NMR spectrum indicated the presence of the nitrile carbon atoms in **II** at δ 114.75.

The solubility of the new phthalocyanines is an obstacle to investigations of the interaction of the heterodonor (N, O and S) groups with metal ions under similar conditions to those of their oxa, aza or thia analogues. The electronic spectra in dmso show the characteristic features of phthalocyanines with absorptions in the red (Q band) and near UV (B band) regions.[22] They are also very similar to those of crown ether-,[15,23] alkyl chain-,[24] and alkylsulfanyl-[25,26] and azamacrocycle-substituted[4–7] phthalocyanines. Although the symmetry of the phthalocyanines is lowered by the heteroatom substituent on each benzene group, **III** still shows Q-band absorptions of D_{2h} symmetry in organic solvents.[1] These complexes showed an intense absorption at 719 nm and a second band of lower intensity at 605 nm. However the intensity of the d–d transitions in the complexes of the saturated cyclic amines is very low when compared with the Q absorptions of phthalocyanines, thus there should be no appreciable difference upon complexation of the macroaza groups[27] and any variation is the result of aggregation phenomena.

The thermal properties of the new phthalocyanines **III** and **1**–**5** were investigated by thermogravimetric analysis (TGA) under nitrogen and the decomposition temperatures are given in Table 3. The present phthalocyanines containing heteroatoms can also be considered as non-substituted phthalocyanines having high thermal stability.[28] Initial decomposition occurs at *ca.* 190–300 °C and then extensive decomposition occurs at temperatures between 320 and 450 °C. The thermal stability of the present metal phthalocyaninates is similar to those of corresponding substituent-containing (crown ether,[19] alkyl chains,[24] alkylsulfanyl,[25,26] sulfonyl chains[29] and azamacrocycle[5–7,30]) and transition-metal phthalocyaninates. Thus, the decomposition temperatures of the phthalocyanine complexes are not decreased significantly by the groups symmetrically attached to the heteroatoms of the ether rings.

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

Table 1 Analytical data for the starting materials and the phthalocyanines

	Found (%)				Calc. (%)			
Compound	C	H	N	S	C	H	N	S
I	49.7	5.9	5.3	24.15	49.6	6.0	5.25	24.1
II	54.95	4.9	8.5	19.5	54.85	4.85	8.55	19.5
III	54.9	5.0	8.6	19.6	54.85	4.95	8.55	19.5
1	53.65	4.7	8.4	19.15	53.6	4.75	8.35	19.05
2	53.7	4.75	8.35	19.05	53.65	4.75	8.35	19.1
3	53.75	4.7	8.3	19.15	53.65	4.75	8.35	19.1
4	53.65	4.7	8.35	19.1	53.55	4.75	8.35	19.05
5	53.8	4.75	8.4	19.2	53.75	4.75	8.35	19.15

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 ^1H and ^{13}C NMR spectra on a Bruker AC-200 Fourier-transform spectrometer. Thermogravimetric analyses were obtained on a Rikagu TG 8110 simultaneous thermal analyser combined with a TAS 100 thermal analyser at 10 °C min^{-1} in a nitrogen flow. Elemental analysis was performed by the Instrumental Analysis Laboratory of TÜBİTAK Gebze Research Center. 1,2-Dichloro-4,5-dicyanobenzene[13] and 6-oxa-3,9-dithiaundecane-1,11-diamine dihydrochloride[31] were synthesized according to the reported procedures.

Syntheses

***N*,*N*′-Di(*p*-tolylsulfonyl)-6-oxa-3,9-dithiaundecane-1,11-diamine I.** 6-Oxa-3,9-dithiaundecane-1,11-diamine dihydrochloride (11.38 g, 38.3 mmol) and sodium hydroxide (6.20 g, 155 mmol) was dissolved in water (150 cm^3). A solution of toluene-*p*-sulfonyl chloride (14.60 g, 76.6 mmol) in CH_2Cl_2 (150 cm^3) was added dropwise over 4 h. The mixture was then stirred at room temperature for 24 h. The combined organic phases were dried over Na_2SO_4 and evaporated to produce a viscous residue, which was washed with NaOH solution (20% w/w) to separate any organic residue. The brown product was washed with water and diethyl ether and recrystallization from ethanol gave

Table 2 Electronic spectral data for the phthalocyanines in dmso

Compound	λ_{max}/nm (10^{-4} ε/dm^3 mol^{-1} cm^{-1})					
III	709 (0.93)	649 (0.91)	609 (sh) (0.83)	349 (1.76)	295 (3.25)	264 (3.69)
1	677 (sh) (1.78)	621 (2.25)	337 (sh) (2.36)	281 (3.84)		
2	694 (sh) (0.74)	612 (0.82)	404 (0.30)	243 (0.43)		
3	680 (3.12)	638 (2.83)	605 (sh) (1.73)	348 (3.44)	259 (2.87)	243 (1.75)
4	662 (1.35)	628 (1.24)	336 (3.46)	269 (5.67)	238 (12.43)	
5	719 (sh) (1.52)	664 (1.90)	442 (1.20)	341 (2.29)	243 (3.92)	221 (6.20)

Table 3 Thermal properties of the phthalocyanines

	T/°C	
Compound	Initial decomposition	Main decomposition
III	190	320
1	245	385
2	280	410
3	285	420
4	300	420
5	230	450

pure compound **I**. Yield 8.0 g (45%). It is soluble in chloroform, ethyl acetate, ethanol, dimethyl sulfoxide and dimethylformamide. M.p. 99–101 °C. IR: $\tilde{\nu}_{max}$/cm^{-1} 3300, 3060–2860, 1610, 1500, 1455, 1420, 1370–1300, 1160, 1100, 1010, 960, 905, 830, 725–700, 660 and 560. ^{1}H NMR [$(CD_3)_2SO$]: δ 7.91 (2 H, s, NH), 7.45–7.20 (8 H, m, aryl), 3.60–3.12 (4 H, t, OCH_2), 3.10–2.94 (4 H, t, NCH_2), 2.91–2.38 (8 H, m, SCH_2) and 2.24 (6 H, s, *p*-Me).

15,16-Dicyano-1,13-di(*p*-tolylsulfonyl)-2,3,5,6,8,9,11,12-octahydro-1,4,13,7,10-benzooxadithiadiazacyclopentadecene II. Compound **I** (9 g, 17 mmol) was dissolved in dry dmf (200 cm^3), finely ground anhydrous K_2CO_3 (7 g, 51 mmol) was added and the mixture stirred for 2 h at 50 °C. A solution of 1,2-dichloro-4,5-dicyanobenzene (4.2 g, 21 mmol) in dry dmf (200 cm^3) was added dropwise over 4 h. After stirring for 4 d at 50 °C, the reaction mixture was poured into ice–water (400 g). The precipitated ditosylate was filtered off, washed with water to separate any inorganic residue, then ethanol and hot hexane and dried. Yield 7.0 g (63%). This yellow product is soluble in hot ethanol, methanol, chloroform, benzene, hot 1,4-dioxane, ethyl acetate, dimethyl sulfoxide and dimethylformamide. M.p. 108–110 °C. IR: $\tilde{\nu}_{max}$/cm^{-1} 3090–2820, 2225, 1610, 1560, 1485, 1390–1325, 1280, 1250, 1210–1150, 1090, 965, 920, 850–810, 730–700, 585 and 560. NMR [$(CD_3)_2SO$]: ^{1}H, 7.92–7.34 (10 H, m, aryl), 3.62–3.51 (4 H, t, OCH_2), 3.48–3.10 (4 H, t, NCH_2), 3.00–2.52 (8 H, m, SCH_2) and 2.41 (6 H, s, *p*-Me); ^{13}C, δ 145.61, 143.56, 137.59, 135.48, 129.91, 129.74, 127.72, 114.75, 66.97, 51.23, 39.46, 38.21 and 21.62.

Metal-free phthalocyanine III. A mixture of compound **II** (1.0 g, 1.52 mmol) and hydroquinone (0.17 g, 0.76 mmol) (purified by sublimation) was gently heated under N_2 until melting occurred and then cooled. This mixture was heated to 200 °C under a nitrogen atmosphere and held at this temperature for 1 h. After cooling to room temperature the reaction mixture was treated with hot water to precipitate the product and then filtered. The dark blue product was washed with hot water, ethanol, ethyl acetate, benzene and dried. Yield 0.34 g (34%). It is soluble in hot dmso and hot dmf. IR: $\tilde{\nu}_{max}$/cm^{-1} 3300, 3060–2960, 1605, 1520, 1460, 1385–1325, 1255–1190, 1160, 1110–1060, 1010, 950, 910, 895, 835–820, 760, 740–710, 640, 610 and 555. ^{1}H NMR [$(CD_3)_2SO$]: δ 7.95–7.14 (40 H, m, aryl), 3.83–3.55 (16 H, t, OCH_2), 3.53–3.12 (16 H, t, NCH_2), 2.95–2.54 (32 H, m, SCH_2) and 2.46 (24 H, s, *p*-Me).

Copper(II) phthalocyaninate 1. A mixture of compound **II** (1.0 g, 1.52 mmol) anhydrous CuCl (0.04 g, 0.38 mmol) and 2-(dimethylamino)ethanol (30 cm^3) was heated and stirred at 145–150 °C for 6 h under N_2. After cooling to room temperature the green mixture was diluted with water (100 cm^3) and the crude product precipitated. The mixture was filtered, washed with NH_4OH (24% w/w) to separate any inorganic residue, then with hot water and hot ethanol to remove the unchanged organic material. The green product was washed with water, methanol, hot ethanol, ethyl acetate and benzene and dried. Yield 0.47 g (46%). The product was soluble in hot dmso and hot dmf. IR: $\tilde{\nu}_{max}$/cm^{-1} 3060–2970, 1610, 1590, 1450–1385, 1310, 1285, 1190, 1160, 1115, 960, 910, 810, 760, 735, 670, 640 and 560.

Nickel(II) phthalocyaninate 2. A mixture of compound **II** (1.0 g, 1.52 mmol), anhydrous $NiCl_2$ (0.05 g, 0.38 mmol) and quinoline (40 cm^3) was heated and stirred at 200 °C for 5 h under N_2. After cooling to room temperature, the dark blue mixture was diluted with ethanol (100 cm^3) and the crude product precipitated. It was washed with methanol, ethanol, ethyl acetate and water, and dried. Yield 0.18 g (17%). The product is soluble in hot dmso and hot dmf. IR: $\tilde{\nu}_{max}$/cm^{-1} 3070–2860, 1605, 1530, 1425–1390, 1345, 1295, 1210, 1165–1140, 1090, 1075, 975, 895, 795, 750, 715, 660 and 560. ^{1}H NMR [$(CD_3)_2SO$]: δ 7.68–7.10 (40 H, m, aryl), 3.76–3.52 (16 H, t, OCH_2), 3.48–3.10 (16 H, t, NCH_2), 2.84–2.43 (32 H, m, SCH_2) and 2.38 (24 H, s, *p*-Me).

Cobalt(II) phthalocyaninate 3. A mixture of compound **II** (1.0 g, 1.52 mmol), anhydrous $CoCl_2$ (0.05 g, 0.38 mmol) and ethylene glycol (50 cm^3) was heated and stirred at 200 °C for 6 h under N_2. After cooling to room temperature, the reaction mixture was treated with ethanol (50 cm^3) to precipitate the dark blue product and then filtered. The product was washed with methanol, ethanol, ethyl acetate and water, and dried. Yield 0.15 g (14%). It is soluble in hot dmso and hot dmf. IR: $\tilde{\nu}_{max}$/cm^{-1} 3080–2860, 1600, 1520, 1435–1335, 1300, 1165, 1105, 1080, 1020, 970, 890, 810, 790, 725, 665, 615 and 555.

Zinc(II) phthalocyaninate 4. A mixture of compound **II** (1.0 g, 1.52 mmol), anhydrous zinc acetate (0.07 g, 0.38 mmol) and quinoline (25 cm^3) was heated and stirred at 190–200 °C for 6 h under N_2. After cooling to room temperature, ethanol (100 cm^3) was added in order to precipitate the product. The dark blue product was filtered off and then washed with ethanol, methanol, ethyl acetate and benzene, and dried. Yield 0.20 g (20%). It is soluble in hot dmso and hot dmf. IR: $\tilde{\nu}_{max}$/cm^{-1} 3070–2820, 1600, 1490, 1420, 1380, 1340, 1290, 1190, 1160, 1135, 1100, 1080, 960, 905, 850, 815, 790, 750, 715, 675 and 560. ^{1}H NMR [$(CD_3)_2SO$]: δ 8.35–7.38 (40 H, m, aryl), 3.95–3.50 (16 H, t, OCH_2), 3.47–3.15 (16 H, t, NCH_2), 2.95–2.51 (32 H, m, SCH_2) and 2.41 (24 H, s, *p*-Me).

Iron(II) phthalocyaninate 5. A mixture of compound **II** (1 g, 1.52 mmol) and ethylene glycol (30 cm^3) under nitrogen was rapidly heated and stirred at 200 °C. At this temperature [$Fe(CO)_5$] (0.05 cm^3, 0.38 mmol) was added slowly by means of a syringe. It was heated at 200 °C for 4 h. After cooling, the reaction mixture was diluted with ethanol and filtered off. The dark blue product was washed with benzene, methanol, hot ethanol and ethyl acetate, and dried. Yield 0.32 g (31%). It is soluble in hot dmso and hot dmf. IR: $\tilde{\nu}_{max}$/cm^{-1} 3070–2860, 1610, 1500, 1420, 1385, 1360, 1340, 1300, 1280, 1160, 1075, 970, 900, 780, 760, 660 and 555.

Acknowledgements

This work was supported by the research fund of the Ondokuz Mayis University of Samsun.

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Received 28*th October* 1996; *Paper* 6/07349B