J. Am. Chem. Soc. 1987, 109, 4261-4265

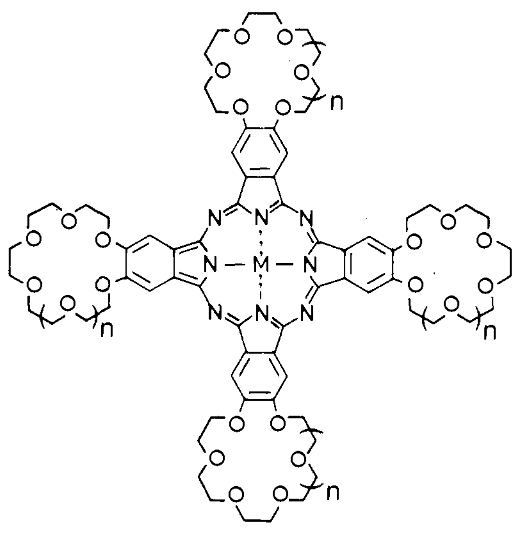
Synthesis and Aggregation Behavior of Hosts Containing Phthalocyanine and Crown Ether Subunits

Ot E. Sielcken, Marcus M. van Tilborg, Maarten F. M. Roks, Ron Hendriks, Wiendelt Drenth, and Roeland J. M. Nolte*

Contribution from the Department of Organic Chemistry, University at Utrecht, 3584 CH Utrecht, The Netherlands. *Received December 24, 1986*

Abstract: Four new organic hosts are described that contain a phthalocyanine core to which four crown ether rings are attached. These hosts include a free base phthalocyanine with 18-crown-6 rings and three copper phthalocyanines with 15-crown-5, 18-crown-6, and 21-crown-7 rings. The macrocycles are synthesized from benzo crown ethers in three steps. In solution the phthalocyanines tend to form aggregates. This aggregation is affected by the polarity of the solvent and the presence of alkali-metal salts, which coordinate to the crowns. Cations with diameters that match the diameters of the crown ether rings form 4:4 host-guest complexes with the new hosts. Complexes with 8:4 host-guest stoichiometry are formed when the diameters of the cations exceed that of the crown ether rings. Binding free energies of the copper phthalocyanine hosts are presented and compared to those of benzo crown ethers. The binding profiles support the results of UV-vis experiments; i.e., that large cations induce aggregation of the macrocycles.

Since the discovery of crown ethers by Pedersen, now 20 years ago,[1] hundreds of papers have been published dealing with the chemistry of these compounds.[2] An even larger number of papers have appeared on phthalocyanines and related macrocycles.[3] Until recently, no papers have been published describing hosts in which both type of ring systems are incorporated.[4] In the course of a program aimed at the development of new ion and electron carriers, we became interested in such mixed-ring systems as possible building blocks for the construction of ion channels. In previous papers we showed that ion channels can be synthesized by arranging crown ether rings in stacks.[5] The stacks remain in a fixed position with the help of a rigid polymer support. Another possible route leading to stacks of crown ether rings could be one in which phthalocyanine rings containing crown ether subunits are polymerized (Figure 1). By chosing different ligands L (e.g., pyrazine, –O–, CN^-) and metals M a great variety of cascade complexes is possible. These complexes can be expected to transport ions and electrons in the direction of the stacks.[5b,6] Here we report on phthalocyanines which have been functionalized with 15-crown-5, 18-crown-6, and 21-crown-7 rings: **1a–d**.[7] Their aggregation behavior in different solvents and in the presence of various alkali-metal salts is described. The construction of ion channels from **1a–d** will be the subject of a separate paper.



1

a, M=2H, n=1
b, M=Cu, n=0
c, M=Cu, n=1
d, M=Cu, n=2

Results

Synthesis. Brominating benzo-18-crown-6[1] (**2c**, Scheme I) with bromine and iron gave 4,5-dibromobenzo-18-crown-6 (**3c**, 53%). The latter compound was refluxed in DMF with 3 equiv of CuCN[8] and a catalytic amount of pyridine[9] to yield the dicyano derivative **4c** (68%). Refluxing **4c** in (dimethylamino)ethanol provided the free base **1a** (26%). Copper complex **1c** was prepared by heating **4c** in DMF with CuCN (36%). Compound **1c** can also be prepared directly from **3c** by treating the latter compound with an excess of CuCN. By similar methods phthalocyanines **1b** and **1d** were synthesized from benzo-15-crown-5 and benzo-21-crown-7, respectively, in overall yields of $\simeq$12%. Macrocycles **1a–d** are solids ranging in color from dark green to black. They are soluble in organic solvents and insoluble in water.

Aggregation. The visible absorption spectra of the free-base phthalocyanine **1a** in various solvents are shown in Figure 2. In chloroform three absorption bands at 700, 660, and 600 nm and a shoulder at 640 nm are visible. We attribute these bands to monomeric phthalocyanine.[10] In polar solvents, e.g., methanol, the spectrum changes and a new band appears at $\simeq$630 nm. This band can be ascribed to the presence of dimeric and oligomeric phthalocyanine species.[10] The metallophthalocyanine compounds **1b–d** show similar solvent-dependent absorption spectra: in apolar solvents a strong band is displayed at 675 nm with a shoulder at

---

(1) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017-7036.

(2) For a recent monograph see: *Progress in Macrocyclic Chemistry*; Wiley-Interscience: New York, 1979; Vol. 1, pp 1-276; 1981; Vol. 2, pp 1-347.

(3) For recent reviews on phthalocyanines see (a) Moser, F. H.; Thomas, A. L. *The Phthalocyanines*; CRC: Boca Raton, FL, 1983: Vols. 1 and 2. (b) Kasuga, K.; Tsidsui, M. *Coord. Chem. Rev.* **1980**, *32*, 67-95.

(4) A porphyrin-containing pendant crown ether rings has been described: Thanabal, V.; Krishnan, V. *J. Am. Chem. Soc.* **1982**, *104*, 3643-3650.

(5) (a) Nolte, R. J. M.; Van Beijnen, A. J. M.; Neevel, J. G.; Zwikker, J. W.; Verkley, A. J.; Drenth, W. *Isr. J. Chem.* **1984**, *24*, 297-301. (b) Kragten, U. F.; Roks, M. F. M.; Nolte, R. J. M. *J. Chem. Soc., Chem. Commun.* **1985**, 1275-1276.

(6) Diel, B. N.; Inabe, T.; Jaggi, N. K.; Lyding, J. W.; Schneider, O.; Hanack, M.; Kannewurf, C. R.; Marks, T. J.; Schwartz, L. H. *J. Am. Chem. Soc.* **1984** *106*, 3207-3214.

(7) Part of this work has been described in a short communication: Hendriks, R.; Sielcken, O. E.; Drenth, W.; Nolte, R. J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1464-1465. Since the submission of this communication related work was published independently by two other groups: Koray, A. R.; Ashen, V.; Bekaroglu, O. *J. Chem. Soc., Chem. Commun.* **1986**, 932-933. Kobayashi, Y. *Ibid.* **1986**, 1462-1463.

(8) Clark, H. J.; Duke, C. V. A.; Miller, J. M.; Brown, S. J. *J. Chem. Soc., Chem. Commun.* **1986**, 877-878.

(9) Friedman, L.; Hechter, H. S. *J. Org. Chem.* **1961**, *26*, 2522-2524.

(10) (a) Monahan, A. R.; Brado, J. A.; Deluca, A. F. *J. Phys. Chem.* **1972**, *76*, 446-449. (b) Cuellar, E. A.; Marks, T. J. *Inorg. Chem.* **1981**, *20*, 3766-3770.

0002-7863/87/1509-4261$01.50/0

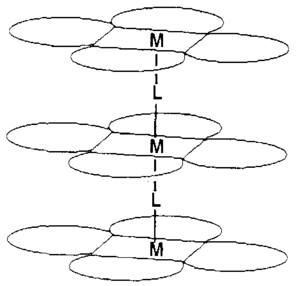


Figure 1. Cascade complexes from phthalocyanines containing crown ether subunits.

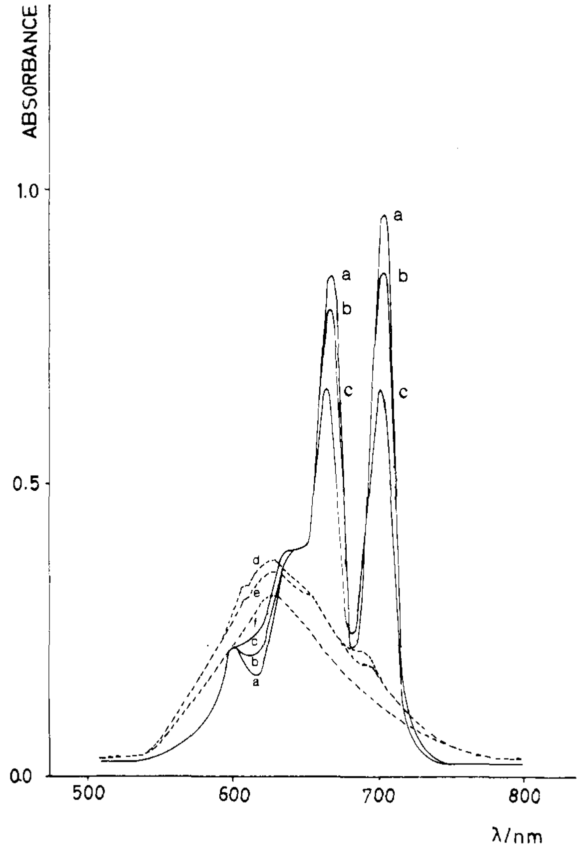


Figure 2. Visible absorption spectra of the free base phthalocyanine **1a** in various solvents: chloroform (a), dichloromethane (b), pyridine (c), ethanol (d), 1-butanol (e), methanol (f).

640 nm and a weak band at 610 nm; in polar solvents a broad band in the 630-nm region predominates (Figure 3). The bands at 675 and 630 nm can, likewise, be attributed to monomeric and oligomeric phthalocyanine species, respectively.

Addition of a metal salt, e.g., KCl, to solutions of phthalocyanines **1c** in dry chloroform causes the absorption band of the monomer at 675 nm to decrease in intensity whereas that of oligomeric species at ≃630 nm increases. The number of aggregated species formed is correlated to the type of salt added. In Table I we present the relative intensity of the 630-nm band of chloroform solutions of **1c** which had been equilibrated with various metal salts. Table I reveals that aggregation of the phthalocyanine in dry chloroform is cation as well as anion dependent. A different situation occurs when the chloroform solutions are saturated with water or when methanol is added. In these solvent mixtures the aggregation process seems to be anion independent. Cations still induce aggregation, but to a lesser extent (vide infra).

Complexation. The stoichiometry of complexation of various metal salts with metallophthalocyanines **1b–d** was investigated through UV–vis measurements in chloroform–methanol. The phthalocyanine was dissolved in chloroform–methanol, and the metal salt, dissolved in methanol, was added in small portions.

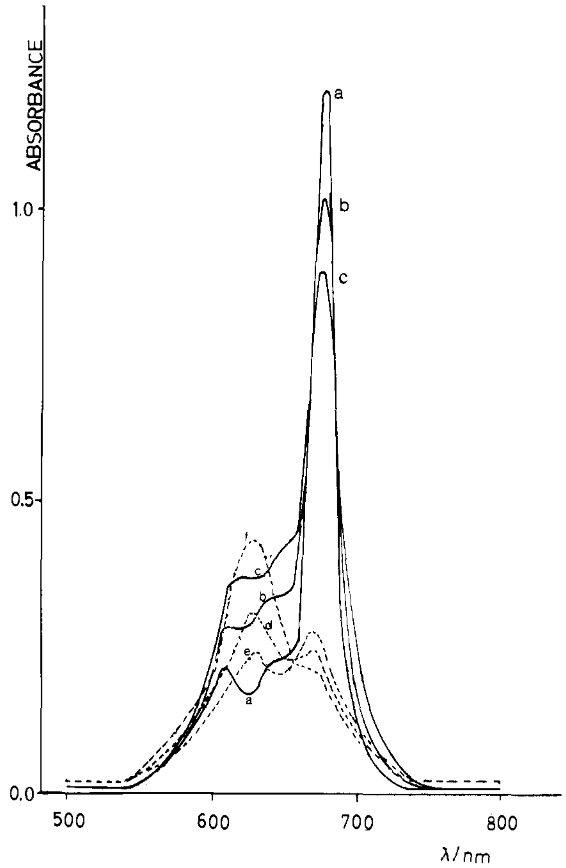


Figure 3. Visible absorption spectra of copper phthalocyanine derivative **1c** in various solvents: chloroform (a), dichloromethane (b), pyridine (c), ethanol (d), 1-butanol (e), methanol (f).

Scheme I

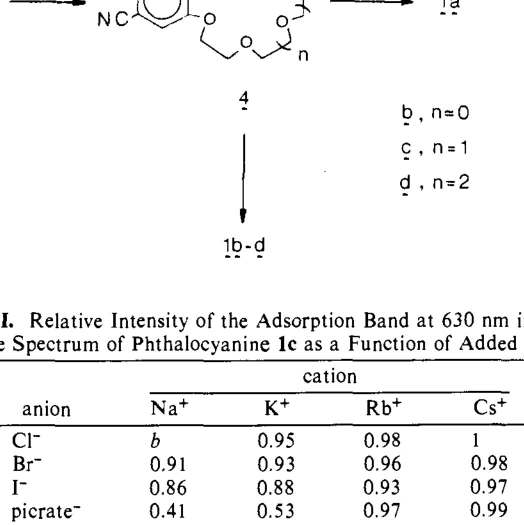


Table I. Relative Intensity of the Adsorption Band at 630 nm in the Visible Spectrum of Phthalocyanine **1c** as a Function of Added Salt[a]

	cation			
anion	Na^+	K^+	Rb^+	Cs^+
Cl^-	b	0.95	0.98	1
Br^-	0.91	0.93	0.96	0.98
I^-	0.86	0.88	0.93	0.97
picrate$^-$	0.41	0.53	0.97	0.99

[a] In chloroform at 25.0 °C; [**1c**] = 2.5×10^{-5} M; alkali-metal salt, 1 mmol; chloroform, 2.5 mL; the absorbances at 630 nm are calibrated to that of **1c**-CsCl (A = 0.235) for which 100% aggregation is observed; estimated error 3%. [b] The crowns are not able to dissolve NaCl.

Table II. Association Constants of Picrate Salt Phthalocyanine Complexes and of Model Compounds[a]

		$10^{-6}K_a$/M^{-1} (or M^{-2})	
host	cation of guest	1:1 complex	2:1 complex
Pc15C5 (**1b**)	Li^+	2.5	11
	Na^+	1.0	180
	K^+		160
	Rb^+		230
	Cs^+		90
B15C (**2b**)	Li^+	1.1	
	Na^+	1.45	
	K^+	0.66	
	Rb^+	0.14	
	Cs^+	0.04	
Pc18C6 (**1c**)	Li^+	5.8	
	Na^+	9.6	
	K^+	64.6	
	Rb^+	17.2	590000
	Cs^+	15.9	35000
B18C6 (**2c**)	Li^+	1.0	
	Na^+	0.62	
	K^+	21.6	
	Rb^+	6.6	
	Cs^+	1.7	
Pc21C7 (**1d**)	Li^+	15.9	
	Na^+	2.9	
	K^+	19.9	
	Rb^+	26.4	
	Cs^+	54.3	
B21C7 (**2d**)	Li^+	1.0	
	Na^+	0.45	
	K^+	1.7	
	Rb^+	4.0	
	Cs^+	4.0	

[a] In chloroform saturated with water at 25.0 °C.

After each addition the changes in absorbance at 630 and 675 nm were determined and plotted against the molar ratio of guest to host. Figure 4 shows two examples of the results. Those experiments indicate that in the solvent mixtures used compound **1b** forms 4:4 (crown–cation) complexes with Li^+ and Na^+, and 8:4 complexes with K^+, Rb^+, and Cs^+, compound **1c** forms 4:4 complexes with Li^+, Na^+, K^+ and 8:4 complexes with Rb^+ and Cs^+, and compound **1d** forms 4:4 complexes with all cations exclusively.

The association constants K_a of the complexes between **1b–d** and various cations were determined by the picrate extraction method in chloroform saturated with water at 25 °C.[11] Table II lists the K_a values for Li^+, Na^+, K^+, Rb^+, and Cs^+ picrates based on an assumed 1:1 crown–cation complex formation and values for the relevant cases based on an assumed 2:1 crown–cation ratio as well. For comparison this table also includes K_a values obtained for benzo-15-crown-5 (**2b**), benzo-18-crown-6 (**2c**), and benzo-21-crown-7 (**2d**).

Discussion

Our results indicate that the solvent, cations, and anions all have an influence on the aggregation behavior of phthalocyanine crowns **1a–d**. Because of the complexity of the system, only tentative conclusions can be drawn with respect to the individual contributions. For the copper-containing phthalocyanines aggregation increases in the solvent series $CHCl_3$ < CH_2Cl_2 < pyridine < 1-butanol < ethanol < methanol. This order parallels the order of increasing solvent polarity as measured by the dielectric constant or the E_T^N solvent polarity parameter.[12] A similar behavior is observed for the free-base phthalocyanine. Apparently, the copper center has qualitatively no influence on the aggregation process.

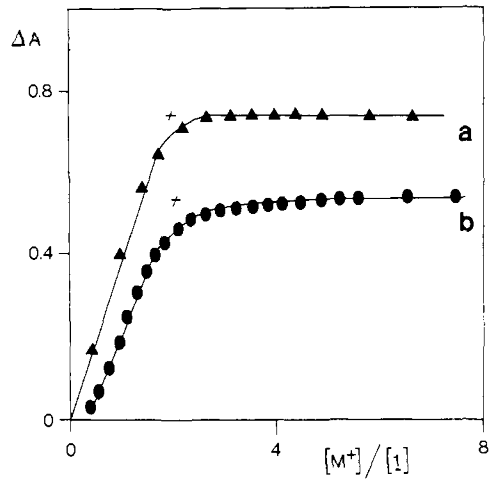
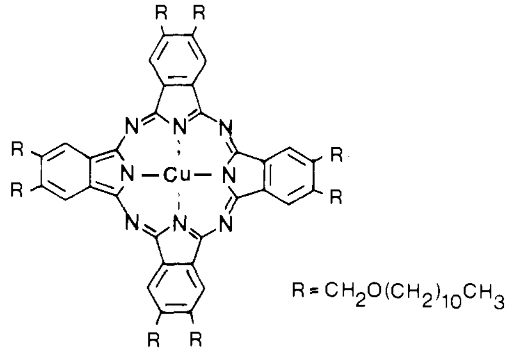


Figure 4. Absorbance increase at 630 nm ratio of cation to crown phthalocyanine: curve a, KCl and **1b** (5.8×10^{-5} M) in $CHCl_3$–MeOH (1:1.5 v/v); curve b, CsCl and **1c** (2.8×10^{-5} M) in $CHCl_3$–MeOH (1:1 v/v).

Aggregation induced by polar solvents is also observed with phthalocyanines that contain no crown ether rings, e.g., compound **5**, which we synthesized separately for comparison.[13,14] Apparently, under our conditions free crown ether rings do not affect the aggregation appreciably.



5

The effect cations and anions have on the aggregation behavior of the phthalocyanine crowns is most pronounced in solvents of low solvating power. The data in Table I show that for various combinations of cations and anions aggregation of **1c** in dry chloroform increases in the series Na^+ < K^+ < Rb^+ < Cs^+ and decreases in the series Cl^- > Br^- > I^- > picrate$^-$. Crown ethers and alkali-metal salts MX are known to form sandwich complexes in the solid state when the size of the cation exceeds that of the crown ether ring. The structure of these complexes is [crown–M–crown]$^+$X$^-$.[15] Sandwich complexes are formed less easily in solution.[16] In compound **1c**, however, four crown ether rings are available for complexation. They can act cooperatively and in this way promote sandwich-like aggregation in solution. Table I suggests that under our conditions with rubidium and cesium salts the aggregation is mainly determined by the cation: virtually no effect of the anion is observed. The opposite is true for the sodium and potassium salts. Here the effect of the anion is appreciable. We explain this anion effect in the following way. Because of their small sizes sodium and potassium can be completely encapsulated by a crown ether ring of **1c**. In this way the cations are sufficiently stabilized and no further profit is obtained

---

(11) (a) Koenig, K. E.; Lein, G. M.; Stueckler, P.; Kaneda, T.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3553–3566. (b) Nolte, R. J. M.; Cram, D. J. *J. Am. Chem. Soc.* **1984**, *106*, 1416–1420.

(12) (a) Reichardt, C.; Harbusch-Goernert, E. *Liebigs Ann. Chem.* **1983**, 721–743. (b) *Handbook of Chemistry and Physics*; CRC: Cleveland OH, 1968; p E-58.

(13) Piechocki, C.; Simon, J. *Nouv. J. Chim.* **1985**, *9*, 159–166.

(14) See also: (a) Gruen, L. C. *Aust. J. Chem.* **1972**, *25*, 1661–1667. (b) Waldmeyer, P.; Prijs, B. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 161–169.

(15) Poonia, N. S.; Bagdi, P.; Sidhu, K. S. *J. Incusion Phenom.* **1986**, *4*, 43–54.

(16) De Jong, F.; Reinhoudt, D. N. *Adv. Phys. Org. Chem.* **1980**, *17*, 279–433.

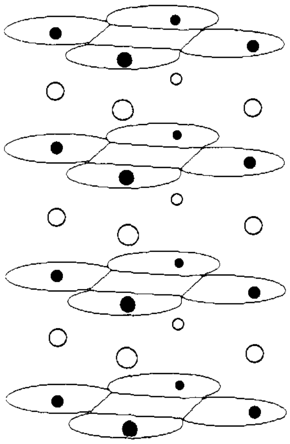


Figure 5. Anion intercalation in stacks of cation–crown phthalocyanine complexes. The cations are represented by full circles and the anions by circles filled with dots.

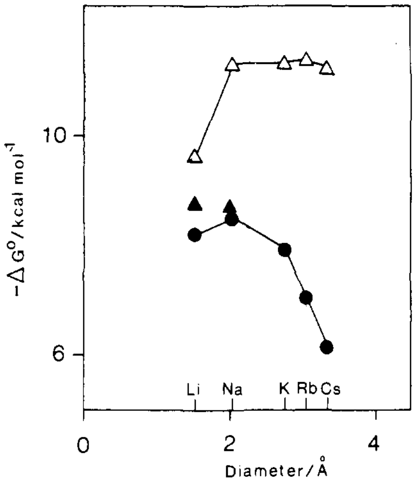


Figure 6. Free energies of binding of picrate salt –**1b** (▲) and of picrate salt –**2b** (●) complexes. Open triangles refer to 2:1 host–guest complexes.

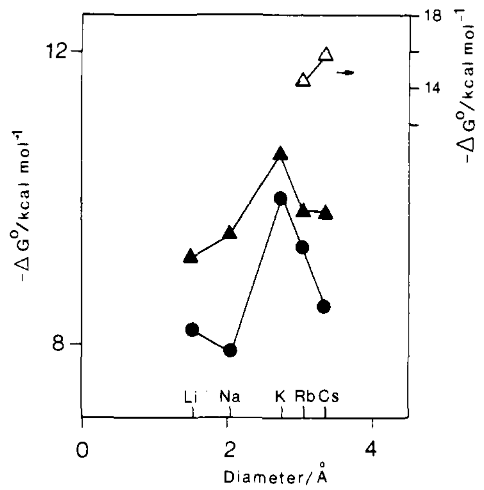


Figure 7. Free energies of binding of picrate salt –**1c** (▲) and of picrate salt –**2c** (●) complexes. Open triangles refer to 2:1 host–guest complexes.

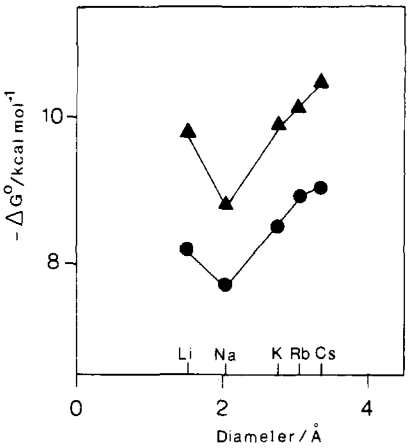


Figure 8. Free energies of binding of picrate salt –**1d** (▲) and of picrate salt –**2d** (●) complexes.

from aggregation. In apolar solvents the anions are present in ion pairs. Aggregation and, therefore, clustering of the ion pairs stabilize the system, in particular for the smaller anions in Table I. This clustering can be imagined to occur through intercalation in stacks of aggregated phthalocyanines as is shown schematically in Figure 5.

As expected, adding methanol to the chloroform solutions of **1** or saturating these solutions with water eliminates the effect of the anions. Only the effect of the cation remains; i.e., cations whose size exceed that of the crown ether ring cause aggregation of the phthalocyanine. Figure 4 shows that under the applied experimental conditions (concentration of **1** $(1-15) \times 10^{-5}$ M) the maximum number of phthalocyanine molecules that aggregate is two; i.e., four cations are sandwiched by eight crown ether rings. At higher phthalocyanine concentrations this number could exceed two. We were unable to test this as such experimental conditions exceed the possibilities of the UV–vis technique.

In Figures 6–8 the binding free energies, ΔG°, of metal picrate salt complexes of phthalocyanines **1b–d** are plotted against the size of the cation. These ΔG° values have been calculated by using the association constants of Table II. For comparison ΔG° values of the model compounds **2b–d** are also included in Figures 6–8. Benzo-15-crown-5 (**2b**) displays the expected binding profile for this type of host; i.e., the $-\Delta G^\circ$ value increases going from Li$^+$ to Na$^+$ and then gradually becomes smaller when the diameter of the guest molecule increases further. Compound **1b** shows a different behavior. It has a high affinity for Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ ions, but a relatively low affinity for Li$^+$ ions. Within the series Na$^+$, K$^+$, Rb$^+$, Cs$^+$ there is little or no structural recognition. This binding pattern supports the idea that large ions induce dimerization of the phthalocyanine rings.

The binding profiles of benzo-18-crown-6 (**2c**) and the phthalocyanine derivative **1c** have similar shapes. The $-\Delta G^\circ$ values calculated for the 1:1 host–guest complexation peak at K$^+$, as for this cation the size of the host and guest match (principle of complementarity).[17] The phthalocyanine-18-crown-6 rings, however, are stronger complexing agents than the benzo-18-crown-6 rings. For the cations tested the differences in ΔG° values vary between –0.5 and –1.6 kcal·mol^{-1}. The origin of this phenomenon is not clear yet. It could be that the picrate ions interact more strongly with the phthalocyanine rings of **1c** than with the benzene rings of **2c**.

The 21-membered-ring hosts **1d** and **2d** bind the larger ions better than the smaller ions as anticipated. The Li$^+$ ion is an exception to this pattern. This cation probably utilizes a molecule of water to fill the cavity of the host molecule. Just as with **1c**, the binding profile of **1d** has shifted to more negative ΔG° values as compared to that of the model compound. The differences in ΔG° values between corresponding complexes of **1d** and **2d** amount to –1 to –1.5 kcal·mol^{-1}.

Experimental Section

^{1}H NMR spectra were recorded on Varian EM-360 and Bruker AW-80 instruments. Infrared and UV–vis spectra were taken on Perkin–Elmer 283 and Perkin-Elmer 555 spectrometers, respectively. DSC thermograms were determined on a Seteram differential scanning calorimeter. FAB mass spectra were recorded on a VG ZAB 2F spectrometer. Elemental analyses were carried out by the Elemental Analytical Section of the Institute for Applied Chemistry TNO, Zeist, The Netherlands. Abbreviations used are as follows: s, singlet; d, doublet; t, triplet;

---

(17) Cram, D. J.; Trueblood, K. N. *Top. Curr. Chem.* **1981**, *98*, 43–106.

m, multiplet; sh, shoulder; v br, very broad.

Benzo-15-crown-5 (2b), benzo-18-crown-6 (2c), and benzo-21-crown-7 (2d) were prepared according to literature procedures.[1]

4,5-Dibromobenzo-18-crown-6 (3c). To a mixture of 20 g (64 mmol) of **2c**, 0.5 g of iron powder, and a catalytic amount of I_2 in 200 mL of dry CH_2Cl_2 was added at 0 °C over a period of 2 h 7.0 mL (0.137 mol) of bromine. The reaction mixture was stirred for 16 h at room temperature, filtered, and poured into 200 mL of 10% aqueous NaOH. The organic layer was separated, washed with water (3 × 200 mL), dried ($MgSO_4$), and concentrated under vacuum to a brown oil. The oil was extracted with dry hexane (3 × 200 mL). The combined hexane extracts were concentrated and cooled to 0 °C, leaving a colorless solid: yield 16 g (53%); mp 78–81 °C; IR (KBr) 1130–1050 (COC), 650 (ArBr) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.6–4.2 (m, 20 H, CH_2O), 6.85 (s, 2 H, ArH).

4,5-Dicyanobenzo-18-crown-6 (4c). A mixture of 10.1 g (21 mmol) of **3c**, 5.7 g (64 mmol) of CuCN, and 1 mL of pyridine in 100 mL of DMF was refluxed, while stirring, for 20 h under an atmosphere of dry nitrogen. The mixture was cooled, poured into 400 mL of 25% aqueous ammonia, and extracted with $CHCl_3$ (3 × 200 mL). The combined organic extracts were washed with water (3 × 300 mL), dried ($MgSO_4$), and concentrated. The resulting solid was purified by column chromatography (neutral alumina, eluent $CHCl_3$) to give a colorless solid: yield 5.5 g (71%); mp 127–131 °C; IR (KBr) 2235 ($C\equiv N$), 1150–1030 (COC) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.6–4.1 (m, 20 H, CH_2O), 6.95 (s, 2 H, ArH).

4,5,4′,5′,4″,5″,4‴,5‴-Tetrakis(1,4,7,10,13,16-hexaoxahexadecamethylene)phthalocyanine (1a). A solution of 1.2 g (3.3 mmol) of **4c** in 2 mL of (dimethylamino)ethanol was refluxed for 20 h. The solvent was evaporated and the resulting dark green, almost black powder was extracted with boiling toluene and subjected to column chromatography (neutral alumina, eluent $CHCl_3$–MeOH (10:1 v/v): yield 0.31 g (26%) of **1a**; mp > 200 °C; FAB MS *m/e* 1451 (M^+); UV–vis ($CHCl_3$) λ_{max} (log ϵ) 700 (4.60), 660 (4.56), 640 (sh), 600 (3.92); IR (KBr) 3295 (N–H), 2905–2870 (CH), 1120–1050 (COC), 1025 (NH) cm^{-1}; ^1H NMR ($CDCl_3$) δ −4.1 to −3.8 (v br, 2 H, NH), 3.5–4.4 (m, 80 H, CH_2O), 7.7 (s, 8 H, ArH); Anal. Calcd for $C_{72}H_{90}N_8O_{24}$: C, 59.67; H, 6.25; N, 7.72; O, 26.46. Found: C, 59.7; H, 6.51; N, 7.5; O, 26.3.

(4,5,4′,5′,4″,5″,4‴,5‴-Tetrakis(1,4,7,10,13,16-hexaoxahexadecamethylene)phthalocyanine)copper(II) (1c). A mixture of 1.2 g (3.3 mmol) of **4c** and 1.0 g (11 mmol) of CuCN in 6 mL of DMF was refluxed for 36 h while stirring. The mixture was poured into 50 mL of 25% aqueous ammonia and extracted with $CHCl_3$ (3 × 50 mL). The combined extracts were washed with water (3 × 100 mL), dried ($MgSO_4$), and evaporated. The resulting green, almost black, powder was extracted with boiling toluene and subjected to column chromatography (neutral alumina, eluent $CHCl_3$–MeOH (10:1 v/v)) to give 0.45 g (36%) of **1c**; mp > 250 °C; FAB MS *m/e* 1512, 1514 (M^+, Cu isotopes); UV–vis ($CHCl_3$) λ_{max} (log ϵ) 675 (4.63), 644–652 (sh), 610 (3.90); IR (KBr) 2900–2865 (CH), 1110–1052 (COC) cm^{-1}. Anal. Calcd for $CuC_{72}H_{88}N_8O_{24}$: C, 59.66; H, 6.12, N, 7.75; O, 26.49. Found: C, 59.0; H, 6.2; N, 8.0; O, 26.9 (different samples gave varying results).

4,5-Dibromobenzo-15-crown-5 (3b). This compound was synthesized from benzo-15-crown-5 (**2b**) as described for **3c**: yield 63%; IR (KBr) as for **3c**; ^1H NMR ($CDCl_3$): δ 3.6-4.2 (m, 16H, CH_2O), 6.9 (s, 2 H, ArH).

(4,5,4′,5′,4″,5″,4‴,5‴-Tetrakis(1,4,7,10,13-pentaoxatridecamethylene)phthalocyanine)copper(II) (1b). A mixture of 0.425 g (1 mmol) of **3b**, 0.45 g (5 mmol) of CuCN, and 0.15 mL of pyridine in 2 mL of DMF was refluxed for 20 h. Aqueous ammonia was added, and the mixture was stirred for 1 h. The resulting solution was extracted with chloroform. The organic layer was concentrated, and the black solid material that resulted was successively extracted with toluene and ether. The dark green solid was purified by column chromatography (neutral alumina, eluent $CHCl_3$–MeOH (10:1 v/v)) yield 0.115 g (34%) of **1b**; mp >250 °C; FAB MS, *m/e* 1240, 1242 (M^+, Cu isotopes); UV–vis ($CHCl_3$) and IR (KBr) as for **1c**. Anal. Calcd for $CuC_{56}H_{72}N_8O_{20}$: C, 57.13; H, 6.17; N, 9.52; O, 27.18. Found: C, 57.3; H, 9.6; N, 6.5; O, 26.5 (different samples gave varying results).

4,5-Dibromobenzo-21-crown-7 (3d). This compound was synthesized from benzo-21-crown-7 (**2d**) as described for **3c**: yield 43%; IR (KBr) as for **3c**; ^1H NMR ($CDCl_3$) δ 3.4–4.3 (m, 24 H, CH_2O), 6.82 (s, 2 H, ArH).

4,5-Dicyanobenzo-21-crown-7 (4d). This compound was synthesized from **3d** as described for **4c**: yield 62%; IR (KBr) as for **4c**; ^1H NMR ($CDCl_3$) δ 3.4–4.2 (m, 24 H, CH_2O), 6.95 (s, 2 H, ArH).

(4,5,4′,5′,4″,5″,4‴,5‴-Tetrakis(1,4,7,10,13,16,19-heptaoxanonadecamethylene)phthalocyanine)copper(II) (1d). This compound was synthesized from **4d** as described for **1b**: yield 41%; mp >250 °C; UV–vis ($CHCl_3$) and IR (KBr) as for **1c**. Anal. Calcd for $CuC_{80}H_{104}N_8O_{28}$: C, 59.11; H, 6.45; N, 6.89; O, 27.55. Found: C, 58.0; H, 6.4; N, 8.2; O, 27.4 (different samples gave varying results).

Determination of K_a and $\Delta G°$ Values. The K_a values were determined by the picrate extraction technique from H_2O into $CHCl_3$ at 25 °C as described in the literature.[11] The $\Delta G°$ values were calculated from the K_a values; the estimated errors are 4%.[11]

Acknowledgment. This research was supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from The Netherlands Organization for the Advancement of Pure Research (Z.W.O.).