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Dioxadiaza macrocycle-substituted phthalocyanines

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Abstract

New metallophthalocyanines (M = Cu, Ni, Co) have been synthesized from a 16-membered dioxadiaza macrocycle using an anhydrous metal salt (CuCN, $NiCl_2$ or $CoCl_2$). The new compounds have been characterized by elemental analyses, IR, NMR and electronic spectroscopy. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Phthalocyanines (Pcs) are widely used as pigments and dyes. In the last decade, much effort has been devoted to the synthesis and characterization of new phthalocyanine derivatives having interesting optical, electrical and catalytic properties by making slight changes on the periphery or on the central metal ion [1–3]. The execution of minor changes on the nature and position of side groups is a practical method of tuning the properties of phthalocyanines [4]. Starting from simple monofunctional substitutents such as halo, alkyl, alkoxy and sulfo groups which cause only small changes in the physical properties of the parent molecules, more complex structures have been introduced on the periphery of the phthalocyanine moiety. Bulky substituents on the periphery enhance solubility and the donor groups of the substituents are capable of binding to additional metal ions.

In addition, since phthalocyanines effectively absorb in the lower energy region of the visible spectrum, they have found extensive application as photoconductors in optical recording material and as photosensitizers in photodynamic therapy [5].

The advantage of using soluble Pcs for the aforementioned applications, in contrast to the insoluble parent Pcs, is the possibility of reaching high degrees of purification by column chromatography or crystallization [6]. The incorporation of macrocyclic groups such as crown ether [7], monoaza crown ether [8], diazatrioxa-macrocycle [9] and also octa-substituted [10–12] onto the periphery of phthalocyanines has enhanced the solubility of these compounds and provided additional binding sites for different kinds of ions.

Preliminary findings on a derivative of phthalocyanine containing four 16-membered-diazadioxa macrocyclic moieties elaborated through O-groups have been reported by our group [13]. In that study we could not synthesize other metallopthalocyanines via nitrile groups because of difficulties in purification. We have now changed the position of the O and N atoms and were able to obtain a

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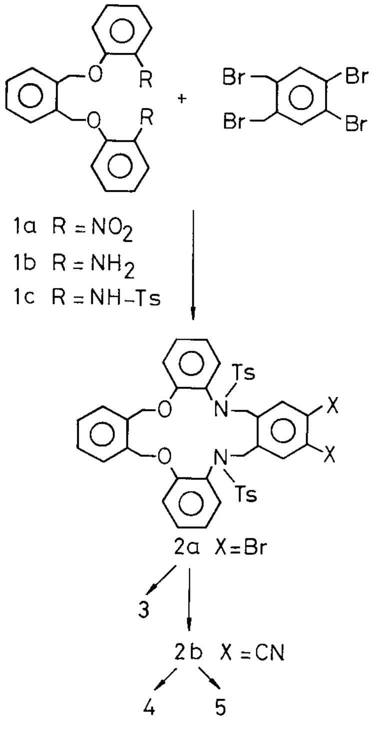
new macrocycle ring. A dinitrile compound was synthesized from this macrocycle and then purified. Therefore, by changing the position of the O and N atoms, we overcame the prior purification problem. In the present paper, new metallophthalocyanines containing [Cu(II), Ni(II), or Co(II)] and four 16-membered-dioxadiaza macrocyclic moieties are described.

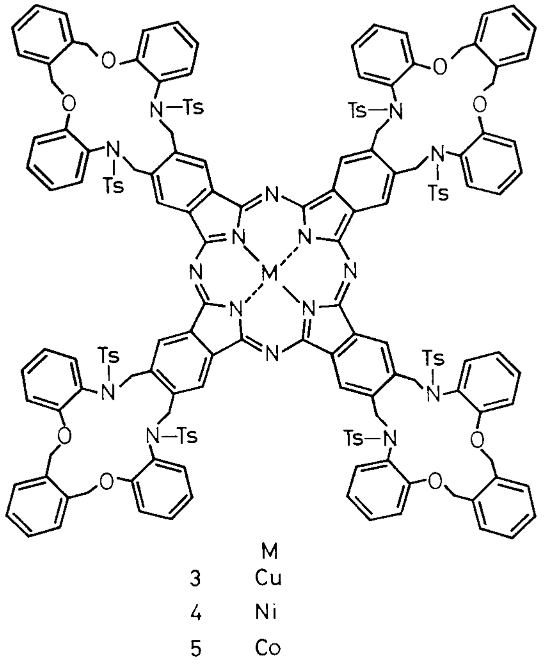
2. Results and discussion

Scheme 1 shows the synthesis of the dioxadiaza macrocycle-substituted phthalocyanines used in this investigation. In step 1, 1,2-bis-(2-nitrophenoxymethyl)benzene (**1a**) was synthesized by treating 2-nitrophenol with 1,2-bis(bromomethyl)-4,5-dibromobenzene [14] in DMF, using anhydrous K_2CO_3 as the base. The reaction was carried out for 60 h at 30°C and gave high yield (81%). Compound **1a** was reduced to the diamino derivative (**1b**) using Fe/HOAc [13].

The amino groups of **1b** were protected by tosylation with *p*-toluenesulfonyl chloride in pyridine at 0°C for subsequent reactions. The usefulness of the tosyl end group of **1c** should be noted because it facilitates the ring-closure reaction, due to the restricted rotation of the tosylamide linkage, and is stable. Under weakly basic conditions, 1,2-bis-(bromomethyl)-4,5-dibromobenzene reacted with the tosylamino groups of **1c** to form the 16-membered dioxadiazamacrocycle **2a**.

Copper(II) phthalocyanine **3** formation was accomplished by the direct reaction of the dibromo derivative **2a** with CuCN in dry tetramethylurea (TMU). The cyano derivative (**2b**) was isolated under mild conditions, according to the Rosenmund von Braun procedure, which might be considered as an intermediate step in the phthalocyanine formation. The reaction of **2b** with the appropriate metal salt in anhydrous solvents (e.g. DMF or ethylene glycol) gave the monomeric phthalocyanines (**4** and **5**) containing Ni(II) and Co(II).





Purification of the phthalocyanines was a laborious process, ultimately requiring column chromatography on neutral alumina. The final yields were lower than those obtained for phthalocyanines having other bulky groups [7,15]. The present phthalocyanines were slightly soluble in CH_2Cl_2, DMF and DMSO.

Characterization of the products involved a combination of several methods, including combustion (Table 1), ^{1}H-NMR (Table 2), UV/VIS (Table 3) and IR analyses. The IR spectrum of the amine-containing compounds exhibited characteristic frequencies at 3480–3380 cm^{-1} for the free NH_2 stretching vibrations. The difference between tosylated and free amino groups was clear from the presence of SO_2 vibrations at 1350 and 1150 cm^{-1} (cf. **1c**).

Comparison of the IR spectra obtained on **2a** and **2b** confirmed the conversion of aromatic bromo groups to cyano groups. In this case, the C-Br band at 630 cm^{-1} has disappeared and a C≡N band at 2240 cm^{-1} appeared. An indication of phthalocyanine formation from the dicyano derivative (**2b**) was the disappearance of the sharp C≡N vibration.

Table 3
Electronic spectra of the phthalocyanines in DMSO

Compound	λ_{max}/nm (10^{-5} ε/dm^3 mol^{-1} cm^{-1})
3	691 (1.068), 620 (0.324), 348 (0.810), 263 (0.989)
4	683 (0.749), 616 (0.268), 334 (0.427), 252 (0.653)
5	687 (1.868), 608 (0.418), 320 (0.624), 243 (0.596)

The ^{1}H-NMR spectra of newly synthesized unmetallised intermediates and nickel(II) phthalocyanine (**4**) were in accord with the proposed structures. In addition to the aromatic protons in dioxadiazamacrocycle **2a**, CH_2-N and CH_2-O protons appeared as singlets at 4.84 and 4.79 ppm, respectively. The ^{1}H-NMR spectra of **4** and **2b** are very similar. The rather broad bands in the case of

Table 1
Elemental analyses result

		Analysis calcd (found)			
Compound	Formula	C	H	N	M
1c	$C_{34}H_{32}N_2O_6S_2$	64.96 (64.45)	5.09 (5.01)	4.46 (4.12)	–
2a	$C_{42}H_{36}Br_2N_2O_6S_2$	56.75 (56.05)	4.05 (3.97)	3.15 (2.98)	–
2b	$C_{44}H_{36}N_4O_6S_2$	67.69 (66.85)	4.61 (4.57)	7.18 (6.93)	–
3	$C_{176}H_{144}CuN_{16}O_{24}S_8$	66.34 (65.93)	4.52 (4.36)	7.03 (7.01)	1.99 (1.72)
4	$C_{176}H_{144}NiN_{16}O_{24}S_8$	66.44 (65.78)	4.53 (4.41)	7.05 (6.86)	1.84 (1.65)
5	$C_{176}H_{144}CoN_{16}O_{24}S_8$	66.64 (66.01)	4.53 (4.29)	7.05 (6.91)	1.85 (1.70)

Table 2
Proton NMR spectral data for the reactants and the phthalocyanines in DMSO

Compound	tosyl-CH_3	OCH_2	NCH_2	Aromatic protons	NH
1c[a]	2.25 (6H,s)	4.86 (4H,s)	–	7.45–6.65 (20H,m)	9.40 (2H,s)
2a	2.36 (6H,s)	4.70 (4H,s)	4.84 (4H,s)	7.61–6.52 (22H,m)	–
2b	2.39 (6H,s)	4.65 (4H,s)	4.76 (4H,s)	7.65–6.76 (22H,m)	–
4[b]	2.34 (24H,s)	4.70 (16H,s)	4.84 (16H,s)	7.75–6.78(88H,m)	–

[a] In [d_6] DMSO.

[b] Broad resonances.

4 were probably due to chemical exchange associated with aggregation–disaggregation equilibria that occurs at the high concentrations used in the NMR measurements. The paramagnetic nature of the copper(II) and cobalt (II) phthalocyanines (**3** and **5**) precluded NMR measurements on these compounds.

Two strong absorption bands were observed for phthalocyanines **3–5**, one in the visible region at 600–700 nm (Q band) that was attributed to the $\pi-\pi^*$ transition from the HOMO to the LUMO of the Pc2$^-$ moiety, and the other in the UV region at 300–350 nm (B band) arising from the deeper π levels →LUMO transition. An increase in dye concentration led to aggregation, causing the Q band to shift to a shorter wavelength and a decrease in the molar absorption coefficient.

In the UV-visible spectrum of dye **3** in DMSO, a characteristic Q band transition with D_{4h} symmetry was observed as a single band of high intensity at 681 nm. The absorption spectra of **4** and **5** in DMSO showed peaks at 685 and 678 nm, respectively.

Fast atom bombardment mass spectrometric analysis gave molecular ion species for **2a**, **2b** and **4**. $M+1$ peaks of *m/z* 889, 781, and 3180 were observed for **2a**, **2b**, and **4**, respectively. In the mass spectrum of **2a**, fragment ions corresponding to the loss of $C_7H_7SO_2$ [M-155], $2C_7H_7SO_2$ [M-310], $C_6H_4ONSO_2C_6H_4CH_3$ [M-261] were easily identified. Fragment ions for **2b** were observed at $C_{10}H_6N_2$ [M-154], $C_7H_7SO_2$ [M-155], $C_6H_4OSO_2C_6H_4CH_3$ $[M\text{-}261]^+$, $C_7H_7SO_2$ $[M\text{-}155]^+$, and a fragment ion of **4** was observed at $3C_{42}H_{36}N_2O_6S_2$ $[M\text{-}2184]^+$. $M+1$ peaks for **3** (m/z 3184.5) and **5** (m/z 3180) were also observed.

3. Experimental

FTIR spectra were recorded in KBr on an ATI Unicam-Mattson 1000 spectrophotometer, UV/visible spectra were recorded on a Unicam UV/visible spectrometer UV 2, ^{1}H-NMR spectra were recorded on a Bruker (200 MHz) Spectrometer, and mass spectra were recorded on a VG Zab-Spectrometer. 1,2-Bis(bromomethyl)-4,5-dibromobenzene was prepared by reported procedures [16,17].

3.1. 1,2-Bis-(2-p-tolysulfonylaminophenoxymethyl)benzene (**1c**)

Compound **1b** (0.750 g, 2.35 mmol) was dissolved in pyridine (15 ml) and the solution was stirred cold under an N_2 atmosphere as a solution of toluene-*p*-sulfonyl chloride (0.9 g, 4.7 mmol) in pyridine (5 ml) was added dropwise over 1 h. The reaction mixture was stirred at room temperature for 1 h and then poured slowly into a stirred mixture of concentrated HCl (25 ml) and ice (200 g). The precipitate was collected by filtration, washed successively with H_2O, EtOH and Et_2O, and dried. Yield: 1.28 g (87%); m.p. 136°C. IR (KBr): ν_{max}/cm^{-1} 3250 (NH), 3060 (CH aromatic), 2950–2870 (CH_2 aliphatic), 1600 (NH bending), 1350 and 1150 (SO_2).

3.2. Dioxadiaza macrocycle (**2a**)

Compound **1c** (1 g, 1.59 mmol) was dissolved in dry DMF (30 ml), anhydrous K_2CO_3 (0.44 g, 3.2 mmol) was added and the mixture was stirred for 1 h at 30°C. A solution of 1,2-bis(bromomethyl)-4,5-dibromobenzene (0.671 g, 1.59 mmol) in dry DMF (20 ml) was added dropwise over 6 h. After the reaction mixture had stirred for 72 h at 30°C, it was poured into ice-water (200 g). The mixture was filtered and the solid was washed successively with H_2O, EtOH and Et_2O. The product was treated with hot THF and filtered. The filtrate was evaporated to dryness and the solid was dried in vacuo. Yield: 0.5 g (35%); m.p. 160°C. IR(KBr): ν_{max}/cm^{-1}, 3060 (CH aromatic), 2980–2820 (CH_2 aliphatic), 1340 and 1150 (SO_2), 620(C-Br).

3.3. Dioxadiaza macrocycle (**2b**)

Under N_2, compound **2a** (0.9 g, 1.02 mmol), CuCN (0.456 g, 5.1 mmol) and anhydrous DMF (15 ml) were heated together at 155–160°C for 10 h in the presence of a catalytic amount of pyridine. During this time the resulting solution became dark brown. After cooling to room temperature the mixture was poured into aqueous NH_3 (25%, 200 ml) and air was passed through the solution for 24 h. The creamy colored precipitate was collected by filtration, washed with water until the wash water was neutral and then with EtOH and Et_2O. The crude product was extracted with EtOAc (5×5 ml), and evaporation of the combined extracts to dryness gave a cream colored solid. Yield: 0.35 g (44%); IR(KBr): ν_{max}/cm^{-1}, 3070 (CH aromatic), 2960–2840 (CH aliphatic), 2240 (C≡N, 1350 and 1150 (SO_2).

3.4. [Tetrakis (macrocycle) phthalocyaninato] copper (II) (**3**)

A mixture of **2a** (0.2 g, 0.23 mmol), CuCN (0.05 g, 0.59 mmol), and dry TMU (0.2 ml) was heated in a sealed tube at 150–160°C for 17 h under N_2. The dark green mixture was cooled to room temperature and diluted with EtOH (10 ml), whereupon the crude product precipitated. The solid was collected and washed with hot EtOH to remove unreacted organic materials. The product was boiled repeatedly (seven times) with a solution of NaCN in H_2O:EtOH (1:2) to remove excess CuCN and then collected by filtration. The dark green product was washed with H_2O and EtOH, extracted three times with CH_2Cl_2, and the filtrate was evaporated to dryness. The product was purified by column chromatography on neutral Al_2O_3, using $CHCl_3$:MeOH 50:1. Yield: 0.045 g (25%); IR(KBr): ν_{max}/cm^{-1}, 3070 (CH aromatic), 2980-2830 (CH aliphatic), 1350 and 1155 (SO_2).

3.5. [Tetrakis (macrocycle)phthalocyaninato] nickel (II) (**4**)

A mixture of dicyano compound **2b** (0.2 g, 0.26 mmol), $NiCl_2$ (0.008 g, 0.06 mmol) and anhydrous DMF (0.6 ml) was heated in a sealed glass tube at 150–160°C for 22 h. After cooling, the reaction mixture was diluted with EtOH (5 ml) and the precipitate was collected. The solid was treated four times with boiling EtOH to dissolve unreacted metal salts. Further purification was accomplished by column chromatography on neutral alumina, using $CHCl_3$:MeOH (50:1) as the eluent. Yield: 0.035 g (20%); IR(KBr): ν_{max}/cm^{-1}, 3070 (CH aromatic), 2980–2830 (CH aliphatic), 1350 and 1155 (SO_2).

3.6. [Tetrakis (macrocycle)phthalocyaninato] cobalt (II) (**5**)

A mixture of dicyano compound **2b** (0.25 g, 0.32 mmol), $CoCl_2$ (0.011 g, 0.08 mmol) and ethylene glycol (1.2 ml) was stirred at 160–170°C for 20 h under nitrogen. After cooling to room temperature the reaction mixture was treated with EtOH (25 ml) and then the crude product was washed with H_2O and EtOH to remove unreacted organic material. The crude product was dried with Et_2O and chromatographed on neutral Al_2O_3 using $CHCl_3$:MeOH (50:1) as the eluent. Yield: 0.040 g (18%); IR(KBr): ν_{max}/cm^{-1}, 3060 (CH aromatic), 2980-2830 (CH aliphatic), 1350 and 1155 (SO_2).

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References

[1] Leznoff CC, Lever ABP. Phthalocyanines properties and applications. VCH: Weinheim, 1989 Vol. 1, 1993 Vol. 2.

[2] Moser FH, Thomas AL. The phthalocyanines. Boca Raton, Florida: CRC, 1983. Vol I and II.

[3] Luk'yanates EA. Mol Mater 1992;1:209.

[4] Schultz H, Lehman H, Rein M, Hanack M. Structure and bonding in Berlin 1991;74:41.

[5] Ben-Hur E. In: Henderson BW, Dougherty TJ, editors. Photodynamic therapy; basic principles and clinical applications. New York: Marcel Dekker, 1992.

[6] Katayose M, Tai S, Kamijima K, Hagiwara H, Hayashi N. J Chem Soc, Perkin Trans 1992;2:403.

[7] Koray AR, Ahsen V, Bekaroglu O. J Chem Soc, Chem Commun 1986:932.

[8] Ahsen V, Gürek A, Musluoglu E, Bekaroglu O. Chem Ber 1989;122:1073.

[9] Gümüs G, Oztürk ZZ, Ahsen V, Gül A, Bekaroglu O. J Chem Soc, Dalton Trans 1992:2485.

[10] Bayır Altuntas Z, Hamuryudan E, Grürek AG, Bekaroglu O. J Porphyrins and Phthalocyanines 1997;1:349.

[11] Gürol I, Ahsen V, Bekaroglu O. J Chem Soc, Dalton Trans 1994:497.

[12] Bekaroglu O. Appl Organomet Chem 1996;10:605.

[13] Hamuryudan E, Bekaroglu O. J Chem Res (S) 1993:460.

[14] Wenner W. J Org Chem 1952;17:523.

[15] Sarıgül S, Bekaroglu O. Chem Ber 1989;122:291.

[16] Klingsberg E. Synthesis 1972:29.

[17] Piechocki C, Simon J. Nouv J Chim 1985;9:159.