Synthesis of Tetraalkylthio-substituted Phthalocyanines and their Complexation with Ag^I and Pd^{II}

İlke Gürol,[a] Vefa Ahsen[a] and Özer Bekaroğlu *,[a,b]
[a] *Department of Chemistry, TUBITAK Marmara Research Center, P.O. Box 21, 41470 Gebze, Kocaeli, Turkey*
[b] *Department of Chemistry, Technical University of Istanbul, Maslak, Istanbul, Turkey*

The synthesis of new metal-free and nickel(II) phthalocyanines substituted with four alkylthio groups SR (R = dodecyl or hexadecyl) is described. The new compounds have been characterized by elemental analyses, and IR, ^1H NMR and UV/VIS spectroscopy. The thio donors co-ordinate to Ag^I and Pd^{II} to give 2:1 metal–nickel phthalocyanine species. The changes in the electronic spectra with respect to increasing concentration of Pd^{II} or Ag^I have been investigated.

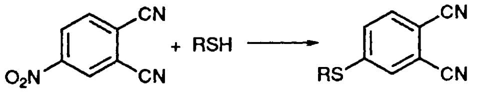
In addition to their extensive use as dyes and pigments, phthalocyanines have found wide applications in catalysis, in optical recording, in photoconductive materials, in photodynamic therapy and as chemical sensors.[1] For this broad range of applications, the stable phthalocyanine core should be amenable to modifications which can be accomplished either by changing the central metal ion or by adding functional groups on the periphery.[2] We are essentially working on the introduction of new peripheral substituents. By a judicious choice of substituents with suitable donor groups on the periphery, one can direct the phthalocyanine interactions with metal ions or with one another; the consequences of these phenomena will appear in affecting the ordering of molecular assemblies in the solid state as well as in solution. Drastic changes occur in the absorption spectra and photophysical properties when strongly conjugated macrocycles such as phthalocyanines are forced to lie in face-to-face conformations.[3]

We have previously reported peripherally substituted phthalocyanines with crown ethers,[4,5] monoaza crown ethers,[6,7] tetraaza-[8,9] and diazatrioxa-macrocycles.[10] These compounds have shown a high tendency to bind alkali- or transition-metal ions and also to form molecular assemblies by intermolecular interactions. Although phthalocyanines with *N*- and *O*-donor substituents have been frequently encountered, those with thioether moieties are rather few.[11,12] The latter group essentially contains products obtained by the cyclotetramerization of thioether-substituted phthalonitriles which themselves have been derived by nucleophilic displacement reactions of dinitriles; also a literature survey[13] shows that most of the recent work on thioether-substituted phthalocyanines has been patented with applications as IR absorbers.[13]

In the present paper we describe the synthesis of metal-free and nickel(II) phthalocyanines with long-chain alkyl thioether substituents. The complexation of thio-donor groups with Ag^I and Pd^{II} has been investigated.

Results and Discussion

The first step in the synthetic procedure was to obtain phthalonitrile (1,2-dicyanobenzene) derivatives containing long alkyl chains; this was accomplished by a base-catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile with dodecane-1-thiol or hexadecane-1-thiol [equation (1)].[11] This reaction has been effectively used in the preparation of a variety of ether or thioether-substituted phthalonitriles or phthalic acids. The reaction was carried out at room temperature in dimethylsulfoxide with K_2CO_3 as the base and the yields were rather high.



(1)

I R = $C_{12}H_{25}$
II R = $C_{16}H_{33}$

Among the many possibilities, preparation of metal-free and nickel(II) phthalocyanines have been especially preferred in order to be able to follow the reaction sequence by NMR spectroscopy for these diamagnetic compounds. The metal-free derivative H_2L^1 was obtained directly by the reaction of phthalonitrile **I** in hydroquinone as a uniphase fused melt; here, the two electrons required in addition to the 16 π electrons of 8 nitriles to yield the 18 π electron system of the phthalocyanine core was supplied by the oxidation of hydroquinone.[11,14] In the case of $[NiL^1]$, cyclotetramerization was carried out in quinoline in the presence of a nickel(II) salt. The most obvious common feature of these two phthalocyanines is their extensive solubility in apolar solvents, such as hexane, light petroleum and carbon tetrachloride. The solubility of $[NiL^1]$ in CCl_4 was determined spectrophotometrically from its saturated solution to be *ca.* 4×10^{-2} mol dm^{-3} [*i.e.* higher than the solubility of a tetrakis(crown ether)-substituted copper(II) phthalocyanine in chloroform].[4] The tetraalkylthiophthalocyanines all have a waxy appearance, so no melting points could be detected up to 300 °C. Although thioethers are known to have poorer co-ordinating ability compared with deprotonated thiols or aza analogues, some metal ions such as Ag^+ and Pd^{2+} show a high tendency to form complexes with thia groups.[15,16] When $[NiL^1]$ was treated with Na_2PdCl_4 or $AgNO_3$ solutions, polynuclear complexes $[NiL^1\{Ag(NO_3)\}_2]$ and $[NiL^1(PdCl_2)_2]$ were isolated, with metal:phthalocyanine ratios of 2:1 even when the phthalocyanine $[NiL^1]$ was treated with an excess of the metal ion. The solubility of both of the heterometallic complexes in apolar solvents is lower than that of $[NiL^1]$.

Characterization of the products involved a combination of methods including elemental analysis (Table 1), ^1H and ^{13}C NMR (Tables 2 and 3), UV/VIS (Table 4) and IR spectroscopy.

Cyclotetramerization of the dinitriles was confirmed by the disappearance of the sharp C≡N vibration at 2240 cm^{-1} of the reagents **I** or **II**. The ^1H NMR spectra of H_2L^1 and $[NiL^1]$ are almost identical, the only difference being the disappearance of the broad NH protons of H_2L^1 at *ca.* δ -4.8 in $[NiL^1]$.[4] Also it should be mentioned that the peaks of both spectra are

Table 1 Analytical[a] and physical data for the starting materials and the phthalocyanines

	Analysis (%)					
Compound	C	H	N	Ni	$T_1{}^b$/°C	$T_2{}^c$/°C
I	73.65	8.10	8.65	—	250	350
	(73.10)	(8.60)	(8.55)			
II	75.10	9.80	6.85	—	260	400
	(74.95)	(9.45)	(7.30)			
H_2L^1	72.75	9.10	8.05	—	250	425
	(73.00)	(8.75)	(8.50)			
$[NiL^1]$	69.10	8.35	8.30	4.00	325	425
	(70.00)	(8.20)	(8.15)	(4.25)		
$[NiL^1(PdCl_2)_2]^d$	55.20	6.30	6.35	3.20	325	425
	(55.60)	(6.55)	(6.50)	(3.40)		
$[NiL^1\{Ag(NO_3)\}_2]^e$	56.30	6.55	7.85	3.05	200	435
	(56.10)	(6.60)	(8.20)	(3.45)		
$[NiL^2]$	71.85	9.40	6.90	3.60	325	425
	(72.20)	(9.10)	(7.00)	(3.65)		

[a] Required values are given in parentheses. [b] Temperature of initial decomposition. [c] Temperature of major decomposition. [d] Pd 12.80 (12.30)%. [e] Ag 12.75 (12.60)%.

Table 2 Proton NMR spectral data for the starting materials and the phthalocyanines in $CDCl_3$

Compound	CH_3	CH_2	SCH_2CH_2	SCH_2	Aromatic
I	0.87 (t, 3 H)	1.25 (s, 18 H)	1.71 (p, 2 H)	3.00 (t, 2 H)	7.65–7.45 (m, 3 H)
II	0.87 (t, 3 H)	1.25 (s, 26 H)	1.71 (p, 2 H)	3.00 (t, 2 H)	7.65–7.45 (m, 3 H)
$H_2L^{1\,a}$	0.89 (s, 12 H)	1.31 (s, 72 H)	2.05 (m, 8 H)	3.34 (m, 8 H)	8.26–7.4 (m, 12 H)
$[NiL^1]$	0.93 (s, 12 H)	1.34 (s, 72 H)	1.94 (m, 8 H)	3.13 (m, 8 H)	7.61–6.93 (m, 12 H)
$[NiL^1(PdCl_2)_2]$	0.94 (br s, 12 H)	1.33 (s, 72 H)	2.16 (m, 8 H)	*b*	*b*
$[NiL^1\{Ag(NO_3)\}_2]$	0.91 (br s, 12 H)	1.25 (t, 72 H)	2.16 (t, 8 H)	2.95 (t, 8 H)	*b*
$[NiL^2]$	0.90 (t, 3 H)	1.29 (s, 104 H)	1.90 (br s, 8 H)	3.07 (br s, 8 H)	7.38–6.83 (m, 12 H)

[a] The chemical shift of inner core NH protons is at δ −4.8. [b] Extremely broad.

Table 3 Carbon-13 NMR spectral data for the starting materials and the phthalocyanines in $CDCl_3$

Compound	C(aromatic) and CN	CH_2S	CH_2	CH_3
I	147.5, 133.2, 129.9, 129.8, 116.2, 115.6, 115.1, 110.6	39.3	28.5, 28.2, 22.7	14.1
II	147.5, 133.1, 129.9, 129.8, 116.1, 115.4, 115.1, 110.5	39.2	31.8, 29.6, 29.3, 28.9, 28.7, 28.4, 28.1, 22.6	14.0
H_2L^1	146.3, 139.7, 135.0, 131.1, 127.3, 121.3, 119.5, 119.0	33.1	32.0, 29.9, 29.7, 29.5, 29.1, 22.7	14.2
$[NiL^1]$	141.3, 138.5, 135.2, 131.3, 126.5, 125.1, 120.9, 118.2	33.0	32.1, 29.9, 29.7, 29.5, 29.1, 22.7	14.2
$[NiL^2]$	142.3, 138.7, 135.8, 131.5, 127.1, 120.8, 119.4, 118.2	34.2	33.1, 31.9, 29.1, 22.7	14.1

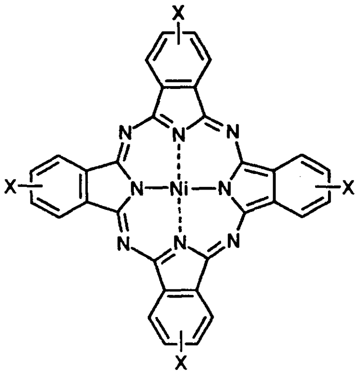
Table 4 Electronic spectra of the phthalocyanines in chloroform

Compound	λ_{max}/nm ($10^{-4}\varepsilon$/dm^3 mol^{-1} cm^{-1})
H_2L^1	716 (12.20), 682 (10.60), 652 (sh) (3.80), 615 (2.50), 410 (2.30), 346 (5.90)
$[NiL^1]$	687 (19.60), 653 (sh) (5.60), 621 (4.50), 402 (3.50), 305 (11.90)
$[NiL^1(PdCl_2)_2]$	680 (sh) (2.63), 643 (7.98)
$[NiL^1\{Ag(NO_3)\}_2]$	680 (sh) (1.93), 634 (6.28), 400 (2.10)
$[NiL^2]$	686 (19.60), 646 (4.20), 618 (4.10), 399 (2.60), 306 (3.93)

broad as encountered in some other soluble phthalocyanines. Tetrasubstituted phthalocyanines obtained from 4′-substituted phthalonitriles are naturally a mixture of isomers which is a primary reason for the broadness of the peaks.[17] Aggregation of the planar phthalocyanine molecules however is also expected to contribute to broadening. In the case of the complexes of $[NiL^1]$ with Pd^{II} and Ag^I, the spectra are further broadened and the aromatic protons are hardly detectable; only the intense peaks of alkyl substituents are observed. In the decoupled and attached proton test ^{13}C NMR spectra of the phthalonitrile derivative **I** the aromatic carbon in the vicinity of thia group is at lowest field (δ 147.5); the protonated aromatic carbons are at δ 133.2, 129.9 and 129.8 while the chemical shifts of the other two aromatic carbons and two nitrile carbons appear at δ 115.6, 115.1 and 110.6. The thermal stability of the phthalocyanines is confirmed by thermogravimetric analysis upon H_2L^1 and $[NiL^1]$, decompositions occurring only above 350 °C. In $[NiL^1\{Ag(NO_3)\}_2]$ the nitrate groups are lost at 220 °C, but the phthalocyanine itself decomposes only above 300 °C.

The electronic spectra of the phthalocyanines show the characteristic Q band absorptions as a single peak at 687 nm and a shoulder at 653 nm in $[NiL^1]$ and as two intense peaks at 716 and 682 nm in H_2L^1. The relative intensity of these peaks are concentration dependent at higher concentrations, but show no appreciable change in the range 10^{-5}–10^{-6} mol dm^{-3}. Solvent effects are also evident in $[NiL^1]$ *e.g.* addition of about 10% methanol into a chloroform solution of $[NiL^1]$ causes drastic changes in the Q band with lowering of intensity of the peak at 687 nm and increasing intensity of a new peak at *ca.* 654 nm.[18] Similar effects have been reported for crown-ether-substituted phthalocyanines as a result of aggregation in polar solvents.[4]

The UV/VIS spectrum of $[NiL^1(PdCl_2)_2]$ exhibits a completely different Q band structure than $[NiL^1]$ itself. Here



X
$[NiL^1]$ $SC_{12}H_{25}$
$[NiL^2]$ $SC_{16}H_{33}$

the higher energy component of the Q band structure, characteristic of aggregated species, is much more intense than in the $[NiL^1]$; a spectrum of $[NiL^1(PdCl_2)_2]$ in chloroform is shown in Fig. 1.

The interaction of $[NiL^1]$ with palladium(II) salts has been followed spectrophotometrically by addition of small increments of $Na_2[PdCl_4]$ to a solution of $[NiL^1]$ in chloroform (Fig. 1). Since the Na_2PdCl_4 was dissolved in ethanol, while $[NiL^1]$ was dissolved in chloroform, a possible solvent effect needs to be taken into account. In order to evaluate its importance, the spectra of $[NiL^1]$ alone in the corresponding solvent mixtures were obtained and indicated that any solvent effect can be safely neglected. The gradual change in the spectra upon the addition of Pd^{II} can be easily observed in Fig. 1. At a Pd^{II}:$[NiL^1]$ ratio of 2:1 the spectrum is identical to that of the isolated $[NiL^1(PdCl_2)_2]$ complex and remained essentially unchanged upon further addition of Pd^{II}. Consequently, the stoichiometry corresponding to two thia groups per palladium(II) ion is verified.

Similar experiments carried out with a 10^{-3} mol dm^{-3} solution of silver nitrate in water–tetrahydrofuran (1:99) are shown in Fig. 2. Here also the solvent effect is found to be negligible. A limiting spectrum is reached at an Ag^I:$[NiL^1]$ ratio of *ca.* 2:1 [Fig. 2 (*f*)]. The spectrum obtained directly from a 10^{-5} mol dm^{-3} solution of $[NiL^1\{Ag(NO_3)\}_2]$ is identical with that obtained upon treatment of a solution of $[NiL^1]$ at the same concentration with 2 equivalents of $AgNO_3$.

Since each of the four thioether groups on the phthalocyanine core are distributed on different benzene moieties, two-co-ordination of the heterometal, Ag^I or Pd^{II}, implies that thia groups from two different molecules co-ordinate to the metal ion, so resulting in a polymeric assembly. Under the concentrations studied spectral evidence also suggests interactions between the assemblies to form aggregates.

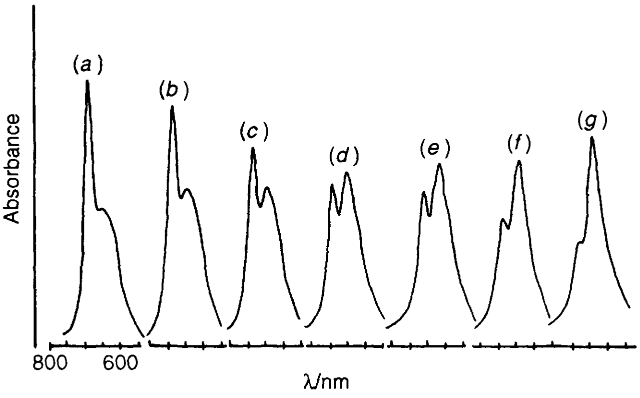


Fig. 1 Spectral changes occurring in the Q band region of a 1×10^{-5} mol dm^{-3} solution of $[NiL^1]$ in the presence of increasing amounts of Pd^{II}. Mole ratio Pd^{II}: $[NiL^1]$; (*a*) 0:1, (*b*) 0.33:1, (*c*) 0.67:1, (*d*) 1.33:1, (*e*) 1.67:1, (*f*) 2:1 and (*g*) 3.33:1

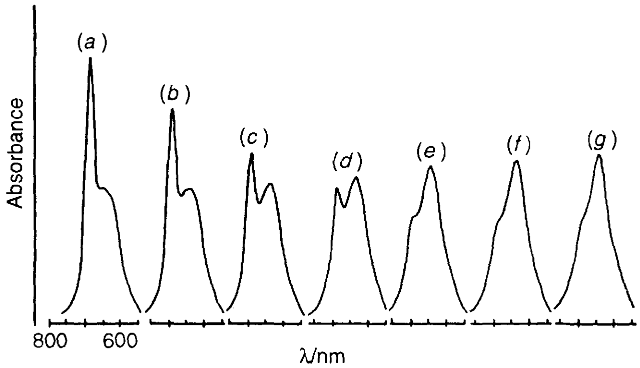


Fig. 2 Spectral changes occurring in the Q band region of a 1×10^{-5} mol dm^{-3} solution of $[NiL^1]$ in the presence of increasing amounts of $AgNO_3$. Mole ratio Ag^I:$[NiL^1]$; (*a*) 0:1, (*b*) 0.33:1, (*c*) 0.67:1, (*d*) 1.33:1, (*e*) 1.67:1, (*f*) 2:1 and (*g*) 3.33:1

Experimental

Routine IR spectra were recorded on a Perkin Elmer 983 spectrophotometer as KBr pellets. Electronic spectra were recorded on a Varian DMS 90 spectrophotometer. Elemental analysis was performed by the Instrumental Analysis Laboratory of TUBITAK Gebze Research Center. Thermogravimetric analyses were run on a DuPont differential thermoinstrument type 990 at 10 °C min^{-1} in a nitrogen flow (10 cm^3 min^{-1}). Proton and ^{13}C NMR spectra were recorded on a Bruker 200 MHz spectrometer. 4-Nitrophthalonitrile was synthesized according to the reported procedure.[19]

Syntheses.—*4-(Alkylthio)phthalonitrile* (*alkyl* = n-*dodecyl* **I** *or* n-*hexadecyl* **II**). The *n*-Alkylthiol [dodecane-1-thiol (6.10 g, 0.03 mol) or hexadecane-1-thiol (7.75 g, 0.03 mol)] was dissolved in absolute dimethyl sulfoxide (30 cm^3) under argon and 4-nitrophthalonitrile (5.2 g, 0.03 mol) was added. After stirring for 10 min, finely ground anhydrous potassium carbonate (6.22 g, 0.045 mol) was added in portions during 2 h with efficient stirring. The reaction mixture was stirred under argon at room temperature for 16 h, after which the solvent was evaporated under reduced pressure. Water (50 cm^3) was added and the aqueous phase was extracted with dichloromethane (3 × 25 cm^3). The combined extracts were treated first with sodium carbonate solution (5%), then with water and dried over anhydrous sodium sulfate. Evaporation of the solvent gave the desired product. **I**: Yield, 6.11 g (62%), m.p. 63 °C, $\tilde{\nu}_{max}/cm^{-1}$ 2980, 2940, 2870, 2240, 1590, 1475, 1195, 1140, 1075, 880, 850, 725 and 525. **II**: Yield, 7.61 g (66%), m.p. 69 °C, $\tilde{\nu}_{max}/cm^{-1}$ 2920, 2860, 2240, 1585, 1475, 1190, 1130, 1070, 875, 835, 720 and 520.

H_2L^1. A mixture of 4-(dodecylthio)phthalonitrile **I** (0.250 g, 0.76 mmol) and freshly sublimed hydroquinone was fused in a glass tube under argon by gentle heating, cooled and sealed under vacuum. The mixture was heated at 200 °C for 5 h. After cooling to room temperature, the tube was opened and the reaction mixture was treated with ethanol to precipitate the product and then filtered. Purification of the product H_2L^1 was accomplished by column chromatography with silica gel (eluent: dichloromethane–hexane, 5:2). Yield 0.060 g (24%); $\tilde{\nu}_{max}/cm^{-1}$ 3310, 2940, 2870, 1605, 1505, 1470, 1450, 1310, 1265, 1080, 1020, 820, 805 and 755.

$[NiL^1]$ *and* $[NiL^2]$. A mixture of 4-(alkylthio)phthalonitrile [**I** (0.250 g, 0.76 mmol) or **II** (0.292 g, 0.76 mmol)], anhydrous $NiCl_2$ (0.028 g, 0.22 mmol) and quinoline (0.4 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 filtered off and washed successively with the same solvent. Isolation of the metallophthalocyanine was carried out using a silica gel column with hexane–dichloromethane (5:3) as the eluent. [NiL^1]: Yield, 0.067 g (26%); $\tilde{\nu}_{max}$/cm^{-1} 2940, 2870, 1605, 1460, 1410, 1120, 1095, 1045, 940, 820 and 750. [NiL^2]: Yield, 0.103 g (34%); $\tilde{\nu}_{max}$/cm^{-1} 2940, 2870, 1605, 1465, 1415, 1125, 1100, 1045, 945, 825 and 750.

[NiL^1(PdCl$_2$)$_2$]. The phthalocyanine [NiL^1] (0.1 g, 0.073 mmol) was dissolved in tetrahydrofuran–water (4 cm^3 : 0.1 cm^3) and a solution of Na$_2$[PdCl$_4$]·3H$_2$O (0.101 g, 0.29 mmol) in the same solvent mixture was added. The reaction mixture became dark green while refluxing for 4 h and precipitation occurred. The product was separated by centrifugation and was washed several times with ethanol. The crude product was then dissolved in CCl$_4$ to separate it from NaCl and precipitated upon addition of acetone after drying over sodium sulfate. The dark green product was obtained upon filtration. Yield, 0.101 g (80%); $\tilde{\nu}_{max}$/cm^{-1} 2920, 2860, 1605, 1460, 1410, 1320, 1150, 1105, 1090, 1050, 940 and 750.

[NiL^1{Ag(NO$_3$)}$_2$]. The phthalocyanine [NiL^1] (0.1 g, 0.073 mmol) was dissolved in tetrahydrofuran–water (4 cm^3 : 0.1 cm^3) and silver nitrate (0.074 g, 0.44 mmol) in the same solvent mixture was added. The mixture was refluxed for 3 h during which all [NiL^1] disappeared (TLC). The reaction mixture was then filtered to separate any silver oxide formed. The crude product was obtained by evaporation of the solvent. It was dissolved in CCl$_4$, filtered and reprecipitated with the addition of acetone. Yield, 0.06 g (48%); $\tilde{\nu}_{max}$/cm^{-1} 2930, 2860, 1605, 1455, 1385, 1150, 1090, 935, 815 and 750.

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Received 26*th August* 1993; *Paper* 3/05160I