Synthesis and Characterization of Metal-free and Metal Derivatives of a Novel Soluble Crown-ether-containing Phthalocyanine

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A straightforward and generalizable synthesis of metal-free and metal (Cu, Co, Ni, or Fe) derivatives of a symmetrically tetrasubstituted phthalocyanine derived from 15,16-dicyano-2,3,5,6,8,9,11,12-octahydro-benzo[1,4,7,10,13]pentaoxacyclopentadecine is described. The new compounds have been characterized by elemental analyses, and i.r., ^{1}H n.m.r., u.v.–visible, and fast atom bombardment mass spectra. The alkali metal ions (sodium and potassium) bound to crown ether groups of the metal complexes force dimerization of the phthalocyanine units in solution as observed in the electronic spectra by the broadening of the *Q*-band transition at *ca.* 630 nm. The solubilities of the metal phthalocyaninates in chloroform were determined to be *ca.* 10^{-3} mol dm^{-3}. The thermal stabilities of the compounds were determined by thermogravimetric and differential thermal analysis. The high affinity of the cobalt(II) derivative for the potassium ion was observed in solvent extraction experiments.

In addition to their industrial importance as pigments, metal phthalocyanine compounds have been extensively studied because of their interesting conductivity, catalytic, photovoltaic, and electrochroic properties.[1] Phthalocyanines have also been studied as models of naturally occurring porphyrins.[2] Another interesting group of compounds used as biological models are crown ethers, which form complexes with alkali and alkaline-earth metal ions as well as with neutral organic molecules.[3]

We concentrated initially on synthesizing and understanding the properties of *vic*-dioxime complexes which contain a planar MN_4 core structure.[4] The addition of crown ether groups into the *vic*-dioxime molecule has provided considerable opportunity to investigate the properties of the complexes by enhancing their solubility in various organic solvents and in water.[5]

The solubility and the physical and chemical properties of phthalocyanines can be 'tailored' by making suitable substitutions on the aromatic rings such as Bu^t, NR_2, OR, COOH, CF_3, SO_3H, CN, or Bu^n.[6] Although Ziolo *et al.*[7] reported that ready solubility in organic solvents was imparted to disodium and dipotassium phthalocyaninates by complexation with macrocyclic polyethers, no phthalocyanine molecule with crown ether groups attached to the aromatic rings has been reported.

The present paper reports the synthesis of free and metal-complexed phthalocyanines containing four 15-crown-5 (1,4,7,10,13-penta-oxacyclopentadecane) moieties in the molecule; a preliminary account of this work has been reported.[8] The capability of binding five cations and their electronic interactions are the major opportunities offered by these new compounds. Metallophthalocyanines with ether substituents are also examples of a new type of liquid crystal, namely the 'discotic mesophases'.[6] Consequently, it is of interest to investigate the properties of these new compounds containing phthalocyanine and crown ether groups simultaneously. The solubilities, spectral data, thermal stability, and alkali metal complexation properties of the novel compounds are also discussed.

Experimental

Benzo-15-crown-5† was prepared by reported procedures.[3] Routine i.r. spectra were recorded on a Perkin-Elmer 983 spectrophotometer as KBr pellets. ^{1}H N.m.r. spectra were recorded on a Bruker 360-MHz spectrometer. Electronic spectra were recorded on a Varian DMS 90 spectrophotometer. Mass spectra were obtained on a Kratos Analytical MS25RFA mass spectrometer equipped with a DS90 data system and fast atom bombardment source. Elemental analysis was performed by the Instrumental Analysis Laboratory of TÜBİTAK Gebze Research Center. Analytical data for metal complexes are given in Table 1. Thermogravimetry and differential thermal analysis were run on a DuPont differential thermo-instrument type 990 at 10 °C min^{-1} in a nitrogen flow (280 cm^3 min^{-1}).

For the solubility measurements, a saturated solution was prepared in chloroform, gravity filtered and diluted. The concentration of solute was determined from the absorbance of the solution and the previously determined molar absorption coefficient using Beer's law.[9]

Synthesis of Dibromobenzo-15-*crown*-5.‡—A solution of bromine (16 cm^3, 49.76 g, 0.31 mol) in acetic acid (80 cm^3) was added dropwise into a solution of benzo-15-crown-5 (44 g, 0.164 mol) in acetic acid (140 cm^3) over 4 h at room temperature. When the mixture was further stirred for 24 h at room temperature, a yellow precipitate formed. It was filtered off and washed with light petroleum (b.p. 40—60 °C). The product was dissolved in ethanol (150 cm^3) and boiled in order to expel bromine complexed in the crown ether ring.[11] Cooling at room temperature gave the product as white needles. Yield: 49.4 g (70%); m.p. 80 °C. This compound was soluble in common

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† Benzo-15-crown-5 = 2,3,5,6,8,9,11,12-octahydro-benzo[1,4,7,10,13]-pentaoxacyclopentadecine; dibromobenzo-15-crown-5 and dicyano-benzo-15-crown-5 are its 15,16-Br_2- and 15,16-$(CN)_2$-substituted derivatives respectively.

‡ This compound was mentioned in ref. 10 but no experimental details were given.

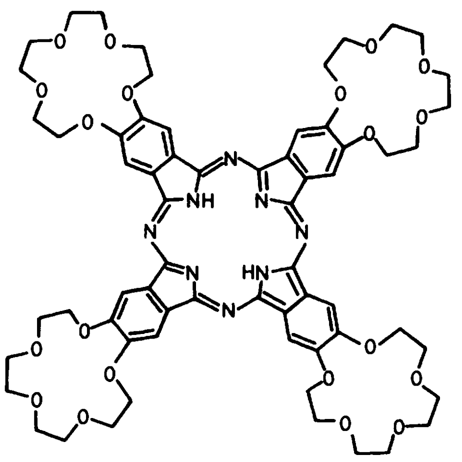
Table 1. Elemental analysis

	Found (%)					Calc. (%)				
Compound	C	H	N	M	Alkali metal	C	H	N	M	Alkali metal
H_2L	60.20	5.60	9.00	—	—	60.30	5.80	8.80	—	—
$H_2L\cdot2NaClO_4$	50.50	4.90	7.10	—	2.90	50.55	4.85	7.35	—	3.00
$H_2L\cdot2NH_4SCN$	55.30	5.60	11.75	—	—	55.55	5.75	11.80	—	—
$H_2L\cdot2KSCN$	52.25	4.85	9.40	—	5.10	53.95	5.05	9.55	—	5.30
[CuL]	56.95	5.45	8.05	4.90	—	57.50	5.45	8.40	4.75	—
[CuL]·4NaSCN	49.50	4.40	10.25	3.70	5.20	49.15	4.35	10.10	3.80	5.55
$[CuL]\cdot2NH_4SCN$	53.00	4.95	10.95	4.30	—	53.20	5.35	11.30	4.25	—
[CuL]·2KSCN	51.90	4.55	8.95	4.05	4.90	51.75	4.70	9.15	4.15	5.10
[CoL]	57.80	5.40	8.35	4.20	—	57.70	5.40	8.40	4.40	—
[CoL]·4NaSCN	49.30	4.55	9.90	3.70	5.80	49.40	4.35	10.15	3.55	5.55
$[CoL]\cdot2NH_4SCN$	53.10	5.20	11.55	4.05	—	53.35	5.40	11.30	3.95	—
[CoL]·2KSCN	51.55	4.60	9.40	3.95	4.95	51.95	4.70	9.20	3.85	5.10
[NiL]	56.10	5.40	8.20	4.30	—	57.65	5.40	8.40	4.40	—
[NiL]·4NaSCN	49.10	4.60	10.30	3.60	5.40	49.30	4.35	10.15	3.55	5.55
$[NiL]\cdot2NH_4SCN$	53.35	5.25	11.60	3.80	—	53.40	5.40	11.35	3.95	—
[NiL]·2KSCN	52.05	4.95	8.90	4.00	5.10	51.90	4.70	9.20	3.85	5.10
[FeL]	58.90	5.45	8.20	4.35	—	57.80	5.40	8.45	4.20	—
[FeL]·4NaSCN	49.25	4.70	9.95	3.55	5.40	49.35	4.35	10.15	3.40	5.55
$[FeL]\cdot2NH_4SCN$	53.30	5.30	10.95	3.80	—	53.45	5.40	11.35	3.80	—
[FeL]·2KSCN	52.10	4.60	9.65	3.50	5.30	52.00	4.70	9.20	3.65	5.10

organic solvents (Found: C, 39.5; H, 3.95; Br, 37.3. Calc. for $C_{14}H_{18}Br_2O_5$: C, 39.45; H, 4.20; Br, 37.55%). Infrared spectrum (KBr pellet): $\nu(C_{aromatic}–O–C)$ 1 210—1 250 and ν(C–O–C) 1 050—1 130 cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 7.07 (2 H, s) and 3.8—4.1 (16 H, m).

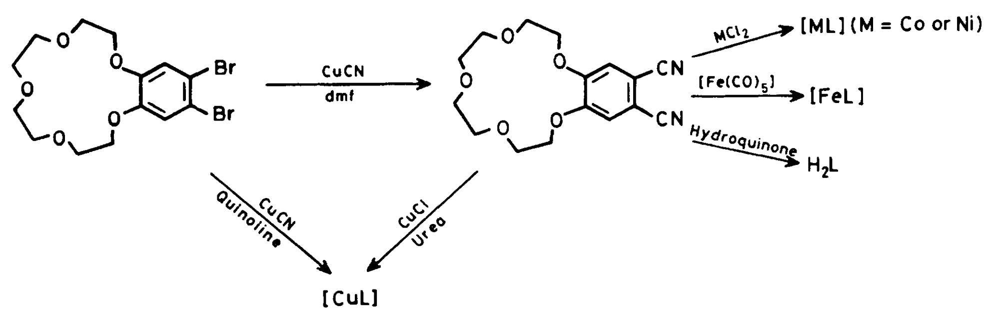
Synthesis of Dicyanobenzo-15-crown-5.—An apparatus consisting of a two-necked, round-bottomed flask (500 cm^3) fitted with a condenser was evacuated and refilled with argon three times and then flamed under high vacuum. Under argon, the flask was charged with CuCN (12.6 g, 0.14 mol), argon-saturated dimethylformamide (dmf, 200 cm^3), and dibromobenzo-15-crown-5 (20 g, 47 mmol), in that order, to give a light green solution. The flask was next immersed in an oil-bath, the temperature raised to 160—170 °C and held overnight. During this time, the solution became dark brown-green. The heating was stopped and the reaction mixture was allowed to cool to room temperature, opened to air and diluted with aqueous NH_4OH (470 cm^3, 25%) and air was passed through the solution for 24 h. The solution became dark blue and a green precipitate formed. The reaction mixture was filtered through Celite and sand and washed with dilute aqueous NH_4OH (10%) and then with water until the filtrate was neutral. The precipitate together with Celite and sand was placed in the thimble of a Soxhlet extractor and extracted for 8 h with toluene. Toluene was evaporated under vacuum, to give bright white crystals. Yield: 9.81 g (66%); m.p. 143—145 °C. This compound was soluble in common organic solvents (Found: C, 60.0; H, 5.75; N, 8.60. Calc. for $C_{16}H_{18}N_2O_5$: C, 60.35; H, 5.65; N, 8.80%). Infrared spectrum (KBr pellet): $\nu(C_{aromatic}–O–C)$ 1 220—1 280, ν(C–O–C) 1 050—1 130 and $\nu(C\equiv N)$ 2 220 cm^{-1}. ^{1}H N.m.r. (CD_2Cl_2): δ 7.14 (2 H, s) and 3.67—4.15 (16 H, m).

Synthesis of the Metal-free Phthalocyanine (H_2L).—A mixture of dicyanobenzo-15-crown-5 (0.94 g, 2.96 mmol) and hydroquinone (0.081 g, 0.74 mmol; purified by sublimation) was fused in a glass tube (10 × 75 mm) under argon by gentle heating, cooled and sealed under vacuum. The mixture was heated at 180 °C for 16 h. After it was cooled to room temperature, the tube was opened and a dark green powder was obtained. This product was dissolved in chloroform–dichloromethane–ethanol (2:1:1, 100 cm^3) and added dropwise into stirred ethyl acetate (250 cm^3). The resulting dark green precipitate was filtered off, washed with ethyl acetate and then with diethyl ether and dried. Yield: 0.34 g (32.16%). This compound was soluble in chloroform, dichloromethane, dmf, Me_2SO and slightly soluble in ethanol and benzene. Infrared spectrum (KBr pellet): $\nu(C_{aromatic}–O–C)$ 1 200—1 280, ν(C–O–C) 1 060—1 130, ν(N–H) 3 300, and δ(N–H) 1 030 cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 8.3 (8 H, s), 3.9—3.2 (64 H, m), and −4.8 (2 H, br, s).



H_2L

Synthesis of [CuL].—*Method A*. A mixture of dibromobenzo-15-crown-5 (3.5 g, 8.21 mmol), CuCN (1.93 g, 21.56 mmol), and quinoline (6 cm^3) was heated and stirred at 220 °C for 16 h under N_2. (When pyridine was used as the solvent instead of quinoline, the reaction was carried out in a sealed tube at the same temperature.) After it was cooled to room temperature, the reaction mixture was treated with ethanol and the crude product was precipitated. It was filtered off and washed with ethanol and diethyl ether to remove the unreacted organic material. The excess CuCN was dissolved by treating the precipitate with a solution of NaCN in water–ethanol (1:2).



Scheme. Synthesis of [CuL]

This solution was extracted with chloroform (5 × 20 cm^3) and the chloroform solution was dried over $MgSO_4$ and evaporated to dryness to afford the pure product. Yield: 1.03 g (38%).

Method B. A mixture of dicyanobenzo-15-crown-5 (0.25 g, 0.78 mmol), CuCl (0.02 g, 0.2 mmol), and urea (0.02 g, 0.33 mmol) was ground well in a ball-mill and placed in a flask. The reaction temperature was brought to 160 °C and held for 10 min, then cooled to room temperature. The crude product was dissolved in CH_2Cl_2 and added dropwise into ethyl acetate (*ca.* 150 cm^3) and stirred for 10 min. The precipitate was filtered off, washed with ethyl acetate, and dried with diethyl ether. Yield: 0.29 g (38.1%). The products obtained by methods A and B are identical. Infrared spectrum (KBr pellet): $\nu(\mathrm{C_{aromatic}{-}O{-}C})$ 1 205—1 285 and ν(C–O–C) 1 050—1 125 cm^{-1}.

Synthesis of [CoL].—A mixture of dicyanobenzo-15-crown-5 (0.82 g, 2.58 mmol) and $CoCl_2{\cdot}6H_2O$ (0.1 g, 0.42 mmol) was ground in a ball-mill and then the mixture was heated in ethylene glycol (6.4 cm^3) at 185—190 °C for 5 h under argon. The mixture was cooled and an equal volume of water was added. The mixture was suction filtered while still hot, and the precipitate was washed with hot water (*ca.* 90 °C) several times followed by ethanol, acetone, and ether. The green powder was dried *in vacuo* (100 °C, 8 h). Yield: 0.39 g (45.5%). Infrared spectrum (KBr pellet): $\nu(\mathrm{C_{aromatic}O{-}C})$ 1 200—1 280 and ν(C–O–C) 1 060—1 130 cm^{-1}.

Synthesis of [NiL].—A round-bottomed flask was charged with $NiCl_2{\cdot}6H_2O$ (0.376 g, 1.58 mmol), dicyanodibenzo-15-crown-5 (2 g, 6.3 mmol), and quinoline (4.72 cm^3). The flask was fitted with a stir-bar and condenser, and then immersed in an oil-bath. The bath temperature was brought to 195—200 °C during 1 h and stirred at that temperature for 2.5 h. The resulting dark green suspension was cooled, diluted with methanol, and filtered. The solid product was washed successively with methanol, water, acetone, heptane, and acetone. This crude product was dissolved in $CHCl_3$–CH_2Cl_2–EtOH (2:1:1, 200 cm^3) and the solution added dropwise into ethyl acetate (600 cm^3), with stirring, to precipitate the product. It was filtered off, washed with ethyl acetate and then with ether and dried. Yield: 1.04 g (49.71%). Infrared spectrum (KBr pellet): $\nu(\mathrm{C_{aromatic}{-}O{-}C})$ 1 205—1 285 and ν(C–O–C) 1 060—1 130. ^{1}H N.m.r. ($CDCl_3$): δ 8.2 (8 H, s) and 3.9—3.4 (64 H, m).

Synthesis of [FeL].—A mixture of dicyanobenzo-15-crown-5 (1.272 g, 4 mmol) and ethylene glycol (15 cm^3) was heated to 190—210 °C under argon. $[Fe(CO)_5]$ (0.2 g, 0.137 cm^3, 1.02 mmol) was then added portionwise directly into the solvent. The reaction mixture immediately turned to green. The reaction was held at the above temperature for 3 h, then cooled and diluted with H_2O (15 cm^3). The precipitate which formed was filtered off, and washed with hot ethanol and acetone. The crude product was dissolved in a mixture of CH_2Cl_2 and ethanol, and washed with H_2O. The organic layer was dried with $MgSO_4$ and then evaporated under vacuum to obtain green [FeL]. Yield: 0.215 g (16.2%). The elemental analysis results are given in Table 1. Infrared spectrum (KBr pellet): $\nu(\mathrm{C_{aromatic}{-}O{-}C})$ 1 200—1 280 and ν(C–O–C) 1 050—1 125 cm^{-1}.

Synthesis of the Adducts of Alkali Metal Salts with [ML].—The transition metal phthalocyaninate (0.05 mmol) was dissolved in chloroform–ethanol (4:1, 50 cm^3). To this solution was added a solution of the desired alkali metal salt (NaSCN, $NaClO_4$, KSCN, or NH_4SCN; 10% in excess) in ethanol and the mixture was heated at 50 °C for 10 min, then cooled to room temperature. The precipitate was filtered off, then washed successively with ethanol and ether and dried under vacuum.

Results and Discussion

Synthesis.—Although many substitution reactions on the aromatic rings of phthalocyanines have been reported, the crown ether-containing phthalocyanine H_2L can only be obtained by starting with reactants which already contain these groups. Complexes of L^{2-} have been synthesized either by the template reaction of dibromobenzo-15-crown-5 or by isolating dicyanobenzo-15-crown-5 as an intermediate step[6] (Scheme). The first route which makes use of a high-boiling solvent (*e.g.* quinoline) is especially favourable to obtain only [CuL], but it is not suitable for synthesis of the metal-free species (H_2L) or for [ML] with metal ions other than copper. The critical point in the second route was to isolate the 15,16-dicyano-substituted crown ether which was accomplished by keeping the concentration of the same reactants sufficiently low and by making use of a moderately high-boiling solvent (dmf) to avoid the formation of copper phthalocyaninate.

The ligand H_2L was synthesized by heating a mixture of dicyanobenzo-15-crown-5 with hydroquinone in a sealed tube.[12] The transition metal complexes were prepared from the dicyano compound and the corresponding metal salt, or carbonyl complex, in a high-boiling solvent. In order to introduce the alkali metal salts, [ML] was dissolved in chloroform–ethanol and a solution of alkali metal or ammonium salt (KSCN, NaSCN, $NaClO_4$, NH_4SCN) was added dropwise in excess.[13] Whereas K^+ or ammonium ion formed complexes with a 2:1 ratio of salt:complex, in the case of sodium all four crown ether groups of the phthalocyanine molecule held four sodium ions separately. The only exception was $H_2L{\cdot}2NaClO_4$ and this phenomenon can be explained by the low solubility of the sodium perchlorate complexes of crown ethers, such that complexation of the second $NaClO_4$ caused precipitation of the compound. The NaSCN complex of H_2L was too soluble to isolate.

The i.r. spectra of H_2L and [ML] (M = Cu, Ni, Co, or Fe)

Table 2. Electronic spectra[a] and solubilities of H_2L and [ML] and their alkali metal adducts

Compound	λ/nm (10^{-4}ε/dm^3 mol^{-1} cm^{-1})						Solubility[b]
H_2L	348 (7.51)	420 (3.03)	601 (2.4)	644 (4.53)	661 (10.34)	701 (12.61)	3.9×10^{-3}
[CuL]	340 (3.71)	382 (2.04)	615 (2.03)	647 (2.13)	680 (4.41)		1.4×10^{-3}
[CoL]	328 (6.04)	398 (2.33)	604 (3.27)	639 (4.73)[c]	669 (10.07)		0.8×10^{-3}
[NiL]	330 (4.13)	406 (2.21)	603 (2.7)	638 (3.51)	669 (12.38)		0.9×10^{-3}
[FeL]	350 (3.83)	412 (2.27)	606 (0.7)[c]	662 (2.06)[c]	682 (2.48)[c]	702 (3.31)	4.1×10^{-3}
H_2L·2NaClO$_4$	340 (4.71)	410 (1.89)		635 (3.69)			
H_2L·2KSCN	332 (2.28)			640 (1.72)			
H_2L·2NH$_4$SCN	352 (3.66)			660 (3.83)		700 (4.3)	
[CoL]·4NaSCN	360 (2.36)		612 (1.48)[c]			698 (2.69)	
[CoL]·2KSCN			628 (2.16)		675 (2.16)		
[CoL]·2NH$_4$SCN	355 (2.67)		620 (2.00)[c]		675 (2.73)		

[a] In chloroform. [b] Of a saturated solution at 25 °C in mol dm^{-3}, where $c = A/\varepsilon l$ and $l = 1$ cm. [c] Shoulder.

Table 3. Molecular ion species obtained by fast atom bombardment mass spectrometry and the theoretical isotopic distributions

Compound	*M*(calc.)	M^+	Theoretical isotopic distributions: Formula	Accurate mass	Relative abundance(%)
[FeL]	1 328.42	1 329.4	$^{12}C_{63}{}^{13}C_1H_{72}{}^{56}Fe_1N_8O_{20}$	1 329.424 50	30.98
			$^{12}C_{64}H_{72}{}^{57}Fe_1N_8O_{20}$	1 329.421 64	1.03
			$^{12}C_{64}H_{72}{}^{56}Fe_1{}^{14}N_7{}^{15}N_1O_{20}$	1 329.418 18	1.28
[CuL]	1 335.5	1 336.4	$^{12}C_{63}{}^{13}C_1H_{72}{}^{63}Cu_1N_8O_{20}$	1 336.419 40	23.33
			$^{12}C_{64}H_{72}{}^{63}Cu^{14}N_7{}^{15}N_1O_{20}$	1 336.413 08	0.96
[CoL]	1 330.93	1 331.4	$^{12}C_{64}H_{72}{}^{59}CoN_8O_{20}$	1 331.419 44	46.45
[NiL]	1 330.71	1 331.5	$^{12}C_{63}{}^{13}C_1H_{72}N_8{}^{58}Ni_1O_{20}$	1 331.424 90	23.66
			$^{12}C_{64}H_{72}{}^{14}N_7{}^{15}N_8{}^{58}Ni_1O_{20}$	1 331.418 58	0.98

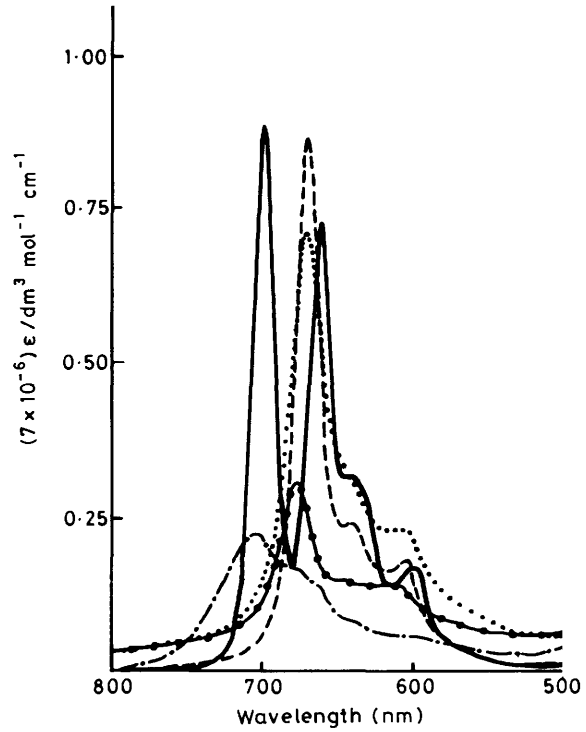


Figure 1. Electronic spectra: H_2L (——), [CuL] (–●–), [CoL] (· · ·), [NiL] (– – –), and [FeL] (— · —)

are very similar. The only difference is the presence of ν(NH) and δ(NH) vibrations assigned to bands at 3 300 and (δ) 1 030 cm^{-1} respectively in the free molecule.[14] These bands are absent in spectra of the metal complexes. The M–N vibrations were expected to appear at 400—100 cm^{-1} but they were not observed in KBr pellets.[15] There is little change in the absorptions due to the crown ether groups [ν(CH) 2 920, ν($C_{aromatic}$–O–C) 1 285, ν(C–O–C) 1 110 cm^{-1}] after adduct formation with alkali metal salts but the characteristic bands of the anions are clearly observed [ν(SCN) 2 060, ν(ClO_4) 1 130 and 620 cm^{-1}].

The ^{1}H n.m.r. spectrum of H_2L indicates aromatic protons (δ 8.3) and aliphatic ether protons (δ 3.9—3.2) as well as the protons of the internal NH groups (δ −4.8). The shift to higher field for the NH protons is a result of the 18 π-electron system of phthalocyanine ring. The reported chemical shift values of NH groups for various substituted metal-free phthalocyanines vary from −2.0 to −9.0.[16] The high upfield shift of the cavity NH protons was also verified by deuterium exchange with D_2O. In contrast to the NH protons, aromatic protons were shifted to lower field because of the π-electron ring current of the phthalocyanine core even after complexation with Ni^{II}.

The solubility of [ML] in various organic solvents enabled investigation of the electronic spectra of these compounds. Optical data for the compounds synthesized in this study are presented in Table 2 and representative electronic spectra are shown in Figure 1. These spectra can be understood in terms of a porphyrinic 'four orbital' with $\pi \longrightarrow \pi^*$ *Q*-band transitions at *ca.* 670 nm and Soret-like $\pi \longrightarrow \pi^*$ bands near 340 nm. It can be seen that a progressive shift of the visible absorption bands to lower energy occurs in the order Co > Ni > Cu > Fe.

The obvious effect of alkali metal ions complexed in the crown groups on the *Q*-band transitions of the phthalocyanine unit should be noted (Figure 2). The broadening of this absorption as well as an hypsochromic effect is observed in the case of sodium and potassium. Similar broadening in the spectra of some water-soluble sulphonated phthalocyanines has been reported and this was explained to be the result of

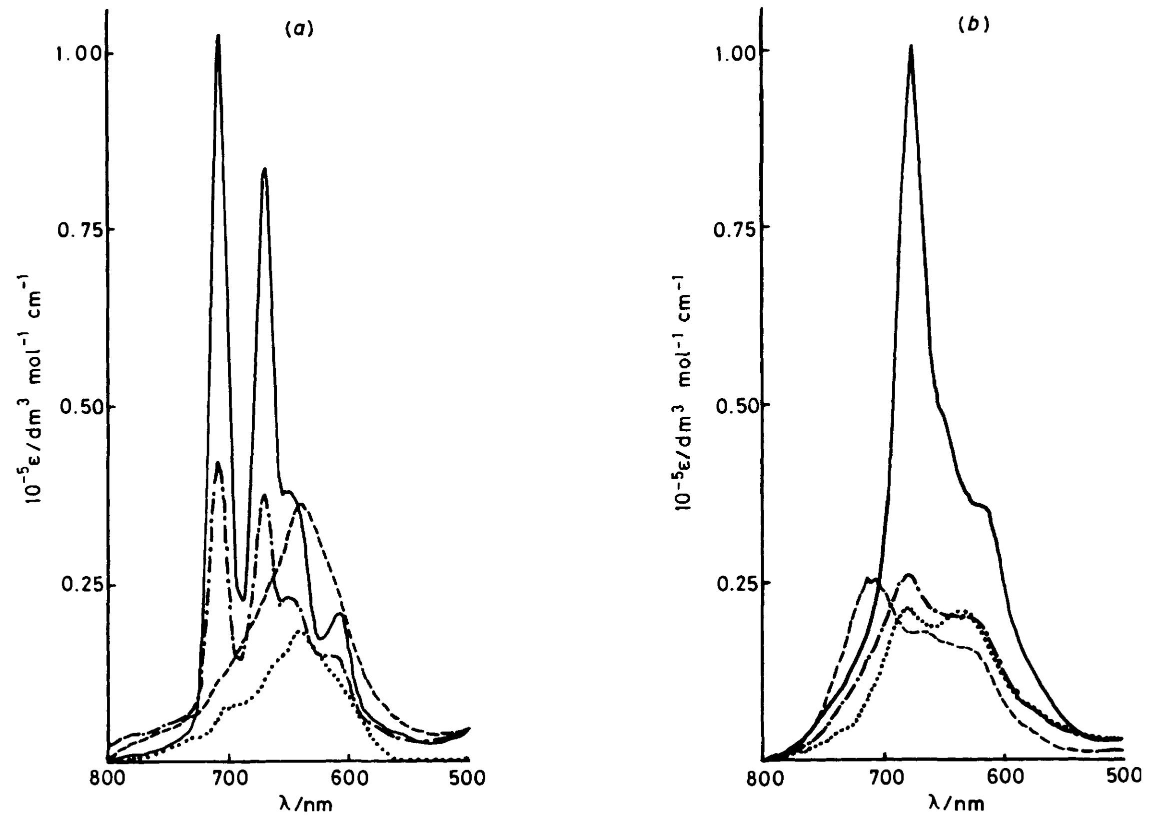


Figure 2. (*a*) Electronic spectra of H_2L (——) and its alkali metal adducts: H_2L·2NaClO$_4$ (– – –), H_2L·2KSCN (• • •), and H_2L·2NH$_4$SCN (–•–). (*b*) Electronic spectra of [CoL] (——) and its alkali metal adducts

Table 4. Solvent extraction[a] of alkali metal (M′) picrates into the organic phase (chloroform) at 25 °C[b]

	M′		
	Li^+	Na^+	K^+
Benzo-15-crown-5	0.9	18.2	33.7
H_2L	4.8	12.3	90.5
[CuL]	7.3	17.9	73.6
[CoL]	2.8	5.4	89.3
[NiL]	2.6	7.2	92.4
[FeL]	6.5	13.8	90.4

[a] Percentage extracted picrate. [b] Organic phase: [crown ether unit] 7.0 × 10^{-4} mol dm^{-3}. Aqueous phase: [M′OH] = 0.1 mol dm^{-3}, [picric acid] = 7.0 × 10^{-5} mol dm^{-3}.

dimerization.[1a] Since crown ethers are known to form relatively stable, sandwich-type complexes with alkali metal cations, dimerization is more easily accomplished when sodium or potassium cations are present. In the case of ammonium ion, similar changes occur in the spectra, but the shifts are not so distinct.

Fast atom bombardment mass spectrometry is a powerful tool for the analysis of polar labile materials such as phthalocyanines. The [ML] samples were used as solutions in a viscous liquid (thioglycerol–dichloromethane–trifluoroacetic acid as the matrix) and bombarded with a beam of high-energy xenon atoms (8 kV). Molecular ion species (Table 3) have been observed and provide confirmation for the proposed structures.

Table 5. Thermal properties of [ML] compounds

Compound	Initial decomposition temp. (°C)	Main decomposition temp. (°C)
Benzo-15-crown-5	150	270
H_2L	290	410
[CuL]	280	380
[CoL]	280	410
[NiL]	205	415
[FeL]	210	385

The values of the molecular ions show good agreement with the results of the theoretical isotopic distributions. The major fragment ions of H_2L are *m*/*e* = 1 276, 1 116, 460, 307, 154, and 89.

Solubility.—The novel [ML] compounds are relatively soluble in halogenated hydrocarbons, dmf, Me$_2$SO, aromatic hydrocarbons and slightly soluble in ethanol and tetrahydrofuran. Quantitative data for the solubilities of [ML] in chloroform are given in Table 2. Since it is known that phthalocyanines are only slightly soluble in solvents such as 1-chloronaphthalene, these solubility values in a non-aromatic solvent ($CHCl_3$) are noteworthy. Therefore, crown ether groups can be considered as more effective 'solubilizing' groups than others previously reported such as t-butyl-, methyl-, and dodecyl-ethers which have been shown to be more active in less symmetrically substituted phthalocyanines.[6]

Solvent Extraction of Alkali Metal Cations.—The alkali metal binding ability of [ML], having four crown ether units, was estimated by solvent extraction of alkali metal salts from water to chloroform.[17] Picrate was used as counter anion for all compounds. The results are recorded in Table 4. Examination of the data reveals the following results. (*i*) All four [ML] compounds exhibit the highest affinity for potassium among the alkali metal cations. (*ii*) A considerable change is observed for different metal ions in the phthalocyanine core.[18] (*iii*) Under these conditions the selectivity of [CoL] for potassium cation is the highest. The influence of the core transition metal ions on the binding properties of the crown ether groups is noteworthy but the present data do not enable us to predict the reason for this.

Thermal Properties.—Although the thermal stability of phthalocyanines is well known, benzo-15-crown-5 is not stable at temperatures above 300 °C.[19] Therefore the thermal properties of [ML] are interesting from the point of view of the crown ether groups. The thermal stabilities of [ML] were evaluated by thermogravimetric analysis (t.g.a.) and differential thermal analysis (d.t.a.) with a heating rate of 10 °C min^{-1} in a nitrogen flow. The initial and main decomposition temperatures are given in Table 5.

The d.t.a. curves exhibited exothermic changes for all [ML] complexes in the region investigated;[20] the curves do not show melting points. No obvious correlation between the transition metal ion in the phthalocyanine ring and the corresponding main decomposition temperatures could be estabished, while the initial decomposition temperature decreased in the order $H_2 > Cu > Co > Fe > Ni$. Catalytic properties of the central metal ions might be one of the reasons for these thermal decompositions. The high molecular weight of the [ML] compounds (*ca.* 1 300) implies that the sublimation of these compounds without any decomposition should not be expected, but we have accomplished their sublimation under high vacuum. This also indicates that the combination of the phthalocyanine core and the crown ether groups has formed thermally stable molecules.

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