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Novel crown ether-substituted phthalocyanines

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Abstract

A novel macrocycle has been synthesized from 4′-(α-bromoacetyl)benzo-15-crown-5, 4-nitrophthalonitril and diethyl malonate; its cyclotetramerization gives Cu(II), Co(II) and Pd(II) phthalocyanines (Pcs) with four benzo-15-crown-5 substituents on the periphery. The effects of alkali metal cations with these Pcs has been investigated through the changes in the visible spectra. The newly synthesized compounds have also been characterized by elemental analyses, IR, ^{1}H NMR.

Keywords: Phthalocyanines; Cyclotetramerization; Macrocycle; Crown ether

1. Introduction

Peripherally functionalized phthalocyanines (Pcs) have the potential to exhibit novel magnetic and electronic properties and to serve as building blocks in the assembly of supramolecular systems. The planar structure and intense colour of this family of compounds provide features superior to those encountered in related organic materials. Also, the presence of transition metal ions in the inner core offers new ways to induce, modify and control molecular arrangements.

In prior papers, we decribed the synthesis of novel soluble Pcs in which crown-ether moieties with either integral parts of the periphery [1–6] or connected to the Pc core through flexible alkyloxy-bridges [7,8]. In addition, Pcs carrying fused tetraaza- [9–11], tetrathia- [12], tetraoxamonoaza- [13,14], trioxadiaza- [15], diazadioxa- [16] and diazadithia-macrocycles [17] on the periphery were reported. Even a two-fold macrocycle on the Pc core was accomplished by starting with a dicyano compound carrying a (15-crown-5) moiety together with a 14-membered tetraazamacrocycle [18]. All of these compounds were capable of forming multinuclear complexes with various metal ions.

As a new approach to the synthesis of macrocycle-substituted phthalocyanines, we have designed a molecule carrying acetyl benzo (15-crown-5) units. The combination of four benzo (15-crown-5) moieties with a phthalocyanine core is expected to provide binding sites for alkali cations.

2. Result and discussion

In the present study, we have made use of the potential for exchanging the acidic –CH– protons of diethyl malonate first with the nitro-group of 4-nitrophthalonitrile [19] and then in further reaction with crown ether alkylhalides [20–23] to obtain an *o*-dicyano starting compound with a benzocrown ether substituent. For this purpose, 4-nitro phthalonitrile was first treated with malonic

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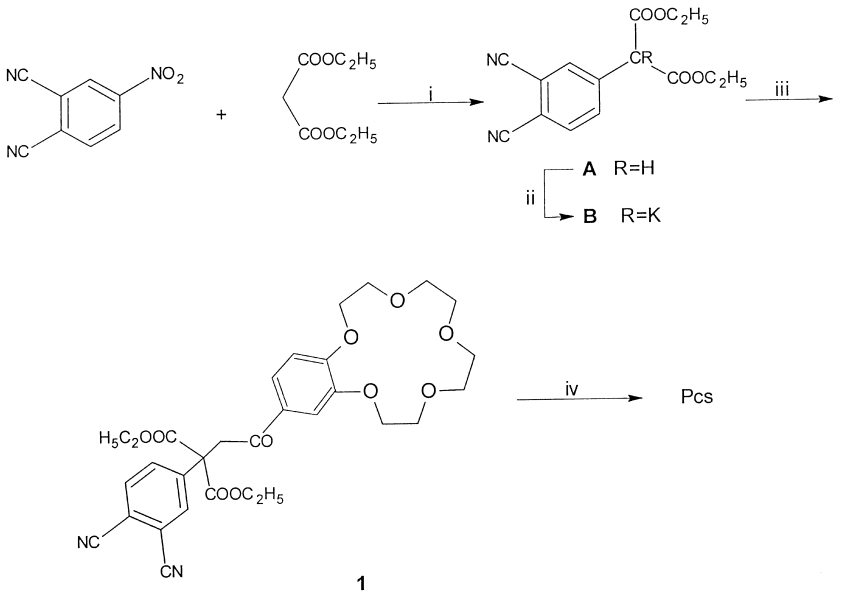

Scheme 1. Synthesis of Pcs **2**–**4**. (i) K_2CO_3, DMF, 50°C; (ii) KOH, ethanol; (iii) acetone/acetonitrile, 4′-bromoacetoxybenzo-15-crown-5, 15 h reflux; (iv) metal salts, 160°C, 6 h.

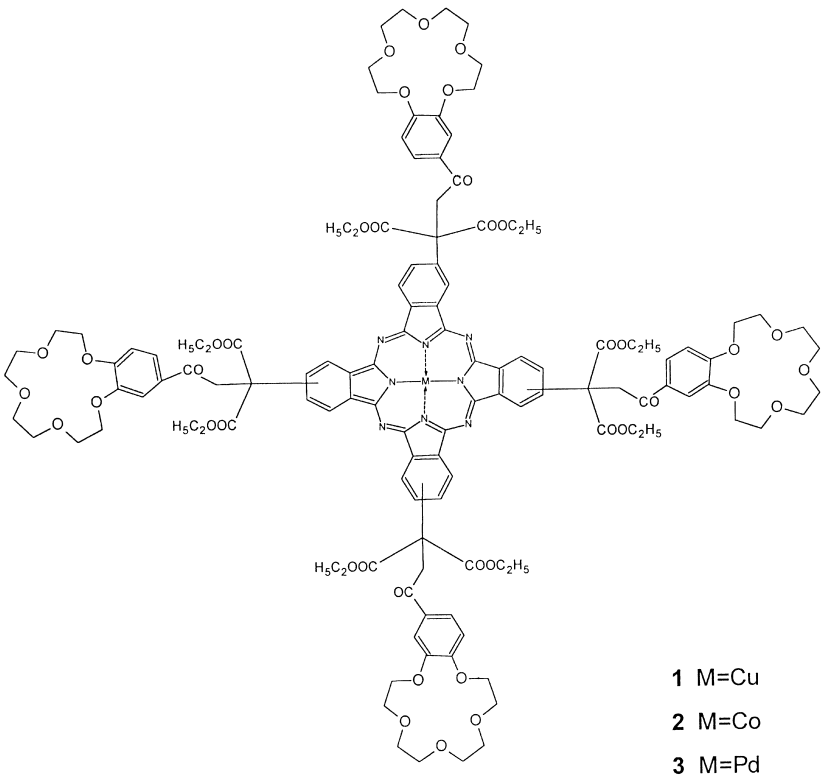

Fig. 1. Metallo-phthalocyanines **2**–**4.**

acid diethyl ester in presence of a base (e.g. K_2CO_3) in anhydrous DMF. Treatment of the product with a strong base and subsequent addition of 4′-(α-bromoacetyl)benzo-15-crown-5 afforded the desired 4-phthalonitrile derivative with crown ether groups **1**. Cyclotetramerization of **1** to the phthalocyanine structure was accomplished by reaction with anhydrous salts in fused state. Cu(II) complex **2**, Co(II) complex **3** and Pd(II) complex **4** were prepared under the same conditions [23,24] (Scheme **1** and Fig. 1).

Spectral data on the newly synthesized intermediates and phthalocyanines are consistent with the proposed structures. For example, in compound **1** we observed C≡N at 2238 cm^{-1}, C=O at 1753 cm^{-1} 1676 cm^{-1}, C–O ester at 1294 cm^{-1}, $C_{aromatic}$–O–C at (1243–1217) cm^{-1}, C–O–C at (1190–1115) cm^{-1}. The IR spectra of **1** and MPc (M=Pd, Cu, Co) were similar and the C≡N at 2230 cm^{-1} had disappeared in each case. In the ^1H NMR spectrum of **1**, the etheral protons of the crown ether group 3.6–4.05 ppm have been assigned on the basis of the results of previous works [4–6,25]. The aromatic protons of benzo 15-crown-5 moiety and phthalonitrile appear at 7–8.5 ppm. In the case of Pd-phthalocyanine, all of the peaks in the ^1H NMR spectrum are some what broader than the corresponding signals in the dicyano derivative **1**. It is likely that broadening is due to chemical exchange caused by agregation–disaggregation equilibria and the fact that the product obtained in these reactions is a mixture of four positional isomers which are expected to show chemical shifts that differ slightly from each other. Even using a high field instrument and multiple scans on dilute solutions ($\sim 5\times10^{-3}$ M) afforded spectra showing broad absorbtions. This would suggest that the presence of an isomeric mixture is the more plausible explanation for peak broadening.

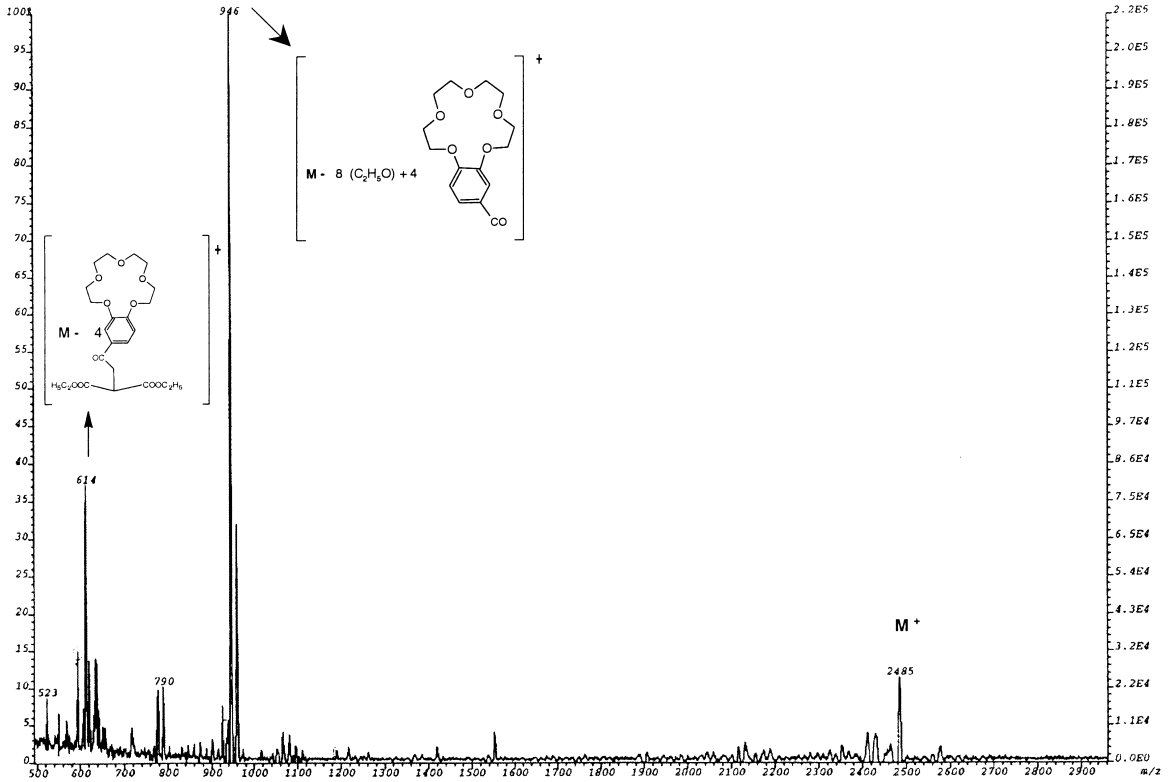

Fig. 2. FAB mass spectrum of **4**.

In the FAB mass spectrum of Pd-Pc (**4**) we observed a molecular ion peak at m/z 2485. (Fig. 2). In addition, the base peak is m/z 946, which corresponds to a decomposition product formed by cleavage of all crown ether and ethoxy groups. An intense peak at m/z 614 is a consequence of the cleavage of all the substituents on the Pc core.

The new metallo phthalocyanines show typical electronic spectra, with a strong absorption regions, at 300–350 nm (B band) and the a second at 650–700 nm (Q band). In exteremely dilute solutions (ca. 10^{-6} mol dm^{-3}), the molecules are present as monomers in chloroform. Increasing the concentrations leads to aggregation, which is easily monitored by shifting of the Q band to shorter wavelength and a decrease in ε max.

Aggregation and dissagregation of Pd-Pc, followed by changes in the visible spectra after the addition of an alkali cation, constitutes an effective route for characterizing the complexation behaviour of the crown etheral substituents [1,4,8,25–28]. For this purpose, the Pd-Pc was dissolved in chloroform (10^{-4} M) and a metal salt (e.g. KNO_3, $NaNO_3$) dissolved in methanol (10^{-2} M) was added. Addition of KNO_3 solution caused slight change in the visible spectrum, diminishing the intensity of the band at around 661 nm. Further addition of KNO_3 salt caused no observable effect. Dimerization of the Pc units in the presence of alkali metal ions, especially with those which have a tendency to form sandwich type complexes such as K^{+1}, forms a clear indication of intermolecular complexation of crown ether units (Fig. 3). On the other hand when we added a solution of $NaNO_3$, a slight increase in the intensity of the band at 661 nm occurred. This observation can be attributed to dissagregation of Pd-Pc by trapped sodium ions in the crown ether units, the radius cavity of which is compatible with this ion [20] (Fig 4).

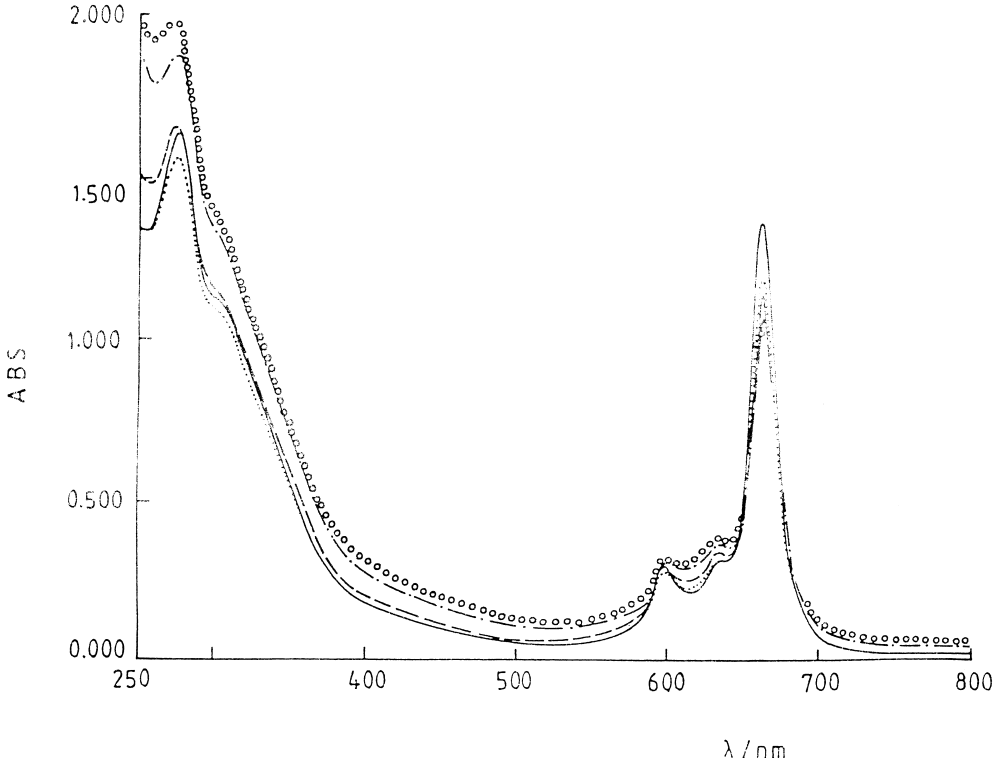

Fig. 3. Changes in the UV–visible spectra of **4** in chloroform (10^{-4} M) after the addition of KNO_3 in methanol (10^{-2} M) in the indicated amounts (— 0 ml, ····· 0.01 ml, - - - 0.03 ml, -·-·-·- 0.06 ml, ○○○○○○ 0.10 ml).

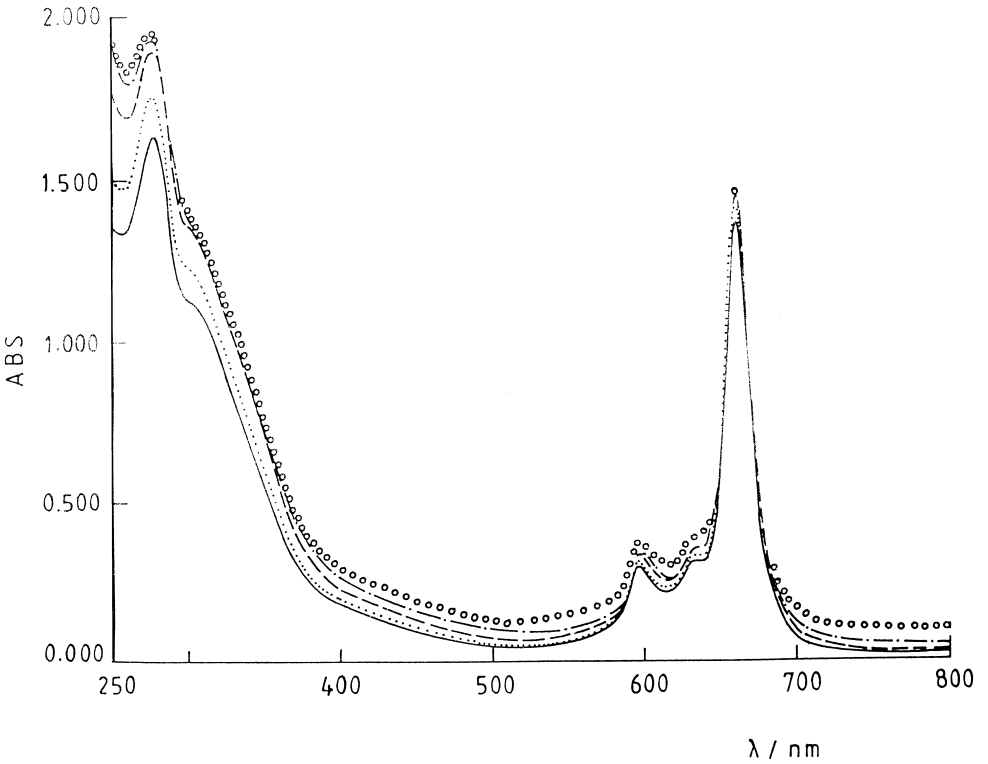

Fig. 4. Changes in the UV–visible spectra of the solution of **4** in chloroform (10^{-4} M) after the addition of $NaNO_3$ in methanol (2×10^{-2} M) in the indicated amounts (— 0 ml, ····· 0.01 ml, - - - 0.03 ml, -·-·-·- 0.06 ml, ○○○○○ 0.10 ml).

3. Experimental

Routine IR spectra were recorded on a Mattson 1000 FTIR spectrometer in KBr pellets, electronic spectra on a Unicam UV2 UV/VIS spectrophotometer. Proton NMR spectra were recorded on a Bruker 200 MHz spectrometer using $SiMe_4$ as the reference. 4-nitrophthalonitrile [19], benzo 15-crown-5 [20], 4′-acetylybenzo-15-crown-5 [21], 4′-bromoacetoxybenzo-15-crown-5 [22], diethyl-3,4-dicyanophenylmalonate [23], potassium salt of diethyl-3,4-dicyanophenylmalonate [23] were synthesized according to published procedures.

All other reagents and solvents were of reagent-grade quality and were obtained from commercial suppliers. All solvents were dried and purified as desribed by Perrin and Armarego [29]. The solvents were stored over molecular sieves (4 Å). The homogeneity of the products was tested by TLC (SiO_2 or Al_2O_3).

3.1. Diethyl (3,4-dicyanophenyl)acetoxybenzo (15-crown-5) malonate (**1**)

To the potassium salt of diethyl 3,4-dicyanophenylmalonate 1.052 g, (3.25 mmol) in 2:1 acetone:acetonitrile (150 cm^3) , was added 4′-bromoacetoxybenzo-15-crown-5 (1.195 g, 3.77 mmol) in acetone (100 cm^3). The mixture was boiled for 20 h and filtered. The solvent was evaporated under reduced pressure to give a creamy solid that was washed with water until the product was free of KBr. After drying in vacuo at 50°C, the crude product was recrystallized from 1-propanol. The compound was soluble in chloroform, dichloromethane, acetone and tetrahydrofuran. Yield: 1.22 g (71.34%); mp = 117°C. ^1H NMR ($CDCl_3$): $\delta = 7$–8.5 (m, 6H, aromatic H), 4.15 (q, 4H, O–CH_2–C), 4.05–3.6 (m, 16H, Ar–O–CH_2, CH_2–O–CH_2), 2.4 (s, 2H, C–CH_2–C), 1.4 (t, 6H, -C–CH_3). ν_{max} (cm^{-1}): 2238 (C≡N), 1753, 1676 (C = O), 1294 (C–O

ester), 1243–1217 ($C_{aromatic}$–O–C), 1190–1115 (C–O–C). $C_{31}H_{34}N_2O_{10}$ (594.6), calcd C 62.62 H 5.76 N 4.71; found C 62.61 H 5.60 N 4.74.

3.2. Synthesis of metallophthalocyanines (2–4)

A mixture of compound **1** (120 mg, 0.2 mmol) and metal salt [0.05 mmol (6.7 mg $CuCl_2$, 6.5 mg $CoCl_2$, 10 mg $PdCl_2$)] was fused in a glass tube (10×75 mm) under N_2 by gentle heating, cooled and sealed under vacuum. Then mixture was heated at 160°C for 6 h. After it was cooled to room temperature, the tube was opened and a dark green powder was obtained. The resulting solid was washed several times with hot methanol to dissolve any unreacted metal salt. Further purification was accomplished by column chromatography on neutral alumina and CH_3COOH: $CHCl_3$ (1:10). These phthalocyanines are soluble in chloroform, dichloromethane, acetone and DMF.

2: Yield, 31 mg (25%). ν_{max} (cm^{-1}): 1753, 1702 (C=O), 1294 (C–O ester), 1243–1210 ($C_{aromatic}$–O–C), 1140–1089 (C–O–C). λ_{max} (nm) $CHCl_3$: 651, 586, 340. $C_{124}H_{136}N_8O_{40}Cu$ (2441.92): calcd C 60.99 H 5.61 N 4.59; found C 61.10 H 5.85 N 4.31.

3: Yield, 25 mg (20.5%). ν_{max} (cm^{-1}): 1753, 1702 (C=O), 1294 (C–O ester), 1240–1217 ($C_{aromatic}$–O–C), 1165–1114 (C–O–C). λ_{max} (nm) in $CHCl_3$: 673, 613, 345. $C_{124}H_{136}N_8O_{40}Co$ (2437.32): calcd C 61.10 H 5.62 N 4.60; found C 61.38 H 5.88 N 4.35.

4: Yield, 35 mg (29%). ν_{max} (cm^{-1}): 1753, 1702 (C=O), 1294 (C–O ester) 1242–1215 ($C_{aromatic}$–O–C), 1160–1115 (C–O–C). λ_{max} (nm) in $CHCl_3$: 661, 596, 335. MS (*m*/*z*): 2845 (M^+, 11), 946 (100), 614 (38). ^1H NMR ($CDCl_3$) δ=8–8.7 (m, 24H, aromatic H), φ.17 (q, 16H, O–CH_2–C) 4.12–3.5 (m, 64H, Ar–O–CH_2, –CH_2–O–CH_2–) 2.45 (s, 8H, –C–CH_2–C–), 1.45 (t, 24H, –C–CH_3). $C_{124}H_{136}N_8O_{40}Pd$ (2484.8): calcd C 59.93 H 5.52 N 4.51; found C 59.72 H 5.31 N 4.27.

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