Pergamon

PII: S0277-5387(96)00593-1

Polyhedron Vol. 16, No. 14, pp. 2335–2339, 1997

0277-5387/97 $17.00+0.00

The synthesis and characterization of novel copper(II) phthalocyanines substituted with four 17-membered macrocyclic ionophores

Yasar Gok* and S. Zeki Yıldız

Department of Chemistry, Karadeniz Technical University, 61080 Trabzon, Turkey

(Received 10 April 1996; accepted 4 December 1996)

Abstract—Copper(II) phthalocyanine containing four 17-membered dioxa-triaza macrocycles has been synthesized starting from copper(II) phthalocyanine substituted 1,2-bis(ethoxycarbonylmetoxy) and 3,3′-diaminodipropylamine. This copper(II) phthalocyanine was used in the extraction of alkali metals and alkaline earth metal picrates from aqueous media. The structures of the compounds are proposed according to elemental analysis, ^{1}H, ^{13}C NMR, IR, UV-VIS and MS spectral data. © 1997 Elsevier Science Ltd

Keywords: phthalocyanines; macrocyclic ionophore; copper(II) complex; N,O-mixed donor; extraction; alkali metals; alkaline earth.

Although the first synthesis of a phythalocyanine was reported in 1907 when Braun and Tcherniac heated *o*-cyanobenzamide at a high temperature [1], the first systematic description for phthalocyanines was introduced by Linstead's group [2]. The growing use of phthalocyanines as commercial dyes [3], catalysts, optical and electrical materials [4], during the last decade has encouraged research on the synthesis of new derivatized materials which differ from one another in the central metal ion or in the peripheral substituents [5]. In spite of this extensive interest, synthetic routes to phthalocyanine derivatives are relatively few, covering mainly phthalonitrile derivatives and aromatic 1,2-dibromo compounds [3,4]. On the other hand, the role of various inbuilt and appended functional groups in the macrocycle on the selective recognition characteristics towards metal cations has led to the design of macrocycles suitable as specific ionophores [6]. The ionophores containing ether and amide moieties exhibit selectivities toward alkaline earth metal cations [7].

Ionophores are small lipophilic molecules that are dissolved in lipid bilayers and carry ions as hydrophobic complexes through the bilayer barrier [8]. The role of various inbuilt and appended functional groups in macrocycles on their selective recognition characteristics towards main groups of transition metal cations has led to the design of macrocycles carrying suitable ionophores [9]. Peripheral substitution of phthalocyanines with ethoxycarbonylmethoxy chains or macrocyclic ionophore moieties dramatically enhances their solubility [10] in organic solvent as chloroform and dichloromethane. Although the "hard" ether-oxygen containing macrocycles show binding preference towards "hard" alkali and alkaline earth metal cations, the incorporation of "soft" sulfide or amine linkages for ether linkages shifts their preference towards "soft" heavy metal cations [11] such as, lead, silver, thallium, etc.

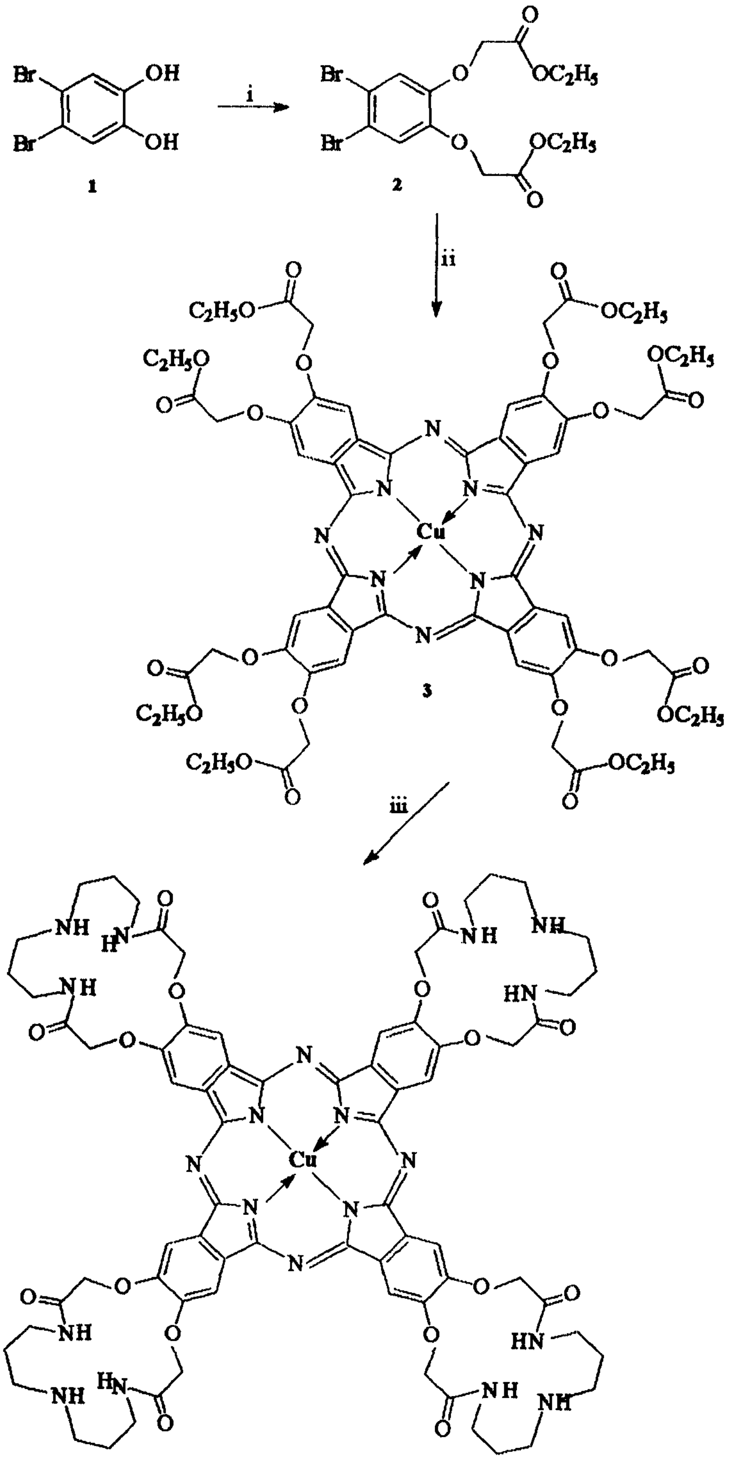
We have previously synthesized nitrogen–oxygen mixed donor macrocycles substituted phthalocyanine which are soluble in common organic solvents. In the present paper, we describe novel phthalocyanines carrying symmetrical ethoxycarbonylmethoxy chains or 17-membered macrocyclic ionophore units.

RESULTS AND DISCUSSION

The first step in the synthetic procedure outlined in Scheme 1 is the formation of the 1,2-bis (ethoxycarbonylmethoxy)-4,5-dibromobenzene **2**. Compound **2** was prepared from 4,5-dibromocatechol [12] and ethyl bromoacetate in dry acetonitrile containing anhydrous K_2CO_3 as the base and tri-

---

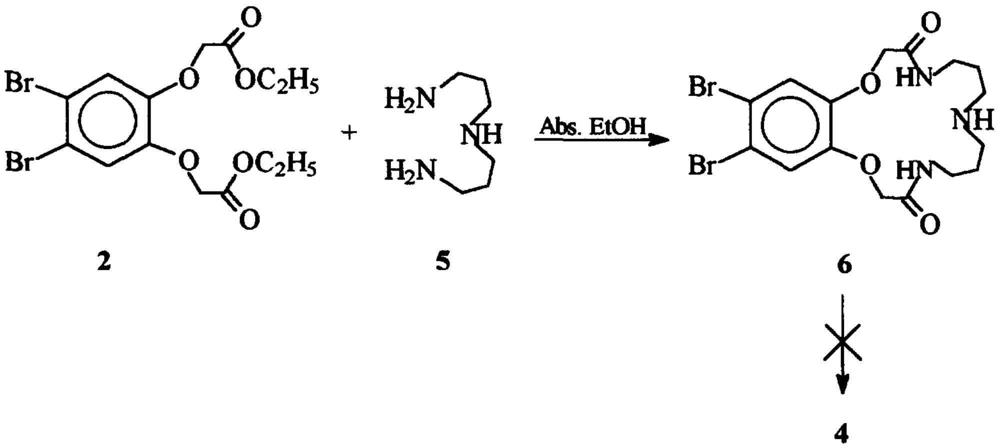
* Author to whom correspondence should be addressed.



i- $BrCH_2COOC_2H_5$ (90 C,dryCH_3CN,K_2CO_3) ii- CuCN (DMF,175 C,24h.) iii- $H_2N(CH_2)_3NH(CH_2)_3NH_2$ (DMSO,90 C)

Scheme 1.

ethylbenzylammonium chloride as the solid–liquid phase-transfer catalyst [6]. Our first goal was to prepare a 17-membered macrocyclic ionophore with 1,2-dibromo substitution on the benzene moiety by a product similar to those reported earlier for the condensation of 1,2-bis(ethoxycarbonylmethoxy)benzene with 3,3′-diaminodipropylamine. The dibromo derivative would then be converted into a copper



Scheme 2.

phthalocyanine. However, all efforts to accomplish this reaction failed in the last step (Scheme 2). No phthalocyanatocopper was detected in a number of trials to convert the dibromo compound carrying the 17-membered macrocyclic ionophore directly in high-boiling solvents such as quinoline, DMF or in pyridine at reflux temperature in a sealed tube. Treatment of **2** with CuCN gave **3** in 24.2% yield after purification. Conversion of **3** into a derivative of ionophore **4** was accomplished by the macrocyclization with 3,3′-diaminodipropylamine in DMSO media by using the high dilution technique.

Characterization of the novel compounds involved a combination of methods including elemental analysis, mass spectrometry, ^{1}H and ^{13}C NMR, UV-VIS and IR spectroscopy. The mass spectrum of **2**, showing a molecular ion at $m/z = 440$, confirmed the proposed structure. The elemental analyses of **2** corresponds to $C_{14}H_{16}O_6Br_2$. Comparison of IR spectral data clearly indicates the conversion of phenolic groups into carbonylethoxy derivatives by the disappearance of OH bands and appearance of the C═O and CH_2 bands at 1750 and 2940 cm^{-1} in **2**, respectively. The ^{1}H NMR spectrum of **2** in $(CD_3)_2SO$ exhibited signals for C—H (aromatic) ($\delta = 7.30$ ppm), OCH_2 ($\delta = 4.86$) and ethyl protons ($\delta = 4.17$ and 1.19 ppm). More detailed information about the structure of **2** was provided by ^{13}C NMR spectroscopy. The amide carbon resonance was found at $\delta = 168.16$ ppm, the aromatic carbon with substituted —OCH_2— groups, resonances at $\delta = 147.30$ ppm, and the protonated aromatic carbons was observed at $\delta = 114.78$ ppm. The carbon resonances which belong to the Br substituted aromatic, —OCH_2— and aliphatic ethyl carbons were observed at $\delta = 118.75, 65.59, 60.69$ and 13.91 ppm, respectively, as expected.

Copper(II) phthalocyanine formation was accomplished directly by the reaction of the dibromo derivative **2** with copper(I) cyanide in DMF and pyridine. Although the synthesis of this compound is rather simple, its isolation is laborious. The overall yield of pure **3** was *ca* 24% and it was soluble in chloroform, dichloromethane, 1,1,2,2-tetrachloroethane and DMF. The reaction sequence in this study is clearly followed by combination of IR and mass spectral data. The fast atom bombardment mass spectrum of this compound shows a molecular ion peak at $m/z = 1392$ $[M+1]^+$. The IR spectral data clearly indicated the formation of compound **3** by the disappearance of C—Br stretching vibration at 650 cm^{-1} in **2**. The other stretching and bending vibrations **3** are very similar to those of **2**. The electronic spectrum of **3** exhibited a partly split Q band absorption in $CHCl_3$ at *ca* 707 and 678 nm due to the $\pi \Rightarrow \pi^*$ transition of this completely conjugated 18π electron system [13]. Thus, the spectrum in $CHCl_3$ is typical of monomeric (Q band at *ca* 678 nm) species [14] in solution and in polar protic solvents such as methanol dimeric or oligomeric (Q band at 627 nm) species prevail.

Copper(II) phthalocyanine containing four 17-membered macrocyclic ionophores **4** was prepared on refluxing **3** with the amine compound in DMSO. The mass spectrum (FAB) of this compound supports the formation of the macrocyclized copper(II) phthalocyanine (**4**), the peak at $m/z = 1548$ corresponding to $[M+1]^+$. Also, the elemental analysis of **4** is in agreement with the calculated value for proposed structure. The IR spectrum of **4** clearly indicates the conversion of ethoxycarbonyl substituted copper(II) phthalocyanine **3** into the macrocyclized derivative as seen by formation of the N—H stretching vibrations at 3340 cm^{-1}. The IR spectrum of this compound shows amide carbonyl absorption in the range 1600–1675 cm^{-1} and does not show any hydrogen bonding between N—H and C═O groups [6]. The electronic spectrum of **4** was recorded in chloroform. This spectrum was the same as that of **3**; however, there was a split band on the lower energy side of the Q band ($\lambda = 682$ nm) and an intense absorption at 629 nm, which are typical of the monomeric species and aggregated phthalocyanine, respectively [15]. Thus, this

Table 1. % Extraction of alkali or earth alkaline metal picrates from aqueous solution in $CHCl_3$[a]

Compound	Na^+	K^+	MG^{2+}	Ca^{2+}	Sr^{2+}
4	83.5	75.2	43.7	57.3	37.8

[a] Organic phase: 1.0×10^{-3} M; aqueous phase: 4.0×10^{-3} M metal picrates.

compound shows a spectrum which is characteristic for either monomeric and dimeric or oligomeric copper phthalocyanine [16].

The role of ionophore group in directing the binding selectivity of macrocycles towards alkali and alkaline earth cations [17] has emphasized the importance of ionophore studies on amide-ether carrying macrocycles. In the present study, we have examined the ability of chloroform solutions of the macrocyclic ionophore carrying phthalocyanatocopper(II) compound to extract alkali and alkaline earth metal picrates from aqueous solution, using the procedure described by Pedersen [18]. The macrocycle **4** extracts metal picrates with significantly higher efficiency, but with selectivity towards Ca^{II} and Sr^{II} (Table 1). This macrocycle, during complexation with metal cations, has to make some compensation for removal of its hydrogen bonding. Picrate salts are preferred in these experiments because the ion pair structure can be identified by analysing their optical spectra.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer as KBr pellets. Elemental analysis of the compounds were determined by a Hewlett-Packard 185 CHN analyzer. Fast atom bombardment mass spectra were measured on a VG AutoSpec from VG Analytical instrument. UV-VIS absorption spectra of the phthalocyanines were measured on a GBC 911 spectrophotometer. 4,5-Dibromocatechol [12] was prepared according to the reported procedure.

1,2-*Bis*(*ethoxycarbonylmetoxy*)-4,5-*dibromobenzene*, (**2**)

A solution of 4,5-dibromocatechol (5.9 g, 25 mmol) and ethylbromoacetate (8.35 g, 50 mmol) in dry acetonitrile (30 cm^3) containing anhydrous K_2CO_3 (6.95 g, 50 mmol) and triethylbenzylammonium chloride (100 mg) was refluxed in an oil-bath at 90°C for 5 h. After completion of the reaction which was monitored by TLC [acetone : petroleum ether (1 : 1)], the reaction mixture was cooled to room temperature and filtered and then was washed with ethyl acetate. The combined solution was removed under reduced pressure and the residue was recrystallized from acetone, giving **1** as a colourless solid and dried *in vacuo*; yield 7.9 g (72%), m.p. 89°C. ^{1}H NMR (DMSO-d_6) : δ 7.30 (s, 2H), 4.86 (s, 4H), 4.17 (q, 4H), 1.19 (t, 6H). ^{13}C NMR (DMSO-d_6) : δ 168.16 (C=O), 147.30 (C—O), 118.75 (C—Br), 114.78 (arom. CH), 65.59 (CH_2O), 60.69 (CH_2), 13.91 (CH_3). IR (KBr pellets) : 3060, 2985, 2940, 1750, 1583, 1550, 1458, 1430, 1345, 1224, 1195, 1158, 1040, 875, 843, 781, 660 cm^{-1}. Mass spectrum (FAB positive) : $m/z = 440$ $[M]^+$. Found : C, 38.0; H, 3.4. Calc. for $C_{14}H_{16}Br_2O_6$: C, 38.2; H, 3.6%.

[2,3,9,10,16,17,23,24-*Octakis*(*ethoxycarbonylmethoxy*) *phthalocyaninato*]*copper*(*II*), (**3**)

1,2-Bis)ethoxycarbonylmethoxy)-4,5-dibromobenzene (**1**) (4.4 g, 10 mmol) was dissolved in 12 cm^3 of DMF and was mixed with CuCN (2.36 g, 26 mmol) and pyridine (3 cm^3) in a Schlenk tube under argon atmosphere at room temperature. When the reaction mixture was heated to 175°C for 2 h and was continued for another 12 h and stirred, the colour of the mixture became dark green. After cooling, concentrated NH_3 (50 cm^3) and ethanol (300 cm^3) were added to this solution and air was passed through for 24 h. The precipitated crude product was filtered off and refluxed with acetone to remove the unchanged organic material. The precipitate was also refluxed with a solution of NaCN in water–ethanol (1 : 2) for 3 h (twice) to remove the excess of CuCN and then was refluxed with ethanol. After cooling to room temperature, the dark green product was filtered off, washed with ethanol and diethyl ether and was completely dried over P_4O_{10} at 60°C in a vacuum oven, yield of a dark green solid 0.84 g (24.2%), m.p. 327°C. IR (KBr pellets) : 3028, 2945, 1743, 1600, 1505, 1422, 1365, 1345, 1270, 1210, 1150, 1121, 1060, 1010, 870 cm^{-1} UV–vis ($CHCl_3$) λ_{max} (log ε) 707 (4.89), 678 (5.09), 605 (4.74), 385 (4.11), 346 (4.51), 278 (4.73), 255 (4.19). Mass spectrum (FAB positive): $m/z = 1392$ $[M+1]^+$. Found : C, 55.0; H, 4.4; N, 7.8. Calc. for $C_{64}H_{64}N_8O_{24}Cu$: C, 55.2; H, 4.6; N, 8.0%.

Tetrakis[*macrocycle-phthalocyaninato*]*copper*(*II*), (**4**)

Compound **3** (0.6695 g, 0.5 mmol) and DMSO (20 cm^3) were mixed in a glass tube which was sealed with argon. When the reaction mixture was heated to 90°C, 3,3′-diaminodipropylamine (0.39 g, 3 mmol) was added for 10 h and the reaction was continued at the same temperature for 48 h. After cooling to room temperature, the dark green product was evaporated under vacuum to yield an oily crude product. Then the product was washed with ethanol and diethyl ether and was purified by column chromatography (silica gel : EtOH-CH_2Cl_2), to yield 0.165 g (21.5%) of dark green solid, m.p. 296°C. IR (KBr pellets) : 3340, 3035, 2953, 1690–1675, 1596, 1514, 1415, 1376, 1349, 1287, 1163, 1120, 1047, 1002, 881 cm^{-1}. UV–vis ($CHCl_3$) λ_{max} (log ε) 682 (5.23), 611 (5.08), 432 (4.38), 379

(4.65), 342 (4.72), 284 (4.89), 251 (4.31). Mass spectrum (FAB positive): $m/z = 1548\ [M+1]^+$. Found: C, 55.6; H, 5.3; N, 17.9. Calc. for $C_{72}H_{84}N_{20}O_{16}Cu$: C, 55.8; H, 5.4; N, 18.1%.

Extraction measurements

In this work, the chloroform solution (25 cm^3) carrying **4** (1.0×10^{-3} M) was shaken with aqueous solution (25 cm^3) containing alkali or earth alkaline metal picrates (4.0×10^{-3} M) for 3 h at 25°C in a constant temperature circulator. The concentration of picrates were determined spectrometrically at λ_{max} 352–356 nm.

Acknowledgement—This study was supported by The Research Fund of Karadeniz Technical University (Trabzon-Turkey).

REFERENCES

1. Braun, A. and Tcherniac, J., *Ann. Ber.* 1907, **40,** 2709.
2. Byrne, G. T., Linstead, R. P. and Lowe, A. R., *J. Chem. Soc.* 1934, 1017.
3. Moser, F. H. and Thomas, A. L., *The Phthalocyanines.* CRC Press, Boca Raton (1983).
4. Leznoff, C. C. and Lever, A. B. P. (eds.), *Phthalocyanines: Properties and Applications.* VCH Weinheim (1993).
5. Hamuryudan, E. and Bekaroglu, O., *J. Chem. Res.* (S), 1993, 460.
6. Kumar, S., Singh, R. and Singh, H., *J. Chem. Soc., Perkin Trans I.* 1992, 3049.
7. Nakatsuji, Y., Okahara, O. and Kobayashi, H., *Chem. Lett.* 1982, 1571; Gok, Y., *Polyhedron* 1996, **15,** 3955; Duro, J. A. and Torres, T., *Chem. Ber.* 1993, **126,** 269.
8. Burbergemeister, W. and Winkler-Oswatitsch, R., *Topp. Curr. Chem.* 1977, **69,** 91; Yamaguchi, K., Kuboniwa, H., Nagami, S., Bando, T., Hiroa, A., Nakahara, S. and Yamazaki, N., *Bull. Chem. Soc. Jpn.* 1995, **68,** 315.
9. Bajaj, A. V. and Poonia, N. S., *Coord. Chem. Rev.* 1988, **87,** 55.
10. Gok, Y., *New J. Chem.* 1996, **20,** 971.
11. De Jong, F. and Reinhoudt, D. N., *Adv. Phys. Org. Chem.* 1981, **17,** 24.
12. Kohn, M., *J. Am. Chem. Soc.* 1951, **73,** 480.
13. Gumus, G., Gul, A. and Bekaroglu, O., *J. Chem. Res.* (S), 1994, 430.
14. Sielcken, O. E., van Tilborg, M. N., Roks, M. F., Hendriks, R., Dreth, W. and Nolte, R. M. J., *J. Am. Chem. Soc.* 1987, **109,** 4261; Ahsen, V., Yılmazer, E., Erbas, M. and Bekaroglu, O., *J. Chem. Soc., Dalton Trans.* 1988, 401; Kobayashi, N. and Nishiyama, Y., *J. Chem. Soc., Chem. Commun.* 1986, 1462.
15. Kobayashi, N., Opallo, M. and Osa, T., *Heterocyclics* 1990, **30,** 389; Stilmann, M. J. and Nyokong, T., In *Phthalocyanines: Properties and Applications,* (Edited by C. C. Leznoff and A. B. P. Lever) p. 133. VCH, New York (1989).
16. Gok, Y. and Yıldız, S. Z., *J. Coord. Chem.* 1995, **36,** 175.
17. Petranek, J. and Kyba, O., *Tetrahedron Lett.* 1977, 4249.
18. Pedersen, C. J., *Fed. Proc.* 1968, **27,** 1305.