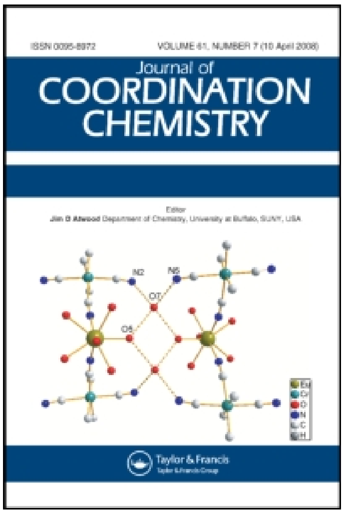

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THE SYNTHESIS AND CHARACTERIZATION OF NEW COPPER(II) PHTHALOCYANINES CONTAINING FOUR 20-MEMBER TETRAAZA-DIOXA MACROCYCLIC MOIETIES

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The synthesis and characterization of a copper(II) phthalocyanate substituted with four 20-membered tetraaza-dioxa macrocycles from 21,22-dibromo-2,8,11,17-tetra(toluene-p-sulphonyl)-1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18-octadecahydrobenzox[*l*] [2,8,11,17]tetraaza[4,13]dioxacyclodi-contine is described. The detosylation of the macrocyclic aza groups provides four tetraaza-dioxa mixed donor sites for binding metal ions. The structures of the compounds were determined by elemental analysis, ^1H, ^{13}C NMR, IR and MS spectral data.

KEYWORDS: phthalocyanine, tetraaza-dioxa macrocycles, copper(II) complexes

INTRODUCTION

Although phthalocyanine was first obtained in 1907 by Braun and Tcherniac,[1] the special natures of the free phthalocyanines and their metal complexes were not realized until 1933.[2] The uses of these compounds as commercial dyes,[3] catalysts, and optical and electrical materials are expanding enormously every year.[4] Phthalocyanines have sufficiently stable cores to permit organizing of binding sites ion a define geometry[5] leading to new products containing additional functionalities. Among these are supra-molecular systems which consist of two identical molecular entities coexisting together without the assistance of covalent bonding.[6] The notable feature of these systems is that they exhibit spectral properties different from those of the individual molecular units.[7]

The chemistry of polyazamacrocycles has been the subject of many recent studies because of interest in the polynuclear metal structures as models of non-heme polymetallic proteins, molecular recognition and "super complex" formation.[8] Dinucleating of macrocycles with two N_3 coordination sites separated by -CH_2CH_2-O-OCH_2CH_2- bridges were investigated.[9] The 16-membered tetraazamacrocyclic moiety provides a strong metal binding site with the special property of conferring ability to bind O_2 on iron(II) and cobalt(II).[10] The large cavity above the metal ion

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is relatively hydrophobic and serves as a site for hydrophobic binding of a substrate molecule in close proximity to the metal ion.[10]

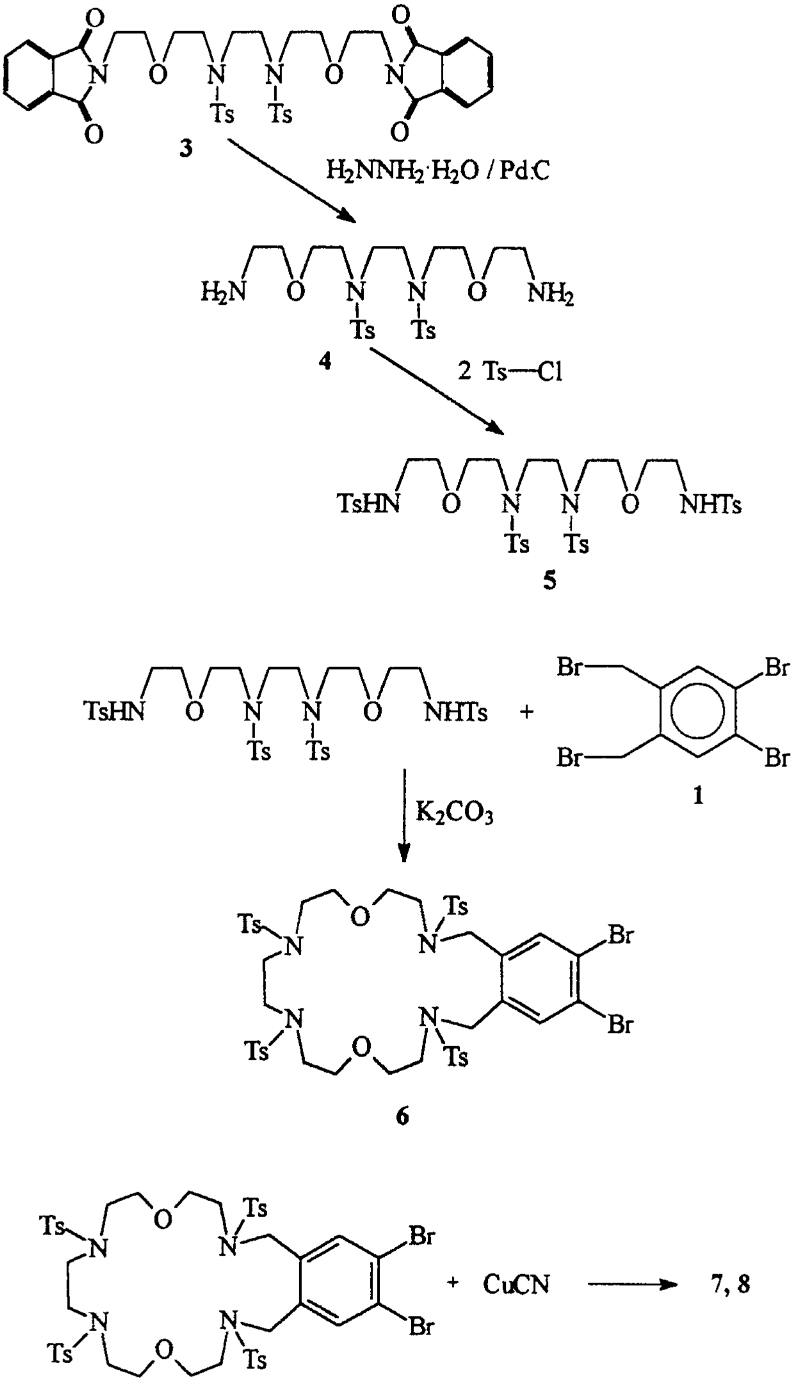
Bekaroglu and co-workers[11] reported the possibility of modifying the complexing ability and selectivity of various donor groups towards metal ions by attaching them as peripheral substituents onto phthalocyanines. It is well known that crown ether substituted phthalocyanines[12] exhibit high affinity toward alkali metal ions, and lead to relatively fixed spatial arrays of macrocycles which form ion channels.[13] Phthalocyanines with 14- or 15-membered tetraaza and diazatrioxa macrocyclic substituents have been synthesized, and their solubilities and complexation abilities toward transition metal ions investigated.[14]

The aim of this study was to synthesize a tetraaza-dioxa mixed macrocycle containing large, cavity substituted phthalocyanine. Thus molecules having various selectivities towards alakali, earth alkali transition metal ions and ammonium cations[15] will be obtained. Toward this goal, 20-membered tetraaza-dioxza mixed macrocycle substituted phthalocyanines have been prepared and their properties investigated by spectral and analytical techniques.

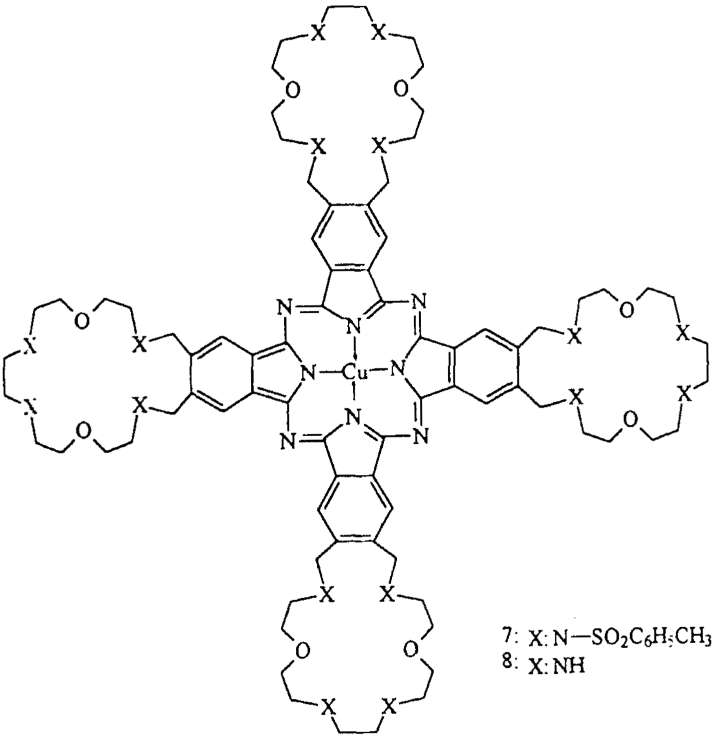
RESULTS AND DISCUSSION

The first step in the synthetic procedure outlined in Scheme 1 is formation of tetraaza-dioxa macrocycle **6**. Starting from 6,9-di(toluene-p-sulfonyl)-1,14-di(toluene-p-sulfonylamino)-3,12-dioxa-6,9-diazatetradecane **5**, which was prepared from 1,14-diamino-6,9-(toluene-p-sulfonyl)-3,12-dioxa-6,9-diazatetradecane **4** by reaction of the di(toluene-p-sulfonyl) derivative of ethylenediamine[16] and an excess of di(2-chloroethyl) ether in dmf in the presence of K_2CO_3 and the condensation of **2** into **4** was carried out *via* the Gabriel[17] and Zip[18] reaction, and 1,2-dibromo-4,5-bis-(bromomethyl)benzene,[19] we have accomplished cyclization in dmf in the presence of K_2CO_3 as the base. The cyclotetramerization of **6** with copper(I)cyanide in tetramethylurea (TMU) gave the proposed copper phthalocyanine containing 16 tosylamino groups. Detosylation of **7** was accomplished in highest yield at 130°C by use of concentrated sulfuric acid for 5 h. Neutralization with sodium hydroxide led to the copper phthalocyanate **8** containing free amino groups (Scheme 2).

In the ^1H NMR spectrum of **6**, the chemical shifts belonging to NH groups at $\delta = 8.75$ ppm disappear after the macrocyclization reaction between **5** and **1**. The singlet at $\delta = 2.39$ ppm and multiplets at $\delta = 7.74$–7.58, 7.43–7.36 correspond to methyl and aromatic protons. It is obvious that the singlet at $\delta = 4.31$ ppm indicates the methylene groups are connected to the phenyl ring.[20] The chemical shifts belonging to methylene protons neighboring nitrogen and oxygen show different values at $\delta = 3.41$–3.35 ppm (CH_2-O) and $\delta = 3.23$–2.97 ppm (CH_2-N) as expected. More detailed information about the formation of **5** is provided by proton-decoupled carbon-13 NMR spectra. The carbon resonances of p-tolyl sulfonyl groups appear at $\delta = 143.65$, 143.41, 135.65, 130.04, 129.93, 129.80, 127.86 and 127.10 ppm. The other carbon resonances appear at $\delta = 143.30$, 132.84 and 126.72 ppm (aromatic), at $\delta = 48.64$ and 47.71 ppm (N-CH_2) and at $\delta = 69.78$, 68.56 and 68.54 (O-CH_2). The carbon resonance which belongs to the methyl groups is observed at $\delta = 20.99$ ppm as expected. The mass spectrum (FAB) of **6** shows the expected molecular ion peak at $m/z = 1111$ $[M+1]^+$. The IR spectrum of this compound exhibits characteristics frequencies at 3047 (Ar-H), 2940–2860 (C-H),



Scheme 1.



7: X: $N-SO_2C_6H_5CH_3$
8: X: NH

Scheme 2.

1337 and 1145 (SO_2) and 632 cm^{-1} (C-Br). The disappearance of N-H stretching vibrations (at 3380 cm^{-1}) belonging to **5** also indicates the formation of **6**.

The cyclotetramerization of **6** in a high-boiling solvent such as tetramethylurea in the presence of copper(I)cyanide gives the desired copper phthalocyanine **7**. Although the synthesis of this compound is rather simple, its isolation and purification are laborious. As expected, this phthalocyanine is soluble in halogenated hydrocarbons such as dichloromethane and chloroform. The fast atomic bombardment mass spectrum of this compound shows a molecular ion peak m/z = 4072 $[M+1]^+$. The IR spectrum of this product gives some hints as to the nature of the copper(II) phthalocyanine. In this context, we may cite the presence of SO_2 vibrations at 1335 and 1149 cm^{-1}, and Ar-H and C-H (aliph.) vibrations at 3040, 2905 cm^{-1}, respectively. This phthalocyanine exhibits a typical electronic spectrum with intense Q and B bands. While the N-tosylated copper(II) phthalocyanine is soluble in $CHCl_3$, its spectrum in this solvent exhibits an intense Q band on the lower energy side (λ = 684 nm) and a shoulder at *ca.* 637 nm indicating aggregation.[14] In addition, this spectrum is very similar to that of crown ether substituted phthalocyanine.[7,13]

Detosylation of **7** in concentrated H_2SO_4 at 130°C for 5 h and subsequent neutralization with 2M NaOH leads to the copper(II) phthalocyanine **8** containing free amino groups which is soluble in chloroform and dichloromethane. The mass spectrum (FAB) of this compound supports the formation of the detosylated copper(II) phthalocyanine, however, the peaks at m/z = 1680 and 1626 indicate $[M+4H_2O+1]^+$ and $[M+H_2O+1]^+$ formation, respectively. Also, the elemental analysis of **8** is in agreement with the calculated values. Comparison of the IR spectral data clearly indicates the conversion of N-tosylated copper(II) phthalocyanine 7 into the detosylated derivative as seen by formation of the N-H stretching vibrations at 3365 cm^{-1}. The electronic spectrum of **8** was recorded in chloroform. This spectrum was the same as that of 7; however, there was a shoulder on the lower energy side of the Q band (λ = 672 nm) and an intense absorption at 643 nm, which are typical of an aggregated phthalocyanine.[14,21]

EXPERIMENTAL

IR and electronic spectra were recorded on a Perkin-Elmer 1600 FT-IR in KBr pellets and a GBC 911 spectrophotometer, respectively. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-300 NMR spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a VG AutoSpec from VG Analytical. The elemental analyses and metal contents of the compounds were determined by a Hewlett-Packard 185 CHN analyzer and a Hitachi 180-80 atomic absorption spectrophotometer, respectively. Ethylenediamine ditoluene-p-sulfonate,[16] 1,14-dichloro-6,9-di(toluene-p-sulfonyl)-3,12-dioxa-6,9-diazatetradecane and 6,9-di(toluene-p-sulfonyl)-1,14-di(toulene-p-sulfonylamino)-3,12-dioxa-6,9-diazatetradecane (5),[17] 1,14-di(phthalimido)-6,9-di(toluene-p-sulfonyl)-3,12-dioxa-6,9-diazatetradecane (3),[18] and 1,2-dibromo-4,5-bis(bromo-methyl)benzene (**1**)[19] were prepared according to reported procedures.

21,22-Dibromo-2,8,11,17-tetra(toluene-p-sulfonyl)-1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18-octadecahydrobenzo[l][1,7,10,16]tetraaza[4,13]dioxacyclodicontine, **6**

Compound **4** (5.5 g, 6.3 mmol) was dissolved in dry ethanol (200 ml) containing finely ground anhydrous K_2CO_3 (2.1 g, 15 mmol) with purging under argon in a Schlenk system and refluxed for 1 h. A solution of **1** (3.4 g, 7.9 mmol) in dry ethanol (80 ml) was added to the refluxing reaction mixture dropwise over a period of 8 h under argon. After the reaction mixture was refluxed for 24 h, the solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2 (140 ml) and filtered. The filtrate was washed with water (3 x 35 mL) and dried with anhydrous $MgSO_4$ and then evaporated to dryness. The oily crude product was isolated as a tannish powder by stirring in n-hexane (200 ml) for 3 days. The powder was collected by filtration, washed with diethyl ether, and dried *in vacuo*. Finally, the product was chromatographed (Silica gel, CH_2Cl_2: MeOH 4:1). Yield: 4.9 g (62 %), m.p. 83-85°C. This compound is soluble in dichloromethane, chloroform, dimethyl formamide and dimethyl sulfoxide. ^1H NMR ($CDCl_3$): δ 7.74-7.58 (m, 10 H, Ar-H), 7.43-7.36 (m, 8H, Ar-H), 4.31 (s, 4H, CH_2-Ar), 3.41-3.35 (m, 8H, O-CH_2), 3.23-2.97 (m, 12H, N-CH_2), 2.39 (s, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ 143.65 (Ts-Ar), 143.41 (Ts-Ar), 143.30 (Ar-CH_2NTs), 135.65 (Ts-Ar), 132.84 (C-Ar), 130.04 (Ts-Ar), 129.93 (Ts-Ar), 129.80 (Ts-Ar), 127.86 (Ts-Ar), 127.10 (Ts-Ar), 126.72 (C-Br), 69.78-68.54 (O-CH_2), 48.64-47.71 (CH_2-N), 20.99 (CH_3). IR (KBr pellets, cm^{-1}): 3047, 2940-2860, 1661, 1585, 1440, 1337, 1145, 1120, 1080, 810 715, 632. *Anal.* Calcd. for $C_{46}H_{54}N_4Br_2O_{10}S_4$(%): C, 49.73; H, 4.86; N, 5.05 Found: C, 49.58; H, 4.61; N, 4.80. Mass spectrum (FAB): m/z 1111 $[M+1]^+$.

[Hexadecakis(N-p-tosyl)-tetrakis-macrocycle-phthalocyaninato]copper(II), 7

Compound **5** (3.6 g, 3.3 mmol), CuCN (0.6 g, 8.5 mmol) and dry tetramethyl urea (2.4 mL) were mixed in a well-stoppered Schlenk tube under an argon atmoshpere. The mixture was heated and stirred at 180–185°C for 8 h under inert conditions. After cooling to room temperature the dark blue product was precipitated with dilute ethanol (10 mL). The precipitate was filtered off and washed with water and hot ethanol to remove unreacted materials. The crude product was then refluxed several times with a solution of NaCN in a mixture of water/ethanol (1:2) to remove the excess CuCN. The oily product thus obtained (after decanting while hot) was precipitated by refluxing with ethanol. The greenish-blue powder was filtered, washed with ethanol and diethyl ether, and then dried *in vacuo.* Yield 1.44 g (43%). This compound is soluble in chloroform, dichloromethane, pyridine, dimethyl formamide and dimethyl sulfoxide. IR (KBr pellets, cm^{-1}): 3040, 2905–2855, 1640, 1590, 1435, 1335, 1149, 1132, 1080, 990, 812, 710. Electronic spectra ($CHCl_3$ logε): 684 (4.69), 637 (4.24), 554 (4.13), 417 (4.26), 346 (5.07), 317 (4.52), 275 (4.76), 243 (5.16). *Anal.* Calcd. for $C_{192}H_{216}N_{24}O_{40}S_{16}Cu$(%): C, 56.58; H, 5.30; N, 8.25; Cu, 1.55. Found: C, 56.38; H, 5.09; N, 8.03; Cu, 1.27. Mass spectrum (FAB): m/z 4072 $[M+1]^+$

[Tetrakis-macrocycle-phthalocyaninato]copper(II), 8

Compound 7 (0.2 g, 0.049 mmol) was suspended in H_2SO_4 (98%, 7.5 mL) in a well-stoppered Schlenk tube. The tube was degassed, filled with argon and heated 130°C for 5 h in an oil bath. After cooling to room temperature, the mixture was poured into cold ethanol (75 mL) and stirred to remove excess H_2SO_4. To the greenish blue precipitate, water was added (20 mL) the mixture stirred and then filtered. The pH of this solution was adjusted to *ca.* 12.00 with an aqueous solution of 2M NaOH which resulted in partial precipitation of the phthalocyanine. The mixture was extracted with chloroform (3×50 mL), and evaporation of the combined extracts after drying over anhydrous $MgSO_4$ gave the dark green copper(II) phthalocyanine. Yield: 0.051 g (65%). This compound is soluble in chloroform, dichloromethane, dimethyl formamide and dimethysulfoxide. IR (KBr pellets, cm^{-1}): 3365, 3032, 2915–2897, 1645, 1596, 1440, 1341, 1152, 1135, 1090, 832, 718. Electronic spectra ($CDCl_3$ logε): 672 (4.81), 643 (4.23), 545 (3.85), 515 (3.90), 473 (4.08), 437 (4.23), 353 (4.87), 302 (7.74), 275 (4.81), 252 (4.47) *Anal.* Calcd. for $C_{80}H_{120}N_{24}O_8Cu$(%): C, 59.72; H, 7.46; N, 20.90; Cu, 3.95. Found: C, 59.54; H, 7.24; N, 20.72; Cu, 3.70. Mass spectrum (FAB): m/z 1680 $[M+4H_2O+1]^+$, 1626 $[M+H_2O+1]^+$.

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