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Synthesis and Characterization of New Phthalocyanines Containing Thio-Oxa-Ether Moieties

Selami Şaşmaz, Erbil Ağar,* Nesuhi Akdemir & İbrahim Keskin

Ondokuz Mayis University, Department of Chemistry, 55139-Kurupelit, Samsun, Turkey

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ABSTRACT

Metal-free and metal phthalocyanines (M: H_2, Ni, Co, Zn) 4–7 containing four 9-membered dithiaoxa macrocycles were prepared. The new compounds were characterized by elemental analyses, and IR, ^{1}H-NMR, UV-VIS and DTA. The dithiaoxa-substituted phthalocyanines are less soluble than the aza and oxa-substituted ones. © 1998 Elsevier Science Ltd

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INTRODUCTION

Since their discovery, phthalocyanines have become one of the most extensively studied classes of compounds because of their unique structure, their extremely high stability and their potential for commercial exploitation [1–4]. In addition to their extensive use as dyes and pigments, phthalocyanines have found wide applications in catalysis, in optical recording, in photoconductive materials, in photodynamic therapy and as chemical sensors [4]. One of the important aims of research on the chemistry of phthalocyanines (Pc) is to enhance their solubility in various solvents. While peripheral substitution with bulky groups [5] or long alkyl chains [6] leads to Pc derivatives soluble in common organic solvents, the introduction of sulfonyl [7], carboxyl [8] or amino [9] groups gives water-soluble products. An additional advantage of using monoazacrown-ether [10, 11], 8 or 9-membered diaza and 11 or 13-membered triaza [12], 14 or 15-membered tetraazamacrocycles [13] was

*Corresponding author.

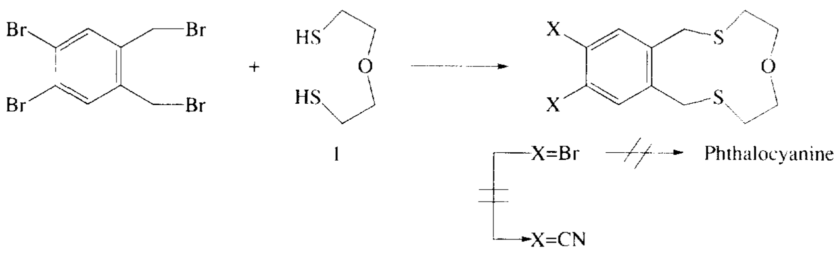
that solubility in water is obtained by quaternization of the aza function. Preliminary findings for phthalocyanines with a detailed study of 12-membered derivative have been reported recently by our group [14, 15]. Phthalocyanines substituted with 12-membered tetraaza macrocycles provided donor sites for binding transition-metal ions or 4-A group ions, leading to nonanuclear or mononuclear complexes [16]. In addition, tetraaza bridged polymeric phthalocyanines were also synthesized [17]. These phthalocyanines were soluble in common organic solvents such as chloroform, dichloromethane, DMF and DMSO, but insoluble in water.

As donors, thioether moieties can be placed between the oxa and aza groups for their tendency to complex with alkali and transition-metal ions [18]. Phthalocyanines substituted with sulfur donors are rather few [19–22]. The shift of the high intensity Q bands to longer wavelengths is a common feature of these compounds [23, 24].

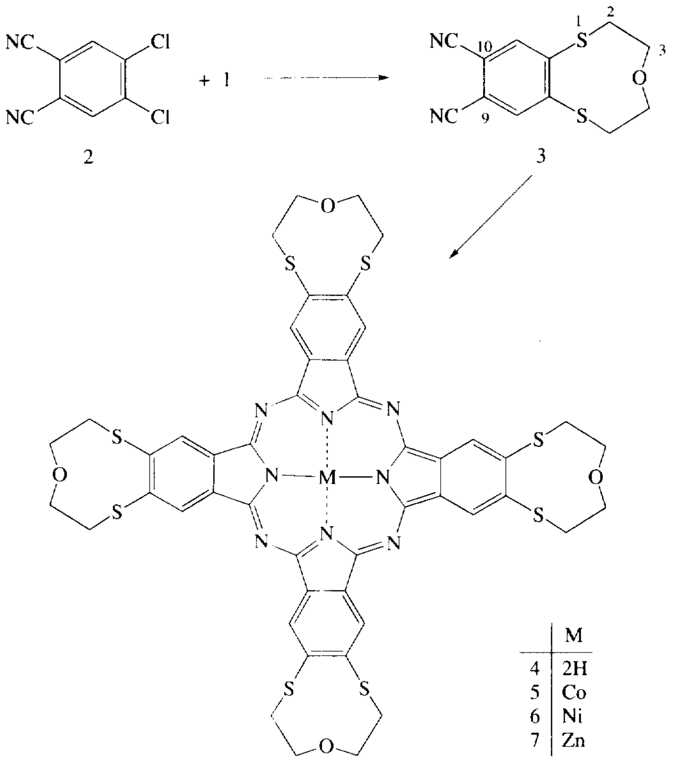
RESULTS AND DISCUSSION

Our primary aim was to prepare a benzofused 9-membered dithiaoxamacrocycle with 1,2-dibromo substitution on the benzene moiety. The dibromo derivative would not be converted into a phthalodinitrile by Rosenmund von Braun reaction. All efforts to accomplish these reactions failed in the second step and no formation of phthalodinitriles was observed (Scheme 1). Similarly, no phthalocyaninatocopper was detected on converting the bromo compound directly in high-boiling solvents such as quinoline or DMF or pyridine at reflux temperature.

To overcome these difficulties, a new macrocycle was designed which would initially carry the phthalodinitrile unit [25]. By nucleophilic displacement, the dinitrile **2** was converted with an excess of **1** in the presence of an excess of Na_2C0_3 in DMSO to the dinitrile **3** (Scheme 2) and the yield was high (80%) Cyclotetramerization of the phthalodinitrile **3** to the metal-free phthalocyanine **4** was accomplished in diethylaminoethanol at reflux tem-



Scheme 1.



	M
4	2H
5	Co
6	Ni
7	Zn

Scheme 2.

perature. The metal phthalocyanines **5**–**7** were obtained by using the anhydrous metal salts (Co, Ni and Zn). Many attempts to obtain CuPc and FePc did not give intensely coloured products.

The high boiling solvents of choice for these reactans were quinoline for Ni (II) **6** and Zn (II) **7** and ethylene glycol for Co (II) **5**.

All new compounds were characterized by their elemental analyses (Table 1).

In contrast to the aza or oxamacrocycle-fused analogs, the solubility of these phthalocyanines is very low in DMSO and DMF, and they are insoluble in pyridine. The low solubility of the phthalocyanines **4**–**7** means that their NMR spectra could not be obtained in hot $CDCl_3$ and hot DMSO (d_6).

The IR spectrum of **3** clearly indicates the presence of alkyl and CN groups by the intense stretching bands at 2920–2860 (C–H) and 2220 cm^{-1} (CN) and CN absorptions disappear after the phthalocyanine formation. The IR spectra of phthalocyanines **5**–**7** are very similar, with the exception of the metal-free **4** showing an NH stretching band at 3250 and 1010 cm^{-1} due to the inner core.

TABLE 1

Analytical Data for the Starting Material and the Phthalocyanines[a]

Compound		*C*	*H*	*N*	*S*
$C_{12}H_{10}N_2S_2O$	(3)	54.96	3.82	10.69	24.43
		(54.90)	(3.80)	(10.65)	(24.40)
$C_{48}H_{42}N_8S_8O_4$	(4)	54.86	4.00	10.67	24.38
		(54.91)	(3.96)	(10.54)	(24.23)
$C_{48}H_{40}N_8S_8O_4Co$	(5)	52.05	3.61	10.12	23.13
		(51.98)	(3.55)	(10.06)	(23.08)
$C_{48}H_{40}N_8S_8O_4Ni$	(6)	52.04	3.61	10.12	23.13
		(52.15)	(3.53)	(10.07)	(23.04)
$C_{48}H_{40}N_8S_8O_4Zn$	(7)	51.73	3.59	10.06	22.99
		(51.64)	(3.53)	(9.97)	(22.86)

[a] Found.

In the ^1H-NMR spectrum in DMS0 (d_6) of **3**, the aromatic protons appear as a singlet at 8.16 ppm and the aliphatic protons as two triplets between 3.85–3.60 (–CH_2–O–CH_2–) and 3.55–3.35 ppm (Ar–S–CH_2-) as expected.

The ^{13}C-NMR spectrum of **3** shows four different signals for the unsaturated C-atoms, one arising from CN (115.48 ppm). Aliphatic C-atoms also give signals at 67.10 (C–O–C) and 32.15 ppm (S–C).

The thio-oxa phthalocyanine complexes **4**–**7** are insoluble in organic solvents such a chloroform, dichloromethane, acetone and ethyl acetate but slightly soluble in DMSO and DMF. The UV-VIS absorption spectra of the metal-free and metal phthalocyanine complexes exhibited characteristic Q and B bands [26]. The results obtained are given in Table 2; the absorption patterns of these complexes were very similar.

The thermal stabilities of the synthesised phthalocyanines were evaluated by TGA and DTA with a heating rate of 10°C min^{-1} in a nitrogen flow. Initial and main decompositions of **3**–**7** occur at approximately 250–426°C (Table 3). These thermal data indicate that the phthalocyanine complexes formed more thermally stable molecules than crown-ether substituted phthalocyanine [27].

TABLE 2

Electronic Spectral Data for the Phthalocyanine Complexes in DMF.

Compound	λ_{max} (nm) (ε/dm^3 mol^{-1} cm^{-1})
4	712(91), 671(69), 642(55)[a], 472(45)[a], 280(1333)
5	698(342), 635(160)[a], 468(140)[a], 280(2204)
6	705(1506), 638(750)[a], 422(680)[a], 330(2330), 291(2951)
7	714(23), 642(13)[a], 471(16)[a], 284(424)

[a] Shoulder.

TABLE 3
Thermal Properties of Starting Materials and the Phthalocyanines

Compound	*Initial decomposition temp. (°C)*	*Main decomposition temp. (°C)*
3	295	372
4	252	426
5	250	384
6	270	384
7	325	423

EXPERIMENTAL

4,5-Dichloro-1,2-dicyanobenzene **2** was prepared using reported procedures [25]. 2-Mercapto ethylether was purchased from Aldrich Chemical Co. Routine IR spectra were recorded on a Perkin–Elmer 1430 spectrophotometer (KBr). UV-VIS spectra were recorded on a Varian DMS 100 Spectrometer. ^{1}H-NMR and ^{13}C-NMR studies were made on a Bruker AC-200 FT-NMR spectrometer. Thermogravimetric analyses were obtained on a RIGAKU TG 8110 simultaneous thermal analyser combined with a TAS 100 at 10°C min^{-1} in a nitrogen flow. Elemental analysis was performed by the Instrumental Analysis Laboratory of TUBITAK Gebze Research Center.

3,5,6-Trihydro-2H-1,7-benzodithia-4-oxacyclodecine-9,10-dicarbonitrile (3)

Dry DMSO (300 ml) containing anhydrous Na_2CO_3 (20 g, 188 mmol) was heated and stirred at 30°C under N_2 for 1 h. A solution of **2** (7.92 g, 40 mmol) and **1** (5.52 g, 40 mmol) in dry DMSO (300 ml) was then gradually added over 5 h and the reaction continued for over 3 days. After evaporation the residue was washed with water and dried. It was extracted with DMF (150 ml) at 100°C and evaporated to dryness. The precipitate was refluxed with acetone for 3 h to remove unreacted organic materials. After filtering the precipitate was washed with hot acetone and dried. Yield: 8.38 g (80%). This compound was soluble in hot DMSO. IR (KBr) ν cm^{-1}: 2920-2860 (CH_2), 2220 ($C{\equiv}N$), 1565, 1530, 1460, 1420, 1410, 1360, 1350, 1275, 1230, 1200, 1110, 920, 880, 740, 710, 700, 530. ^{1}H-NMR (DMSO-d_6) δ ppm: 8.16 (s, 2H, aromatic), 3.85–3.60 (t, 4H, CH_2–O–CH_2), 3.55–3.35 (t, 4H, Ar-SCH_2) ^{13}C-NMR (DMSO-d_6) δ ppm: 143.21, 133.30, 115.48, 112.10, 67.10, 32.15.

Metal-free phthalocyanine (4)

Compound **3** (1.31 g, 5.0 mmol) was refluxed for 12 h under stirring and N_2 in diethylaminoethanol (50 ml). After cooling to room temperature, the dark green mixture was diluted with EtOH (25 ml) and filtered. The dark green precipitate was heated at 40°C with DMF (3×20 ml), filtered and the dark green product washed with hot EtOH and Et_2O and dried in vacuo. Yield: 0.98 g (75%). This compound was slightly soluble in DMSO and DMF. IR (KBr) ν cm^{-1}: 3250 (NH), 2930–2860 (CH_2), 1610, 1510, 1420, 1400, 1380, 1350, 1290, 1200, 1190, 1130, 1090, 1010, 940, 760, 740, 680.

Phthalocyaninatocobalt (II) (5)

A mixture of **3** (0.55 g, 2.1 mmol), anhyd. $CoCl_2$ (0.13 g, 1.01 mmol) and dry ethylene glycol (80 ml) was heated and stirred at 200°C for 6 h under N_2. After cooling to room temperature, the dark green mixture was diluted with EtOH (15 ml) and the crude product precipitated. This was filtered and then heated at 40°C with DMF (3×20 ml) and filtered. The dark green product was washed with hot EtOH and Et_2O and dried in vacuo. Yield: 0.11 g (20%). This compound was slightly soluble in DMSO and DMF. IR (KBr) ν cm^{-1}: 2930–2855 (CH_2), 1620, 1580, 1550, 1420, 1380, 1330, 1290, 1205, 1150, 1100, 940, 780, 750, 705.

Phthalocyaninatonickel (II) (6)

A mixture of **3** (0.55 g, 2.1 mmol) anhyd. $NiCl_2$ (0.14 g, 1.08 mmol) and quinoline (3 ml) was heated and stirred at 190°C for 6 h under N_2. After cooling to room temperature, the dark green mixture was diluted with EtOH (10 ml) and the crude product precipitated. The precipitate was then heated at 40°C with DMF (3×20 ml) and filtered off. The dark green product was washed with hot EtOH and Et_2O and dried in vacuo. Yield: 0.23 g (40%). This compound was slightly soluble in DMSO and DMF. IR (KBr) ν cm^{-1}: 2935–2865 (CH_2), 1610, 1560, 1450, 1350, 1250, 1205, 1135, 1100, 1080, 970, 860, 800, 760, 700.

Phthalocyaninatozinc (II) (7)

A mixture of **3** (0.55 g, 2.1 mmol) anhyd. zinc (II) acetate (0.18 g, 1.01 mmol) and dry quinoline (3.3 ml) was heated and stirred at 185–190°C for 16 h under N_2. After cooling to room temperature, the greenish yellow mixture was diluted with EtOH (15 ml) and filtered off. The greenish precipitate was heated at 80°C with DMF (3×20 ml) and filtered. The greenish product was washed with hot EtOH and Et_2O and dried in vacuo. Yield: 0.32 g (55%). This compound was slightly soluble in DMSO and DMF. IR (KBr) ν cm^{-1}: 2930–2860 (CH_2), 1620, 1415, 1370, 1330, 1290, 1150, 1100, 1080, 930, 750, 730.

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REFERENCES

1. Moser, F. H. and Thomas, L., *Phthalocyanine Compounds*. Reinhold Publishing Corporation, New York, 1963.
2. Smith, H. M., Phthalocyanines. In *The Pigment Handbook*, 2nd edn, Vol. 1, ed. P. A., Lewis, John Wiley, New York, 1988, p. 663.
3. Moser, F. H. and Thomas, A. L., *The Phthalocyanines*. Vols. 1 and 2, CRC Press, Boca Raton, Florida, 1983.
4. Leznoff, C. C. and Lever, A. B. P., *Phthalocyanines: Properties and Applications*. VCH, Weinheim, 1989.
5. Koçak, M., Okur, A. I. and Bekaroğlu. Ö., *J. Chem. Soc. Dalton Trans.*, 1994, 323.
6. Hanck, M., Gül A., Hirsch, A., Mandal, B. K., Subramanian, L. R. and Witke E., *Mol. Cryst., Liquid Cryst.*, 1990, **187**.
7. Weber, J. H. and Busch. D. H., *Inorg. Chem.*, 1965, 469.
8. Kobayashi, N., Shirai, H. and Hojo, N., *J. Chem. Soc., Dalton Trans.*, 1984, 2107.
9. Derkacheua, V. M., Bundina. N. I., Meekhryakova, N. G., Kaliya, O. L., Gulinat, T. Y. and Lukyanets, E. A., *Russian J. Inorg. Chem.*, English Edn., 1981, **26**, 911.
10. Ahsen, V., Gürek, A., Musluoğlu, E. and Bekaroğlu, Ö., *Chem. Berichte*, 1989, **122**, 1073.
11. Mushoğlu, E., Ahsen, V., Gül, A. and Bekaroğlu, Ö., *Chem. Berichte*, 1991, **124**, 2531.
12. Ağar, E., Şaşmaz, S., Bati, B. and Özdemir, M., *Synthetic Reactions in Inorg. and Metal-Organic Chem.*, 1995, **25** (7), 1165.
13. Koçak, M., Cihan, A., Okur, A. I. and Bekaroğlu, Ö., *J. Chem. Soc., Chem. Comm.*, 1991, 571.
14. Ağar, E., Bati, B., Erdem, E. and Özdemir, M., *J. Chem. Res.*, 1995, S, 16.
15. Ağar, E., Şaşmaz, S. Gümrükçüoğlu, I. E. and Özdemir, M., *Synthetic Reactions in Inorg. and Metal-Organic Chem.*, 1996, **26** (7), 1243.
16. Ağar, E., Şaşmaz, S, Gümrükçüoğlu, I. E. and Özdemir, M., *Dyes and Pigments*, 1998, **36**, 407.
17. Ağar, E., Şaşmaz, S., Keskin, I. and Akdemir, N., *Dyes and Pigments*, 1998, **36**, 249.
18. Murray, S. G. and Hartley, F. R., *Chem. Rev.*, 1981, **81**, 365.
19. Snow, A. W. and Griffith, J. R., *Macromolecules*, 1984, **17**, 1614.
20. Wöhrle D., Schnurpfeil, G. and Knothe, G., *Dyes and Pigments*, 1992, **18**, 91.
21. Ağar, E., Şaşmaz. S., Akdemir, N. and Keskin, I., *J. Chem. Soc., Dalton Trans.*, 1997, 2087.
22. Ağar, E., Şaşmaz, S., Keskin, I. and Karabulut, B., *Dyes and Pigments*, 1998, **36**, 249.

23. Gürek, A. G. and Bekaroğlu, Ö, J. Chem. Soc., Dalton Trans., 1994, 1419.
24. Gürek, A. G. and Bekaroğlu, Ö., *Helvetica Chim. Acta*, 1994, **77**, 1616.
25. Wöhrle, D., Eskes, M., Shigehara, K. and Yamada, A., *Synthesis*, 1993, 194.
26. Stillmann, M. J. and Nyokong, T., In *Phthalocyanines-Properties and Application.* ed. C. C., Leznoff and A. B. P., Lever. VCH, New York, 1989, p. 133.
27. Lawtor, E. A., *J. Phys. Chem.*, 1958, **62**, 384.