Octakis(alkylthio)-substituted Phthalocyanines and their Interactions with Silver(I) and Palladium(II) Ions

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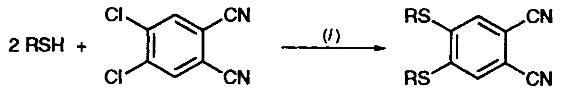
Metal-free phthalocyanines and metal phthalocyaninates (M = Ni, Cu, Co or Zn) carrying eight alkylthio-groups on peripheral positions have been synthesised from 4,5-bis(alkylthio)phthalonitrile and 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) or the corresponding anhydrous metal salt [$NiCl_2$, CuCl, $CoCl_2$ or $Zn(O_2CMe)_2$]. The resulting compounds reacted with silver(I) or palladium(II) salts to form complexes with a phthalocyanine:metal ratio of 1:4. Spectrophotochemical investigation of these reactions revealed that complexation with Ag^I results in aggregation, while the addition of Pd^{II} destroys the aggregation and yields a new Q band at 720 nm.

Although the special nature of phthalocyanines and their metal complexes has been known for about 60 years, their uses as commercial dyes, catalysts, optical and electrical materials are expanding enormously every year.[1] The rich co-ordination chemistry of phthalocyanine complexes has encouraged researchers to 'tailor' specific products with certain properties which are required for high-technology applications. The two variables are the central metal ion and the peripheral substituents: when the possibility of inserting a great number of different metal ions into the phthalocyanine core is combined with the unlimited number and type of substituents the variety of novel products is infinite.

Our primary aim has been the synthesis of new phthalocyanines with various functional groups and/or macrocycles. Among these we may cite the N- and O-containing functionalities such as crown ethers,[2,3] azacrown ethers,[4] diazatrioxa-[5] or tetraaza-macrocycles.[6,7] Substitution with four or eight long-chain alkoxy groups has also been frequently encountered.[8] The consequences of these substituents have been enhanced solubility, alkali- or transition-metal-ion binding, ion channel and discotic mesophase formation.[9] During the progress of our studies, reports by two other groups on the synthesis and properties of crowned phthalocyanines should be cited.[10,11]

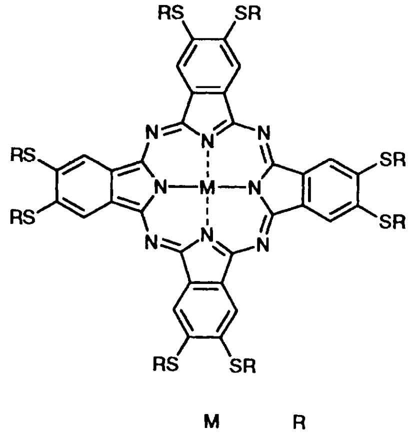
Phthalocyanines substituted with sulfur donors are rather few.[12,13] Also a small number of recent patents and proceedings describe the use of these types of compounds as IR absorbers.[14,15] The shift of the high-intensity Q bands to longer wavelengths is a common feature of these compounds.

We have recently reported the synthesis of metal-free and nickel(II) phthalocyanines with four long-chain alkylthioether substituents and their complexation through sulfur-donor groups to Ag^I and Pd^{II}.[16] While the tetrasubstituted phthalocyanines obtained from 4-substituted phthalonitriles are a mixture of three isomers, 4,5-disubstituted starting materials give a single product. The interaction of *o*-bis(thioethers) with metal ions is naturally expected to be different from that of mono derivatives. In the present work phthalocyanines with eight peripheral alkylthioether substituents have been prepared and their complexes with the same metal ions are investigated.



Ia R = C_6H_{13}
Ib R = $C_{12}H_{25}$

Scheme 1 (*i*) K_2CO_3, Me_2SO



	M	R
II	2H	C_6H_{13}
1a	Ni	C_6H_{13}
1b	Ni	$C_{12}H_{25}$
2a	Cu	C_6H_{13}
3a	Co	C_6H_{13}
4a	Zn	C_6H_{13}
1a·$4PdCl_2$	Ni	C_6H_{13}
1a·$4AgNO_3$	Ni	C_6H_{13}
1b·$4PdCl_2$	Ni	$C_{12}H_{25}$
2a·$4PdCl_2$	Cu	C_6H_{13}

Results and Discussion

1,2-Dichloro-4,5-dicyanobenzene was used recently to prepare 4,5-disubstituted phthalonitrile derivatives through base-catalysed nucleophilic aromatic displacement.[14,17] The same route was applied to prepare 4,5-bis(hexylthio)- and 4,5-bis-(dodecylthio)-1,2-dicyanobenzene **Ia** and **Ib** from the corresponding alkanethiols and 1,2-dichloro-4,5-dicyanobenzene (Scheme 1). The reactions were carried out in dimethyl sulfoxide at room temperature and gave high yields (≈80%).

Cyclotetramerization of the phthalonitrile derivative **Ia** to the metal-free phthalocyanine **II** was accomplished in pentanol in the presence of a strong base 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) at reflux temperature.[17,18] The metal phthalocyanin-

Table 1 Analytical* data for the starting materials and the phthalocyanines

	Analysis (%)						
Compound	C	H	N	M	Ag or Pd	S	Cl
Ia	66.80 (66.60)	7.95 (7.85)	7.75 (7.75)	—	—	17.55 (17.80)	—
Ib	72.55 (72.65)	9.90 (9.90)	5.25 (5.30)	—	—	12.10 (12.10)	—
II	66.55 (66.55)	7.95 (7.95)	7.60 (7.75)	—	—	17.25 (17.75)	—
1a	64.00 (64.00)	7.15 (7.50)	7.40 (7.45)	3.40 (3.90)	—	17.00 (17.10)	—
1b	70.40 (70.70)	9.85 (9.65)	5.15 (5.15)	2.10 (2.70)	—	11.50 (11.80)	—
2a	63.45 (63.80)	7.45 (7.50)	7.85 (7.45)	4.30 (4.20)	—	16.90 (17.05)	—
3a	63.95 (64.00)	7.50 (7.50)	7.35 (7.45)	4.00 (3.90)	—	17.90 (17.10)	—
4a	63.50 (63.75)	7.45 (7.50)	7.10 (7.45)	4.35 (4.35)	—	16.85 (17.00)	—
1a·4PdCl$_2$	43.20 (43.45)	5.00 (5.10)	5.10 (5.05)	2.15 (2.65)	19.35 (19.25)	11.35 (11.60)	12.50 (12.85)
1a·4AgNO$_3$	45.00 (44.05)	5.00 (5.20)	7.60 (7.70)	2.65 (2.70)	19.65 (19.80)	11.50 (11.75)	—
1b·4PdCl$_2$	53.20 (53.30)	7.00 (7.25)	3.85 (3.90)	2.10 (2.05)	14.55 (14.75)	8.80 (8.90)	9.80 (9.85)
2a·4PdCl$_2$	43.25 (43.40)	5.10 (5.10)	5.00 (5.05)	2.55 (2.85)	18.95 (19.20)	11.40 (11.60)	12.70 (12.80)

* Required values are given in parentheses.

Table 2 Proton NMR spectral data for the starting materials and the phthalocyanines in CDCl$_3$ (SiMe$_4$, δ 0)

Compound	CH$_3$	CCH$_2$C	SCCH$_2$	SCH$_2$	Aromatic
Ia	0.91 (t, 6 H)	1.26–1.45 (m, 8 H) 1.47–1.56 (m, 4 H)	1.71 (qnt, 4 H)	3.00 (t, 4 H)	7.16 (s, 2 H)
Ib	0.88 (t, 6 H)	1.27 (s, 32 H) 1.41–1.55 (m, 4 H)	1.71 (qnt, 4 H)	3.00 (t, 4 H)	7.41 (s, 2 H)
II*	1.01 (t, 24 H)	1.50–1.52 (m, 32 H) 1.78–1.90 (m, 16 H)	2.07 (qnt, 16 H)	3.41 (t, 16 H)	8.45 (s, 8 H)
1a	1.04 (t, 24 H)	1.51–1.53 (m, 32 H) 1.78–1.91 (m, 16 H)	1.97 (qnt, 16 H)	3.20 (t, 16 H)	7.87 (s, 8 H)
1b	0.86 (t, 24 H)	1.26 (s, 128 H) 1.72–1.90 (m, 16 H)	2.03 (qnt, 16 H)	3.32 (t, 16 H)	8.07 (s, 8 H)
4a	0.96 (t, 24 H)	1.26–1.47 (m, 48 H)	1.71 (qnt, 16 H)	2.90 (t, 16 H)	7.87 (s, 8 H)

* The peak of the inner-core NH protons is at δ −3.21.

Table 3 Carbon-13 NMR spectral data for the starting materials and the phthalocyanines in CDCl$_3$ (SiMe$_4$, δ 0)

Compound	C$_{\text{aromatic}}$	CN	CH$_2$S	CH$_2$	CH$_3$
Ia	144.45, 128.54, 111.27	115.57	32.89	31.22, 28.53, 28.15, 22.42	13.87
Ib	147.37, 129.92, 111.04	115.58	32.78	31.87, 29.65, 29.50, 29.25, 28.93, 22.67	12.85
II	147.98, 140.02, 132.87, 120.18	—	34.12	31.82, 29.19, 28.95, 22.73	14.16
1a	143.22, 139.10, 132.65, 118.67	—	33.89	31.82, 29.17, 28.77, 22.72	14.20
1b	143.48, 139.22, 132.94, 118.87	—	33.99	31.97, 29.83, 29.64, 29.46, 28.93, 22.69	14.15
4a	151.58, 138.72, 134.26, 119.87	—	33.73	31.73, 29.09, 28.64, 22.67	14.14

ates **1**–**4** were obtained by using the anhydrous metal salts [NiCl$_2$, CuCl, CoCl$_2$ or Zn(O$_2$CMe)$_2$]. Column chromatography with silica gel was employed to obtain the pure product from the reaction mixture (Table 1). The intense green products are very soluble in a number of solvents such as chloroform, dichloromethane, carbon tetrachloride, benzene, tetrahydrofuran (thf) and light petroleum (b.p. 40–60 °C). The solubility of **1a** in dichloromethane as determined spectrophotometrically was 7.8 × 10^{-2} mol dm^{-3} which is even higher than that of tetrakis(crown ether)-[2] or tetrakis(dodecylthio)-substituted phthalocyanines.[16] The interaction of silver(I) and palladium(II) ions with the thioether groups of the phthalocyanines gave products with a phthalocyanine : metal ratio of 1 : 4. They can be easily differentiated from the free phthalocyanines by their bluish tone and lower solubility in common solvents, especially in the case of the palladium derivatives.

Elemental analyses, IR, ^{1}H and ^{13}C NMR and UV/VIS spectra confirm the proposed structures of the compounds. In the IR spectra of **Ia** and **Ib** the intense absorption bands at 2240 and 2220 cm^{-1} respectively, corresponding to the C≡N groups, disappear after their conversion into the phthalocyanines. The NH groups in the inner core of the metal-free phthalocyanine **II** give an absorption at 3300 cm^{-1}; these protons are also very well characterized by the ^{1}H NMR spectrum which shows a peak at δ −3.21 as a result of the 18π-electron system of the phthalocyanine ring.[2] A distinct difference encountered in the ^{1}H NMR spectra of the phthalocyanines **II** and **1**–**4** when compared with our previous works with macrocycle-substituted ones is the sharp peaks which indicate a lower tendency to aggregation even at the concentration used for NMR measurements[3–5] (Table 2). The ^{13}C NMR spectral data given in Table 3 are also in accord with the expected structures.

Octakis(alkylthio)-substituted phthalocyanines **II** and **1**–**4** show intense Q absorption bands above 700 nm (Table 4). When compared with octakis(alkyl or alkoxy)-substituted ones, the shift of this intense band is especially important and will receive further attention for various near-IR applications. The characteristic Q band has been considered as a probe in discussing the self-assembling features of phthalocyanines in solution.[19] While the monomeric species with D_{2h} symmetry (*i.e.* metal-free derivative) shows two intense absorptions of comparable intensity around 700 nm, those having D_{4h} symmetry give only a single band in this region. Any increase in the concentration results in the aggregation of phthalocyanine molecules which is accompanied by a blue shift of the Q band with some decrease in intensity. It has also been concluded that aggregation is enhanced by solvent polarity and the presence of aliphatic side chains.[2,8,10,11] When the electronic spectra of the

Table 4 Electronic spectra of the reactants and the phthalocyanines in chloroform

Compound	λ_{max}/nm (10^{-4} ε/dm^3 mol^{-1} cm^{-1})
II	740 (13.44), 700 (12.75), 670 (5.20), 636 (3.39), 448 (3.44), 360 (6.70), 330 (7.36)
1a	702 (11.10), 675 (6.46), 634 (4.09), 432 (2.70), 364 (sh) (2.20), 325 (9.77)
1b	702 (13.95), 670 (7.09), 636 (3.86), 434 (3.27), 360 (sh) (2.96), 326 (11.05)
2a	711 (12.93), 675 (5.58), 643 (4.35), 440 (2.73), 327 (8.10)
3a	704 (12.24), 630 (4.00), 423 (2.62), 327 (11.76)
4a	710 (18.75), 675 (sh) (2.86), 638 (3.40), 364 (6.55), 325 (5.10)
1a·4AgNO$_3$	698 (9.48), 661 (10.30), 430 (sh) (3.75), 370 (4.10), 318 (13.35)

sh = Shoulder.

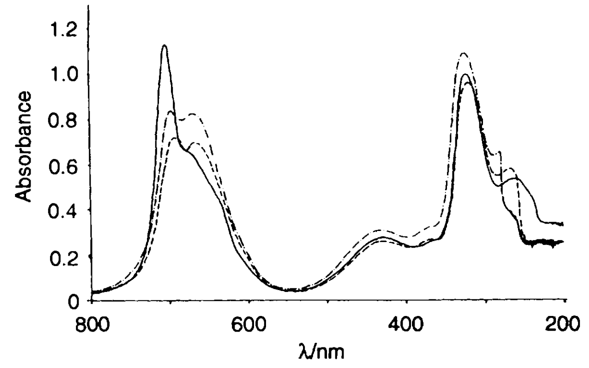


Fig. 1 Electronic spectra of complex **1a** in CHCl$_3$ (——), benzene (– · – · –) and CCl$_4$ (– – –)

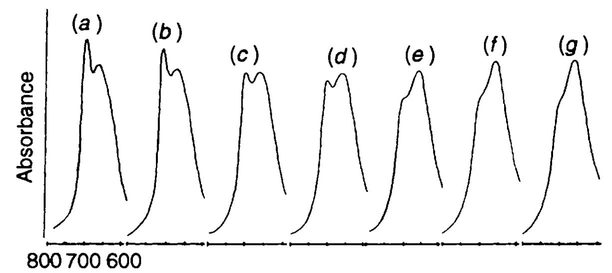


Fig. 2 Spectral changes occurring in the Q band of 10^{-5} mol dm^{-3} complex **1a** in (3 cm^3) in the presence of increasing amounts of AgNO$_3$ solution (10^{-3} mol dm^{-3}): (*a*) 0, (*b*) 20, (*c*) 40, (*d*) 60, (*e*) 80, (*f*) 100 and (*g*) 120 μl

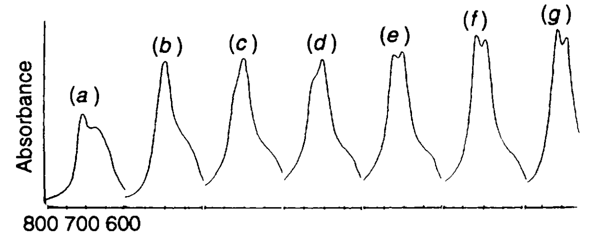


Fig. 3 Spectral changes occurring in the Q band of 10^{-5} mol dm^{-3} complex **1a** (3 cm^3) in the presence of increasing amounts of palladium(II) solution (10^{-3} mol dm^{-3}): (*a*) 0, (*b*) 20, (*c*) 40, (*d*) 60, (*e*) 80, (*f*) 100 and (*g*) 120 μl

phthalocyanines **II** and **1**–**4** were investigated some peculiarities were observed. The two intense Q bands of the metal-free derivative **II** were somewhat distorted leading to a third band of medium intensity around 670 nm. The nickel(II) phthalocyaninate showed a completely novel behaviour at lower energy: while the Q band appeared as an intense peak at 702 nm with a shoulder around 675 nm corresponding to monomeric and aggregated forms in chloroform or thf, in solvents of lower relative permittivity such as CCl$_4$ or benzene the spectra were completely different and contradictory to expectations; an intense Q band was split into a doublet at 669 and 700 nm in these apolar solvents (Fig. 1). These two absorptions cannot be attributed to the monomeric and aggregated species, while solvents of low polarity are known to lead to monomers especially at the concentrations studied (10^{-5} mol dm^{-3}). Also the shape of the Q-band region of complex **1a** in CCl$_4$ (Fig. 1) is completely different from those encountered for many soluble metallophthalocyanines which have a broad absorption for the dimers, trimers, *etc.* at higher energy with a satellite band at higher wavelengths for the monomers.[20] Since similar spectra have been obtained in the cases of both **1a** with C$_6$ and **1b** with C$_{12}$ substituents, the alkyl chain length should not be expected to have any contribution. In order to test the effect of the central metal ion on the changes in the Q band, the spectra of all phthalocyanines **1**–**4** in these solvents have been carefully investigated. It was found that in addition to the nickel(II) phthalocyanine **1a**, a similar splitting of the Q band, but to a lesser extent, occurred only for the copper(II) derivative **2a**. This result might be interpreted in terms of the formation of some intermolecular interactions between the central metal ion of one molecule with the thioether groups of another.

When the interaction of complex **1a** in thf:water 7:0.2 with Pd^{2+} and Ag$^+$ ions in the same solvent mixture was followed spectrophotometrically, two completely different coupling patterns between phthalocyanine units were observed according to the changes in the Q-band region. While addition of small increments of Ag$^+$ leads to gradual disappearance of monomeric species which show absorption at 698 nm, simultaneously enhancing the intensity of aggregated species around 665 nm (Fig. 2), portionwise addition of Pd^{2+} ions immediately results in the disappearance of the shoulder at 665 nm corresponding to the aggregated species and a new absorption band appears at 720 nm, which reaches a higher intensity than that of the original Q band at 700 nm when the Pd: phthalocyanine ratio of 4:1 is employed (Fig. 3). In order to eliminate the possibility of any solvent effect, blank tests were applied but no appreciable changes were observed. The results of the titration with silver ion closely follows those obtained in our previous work with tetra(alkylthio)-substituted phthalocyanines;[16] consequently we propose the interaction of the thioether groups of two different phthalocyanine molecules with silver ion to form network-type polymer units which then will form aggregates. The electronic configuration of the d^8 metal ion Pd^{II} exhibits a preference for square-planar geometry also with some dithioether complexes.[21] While two of the coordination sites are saturated by thio groups, the other two are filled by chloride ions.[22] When the complex obtained from 1,2-bis(alkylthio)benzene with PdCl$_2$ is investigated as a model compound, it is seen that the plane of the complex makes some angle with the plane of the benzene ring. Consequently, we should expect four PdS$_2$Cl$_2$ planes directed out of the plane of phthalocyanines **1a**, **1b** or **2a** which will cause decomposition of aggregates of planar phthalocyanine molecules in solution. The changes observed in the Q band of **1a** upon titration with Na$_2$[PdCl$_4$] closely follow this assumption. The new band at 720 nm is also a consequence of the lowering in the symmetry of the molecule. The insolubility of **1a**·4PdCl$_2$ in solvents such as chloroform, dichloromethane, benzene and thf, prevented attempts to compare the spectra obtained directly from the reactants in solution with those of the isolated complex. The visible spectrum of **1a**·4PdCl$_2$ in dmf was identical with that of the free phthalocyanine indicating that the complex had been decomposed in this solvent. In contrast to the palladium(II) complexes, in the case of silver(I) the Q-band regions of the spectra were very similar in halogenated solvents for both the isolated complex ($1a{\cdot}4AgNO_3$) and that obtained directly in solution from the reagents.

In conclusion, the donor capabilities of the thio groups should be taken into account together with the high solubility and red shift of the Q bands encountered in the octakis-(alkylthio)-substituted phthalocyanines. The mesogenic properties as well as the electrical conductivity of the compounds will be investigated in due course.

Experimental

Routine IR spectra were recorded on a Perkin Elmer 983 spectrophotometer as KBr pellets, electronic spectra on a Varian DMS 90 spectrophotometer. Elemental analysis was performed by the Instrumental Analysis Laboratory of TUBITAK Gebze Research Center. Proton and ^{13}C NMR spectra were recorded on a Bruker 200 MHz spectrometer. 1,2-Dichloro-4,5-dicyanobenzene was synthesised according to the reported procedure.[17]

Preparations.—*1,2-Di(alkylthio)-4,5-dicyanobenzenes* **Ia** *and* **Ib**. The alkanethiol [hexanethiol (7.165 g, 60.6 mmol) or dodecanethiol (12.27 g, 60.6 mmol)] was dissolved in absolute dimethyl sulfoxide (35 cm^3) under argon and 1,2-dichloro-4,5-dicyanobenzene (5.91 g, 30 mmol) was added. After stirring for 15 min, finely ground anhydrous potassium carbonate (15 g, 109 mol) was added portionwise in 2 h with efficient stirring. The reaction mixture was stirred under argon at room temperature for 12 h. Then water (100 cm^3) was added and the aqueous phase extracted with chloroform (3 × 50 cm^3). The combined extracts were treated first with sodium carbonate solution (5%), then with water and dried over anhydrous sodium sulfate. Solvent was evaporated and the oily product was crystallized from EtOH and dried in vacuum (P_2O_5). Compound **Ia**: yield 8.55 g (79%), m.p. 70 °C; ν_{max} 2970, 2950, 2860, 2240, 1560, 1450, 1420, 1350, 1280, 1260, 1230, 1205, 1120, 935, 905 and 715 cm^{-1}. Compound **Ib**: yield 12.61 g (80%), m.p. 58 °C; ν_{max} 3000, 2980, 2900, 2220, 1580, 1480, 1440, 1350, 1320, 1280, 1260, 1240, 1120, 940, 900 and 730 cm^{-1}.

Metal-free phthalocyanine **II**. Compound **Ia** (0.361 g, 1 mmol) was heated in pentanol (50 cm^3) in the presence of dbu (0.15 cm^3, 1 mmol) with stirring and refluxed for 60 h under argon. After cooling the dark green product was filtered off, washed with hot EtOH (3 × 20 cm^3) and then dried in vacuum. Yield: 0.140 g (39%); ν_{max} 3300, 2970, 2950, 2850, 1600, 1500, 1460, 1440, 1400, 1380, 1325, 1295, 1125, 1080, 1020, 940, 875, 750 and 725 cm^{-1}.

Nickel(II) *phthalocyaninates* **1a** *and* **1b**. A mixture of 1,2-di(alkylthio)-4,5-dicyanobenzene [**Ia** (1 g, 2.77 mmol), **Ib** (1.46 g, 2.77 mmol)], anhydrous $NiCl_2$ (0.104 g, 0.80 mmol) and quinoline (1.5 cm^3) was heated and stirred at 200 °C for 5 h under argon. After cooling to room temperature it was treated with ethanol (5 cm^3) and the product filtered off and washed with the same solvent. The dark green metallophthalocyanine was isolated on a silica gel column with $CHCl_3$ as the eluent. Complex **1a**: yield 0.390 g (38%); ν_{max} 3000, 2980, 2840, 1620, 1550, 1480, 1430, 1400, 1360, 1300, 1285, 1130, 1100, 1080, 980, 900, 875, 795, 750 and 715 cm^{-1}. Complex **1b**: Yield 0.292 g (19%); ν_{max} 2960, 2860, 1600, 1525, 1475, 1420, 1395, 1350, 1290, 1130, 1095, 1080, 975, 900, 875, 795, 755 and 705 cm^{-1}.

Copper(II) *phthalocyaninate* **2a**. A mixture of compound **Ia** (1 g, 2.77 mmol), CuCl (0.068 g, 0.69 mmol) and urea (0.071 g, 1.182 mmol) was heated and stirred at 100 °C for 2 h under argon. After cooling to room temperature, it was refluxed in hot ethanol (25 cm^3) and then filtered. The procedure was repeated three times. The dark green product was purified by column chromatography with silica gel (eluent: chloroform). Yield: 0.650 g (62%); ν_{max} 3000, 2980, 2800, 1610, 1520, 1480, 1420, 1395, 1350, 1300, 1275, 1140, 1100, 1080, 975, 900, 875, 795, 750 and 720 cm^{-1}.

Cobalt(II) *phthalocyaninate* **3a**. A mixture of compound **Ia** (1 g, 2.77 mmol), anhydrous $CoCl_2$ (0.091 g, 0.70 mmol) and ethylene glycol (5.5 cm^3) was heated and stirred at 200 °C for 4 h under argon. After cooling to room temperature, the reaction mixture was treated with ethanol to precipitate the dark green product and then filtered. The product was purified by column chromatography with silica gel (eluent: chloroform). Yield: 0.270 g (26%); ν_{max} 3000, 2980, 2800, 1610, 1535, 1480, 1420, 1395, 1355, 1300,1275, 1100, 1080, 975, 900, 875, 795, 755 and 715 cm^{-1}.

Zinc(II) *phthalocyaninate* **4a**. A mixture of compound **Ia** (1 g, 2.77 mmol), anhydrous zinc acetate (0.128 g, 0.70 mmol) and quinoline (2.2 cm^3) was heated and stirred at 200 °C for 6 h under argon. After cooling to room temperature, ethanol (5 cm^3) was added in order to precipitate the product. The dark green product was filtered off and then washed with hot ethanol several times. It was isolated on a silica gel column with chloroform as the eluent. Yield: 0.500 g (48%); ν_{max} 3000, 2980, 2800, 1610, 1500, 1480, 1420, 1390, 1350, 1300, 1275, 1140, 1100, 1080, 975, 900, 880, 785, 750 and 705 cm^{-1}.

Palladium(II) *complexes of* **1a**, **1b** *and* **2a**. The metallophthalocyanines [**1a** (0.098 g, 0.065 mmol), **1b** (0.141 g, 0.065 mmol), **2a** (0.098 g, 0.065 mmol)] were dissolved in tetrahydrofuran–water (7 + 0.2 cm^3) and a solution of $Na_2[PdCl_4]{\cdot}3H_2O$ (0.181 g, 0.52 mmol) in the same solvent mixture (7.2 cm^3) was added. The colour became blue-green while refluxing for 1 h and precipitation occurred. The product was separated by centrifuging and washed several times successively with hot water, hot ethanol and then with diethyl ether. The blue-green product was filtered off. Complex $\mathbf{1a}{\cdot}4PdCl_2$: yield 0.120 g (84%); ν_{max} 2980, 2960, 2840, 1600, 1525, 1460, 1420, 1390, 1350, 1300, 1120, 1080, 965, 780, 760, 705 and 320 cm^{-1}. Complex $\mathbf{1b}{\cdot}4PdCl_2$: yield 0.158 g (85%); ν_{max} 2950, 2860, 1600, 1525, 1460, 1420, 1390, 1350, 1300, 1120, 1080, 960, 780, 760, 705 and 320 cm^{-1}. Complex $\mathbf{2a}{\cdot}4PdCl_2$: yield 0.125 g (87%); ν_{max} 2990, 2980, 2860, 1620, 1520, 1475, 1420, 1390, 1350, 1305, 1120, 1080, 950, 785, 750, 700 and 320 cm^{-1}.

Silver(I) *complex of* **1a**. Complex **1a** (0.1 g, 0.067 mmol) was dissolved in tetrahydrofuran–water (7 + 0.2 cm^3) and silver nitrate (0.091 g, 0.533 mmol) in the same solvent (7 + 0.2 cm^3) was added. The mixture was refluxed for 4 h during which time all **1a** was consumed (TLC). The reaction mixture was filtered to separate any silver oxide formed. The product was obtained by evaporation of the solvent. It was dissolved in $CHCl_3$, filtered and reprecipitated by addition of ethanol. Yield: 0.05 g (34%); ν_{max} 2980, 2960, 2880, 1600, 1530, 1385, 1280, 1130, 1100, 1080, 970, 875, 845, 830, 795, 750 and 710 cm^{-1}.

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