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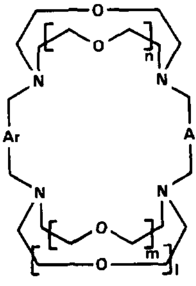
CATION BINDING BY A CROWN-CAPPED PORPHYRIN

Neil M Richardson and Ian O Sutherland*
Department of Organic Chemistry, University of Liverpool,
PO Box 147, Liverpool L69 3BX
Patrick Camilleri* and Janet A Page
Shell Research Ltd., Sittingbourne Research Centre, Sittingbourne ME9 8AG

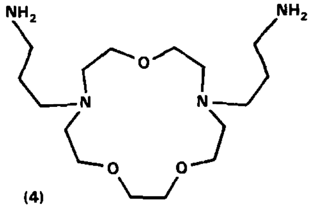
SUMMARY: The crown ether capped metalloporphyrins (6) form complexes with metal cations; complex formation may be detected by fluorescence quenching for (6, M=ZnII or CuII) and paramagnetic guest cations or, in some cases, by FAB mass spectrometry. Complexation with alkyl ammonium cations was also examined using absorption spectrometry.

The chemical and physical properties of a wide range of fenced, bridged, and capped metalloporphyrins have been studied[1] in the search for simple chemical models for haemoglobins and the cytochromes. Recently a porphyrin-bridged crown ether has been used as a synthetic receptor molecule[2]. We have previously[3] used the tricylic crown ether systems (1) as ditopic receptors in which both active sites are potential cation receptors; related ditopic receptors having two positively charged receptor sites have also been used as selective hosts for di-anions[4]. We now wish to describe a ditopic receptor (2) in which the two receptor sites are appropriate for a cation and an anion respectively. The cation receptor is an aza crown ether and the anion receptor is a metalloporphyrin. The ditopic receptor (2) is similar to a capped porphyrin (3) which has been studied as a haemoglobin model[5]. The host (2)[6] was synthesised (50% yield) by the reaction[7] of the tetra-amine (4) with the bis-*p*-nitrophenyl ester (5) in pyridine at 55°C. Metallated derivatives of (2), shown diagramatically in (6), were readily prepared by conventional metallation procedures.
The metalloporphyrin (6) is potentially a host for anionic and cationic species, as indicated in (7), and initially complexes with a variety of metal cations were investigated. Bimetal complexes (7, X=metal) were not obtained as crystalline compounds but evidence for their formation was obtained from the quenching of the fluorescence spectrum of the porphyrins (6, M=ZnII or CuII) in the presence of the metal ions listed in Table 1; association constants and details of fluorescence quenching are given in the Table. The degree of

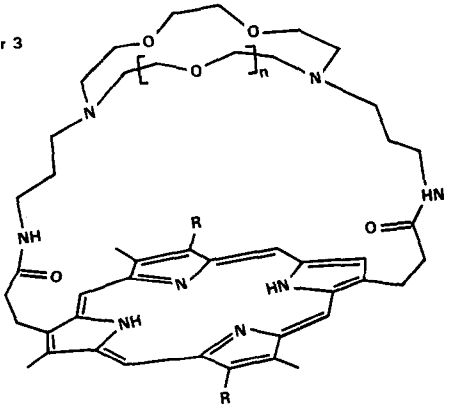


(1)

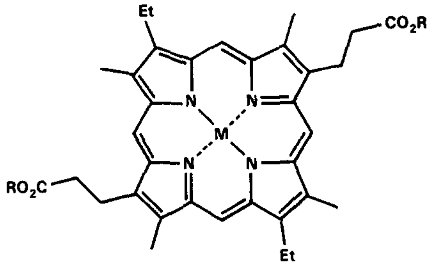
n = 1 or 2
l,m = 1, 2 or 3



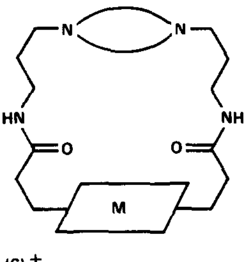
(4)



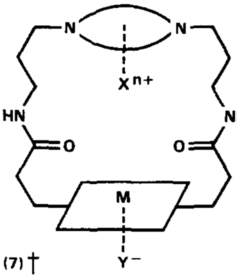
(2) R = Et, n = 1
(3) R = n-hexyl, n = 2



(5) R = $-C_6H_4-NO_2$, M = H_2
(8) R = Et, M = Zn



(6)†



(7)†

quenching is thought to depend mainly on two factors: the extent of complexation and the quenching ability of the metal ion in the crown ether cavity. Fluorescence quenching was observed only for paramagnetic guest metal cations [X^{n+} in (7)] and it seems likely that the quenching is associated with the magnetic effect[8] of the guest cation since the effect was not observed for Na^+, Zn^{2+}, Mg^{2+} or Ba^{2+} (cf. refs 8 and 9), although electron transfer cannot be completely ruled out at this stage[10]. The values for association constants have relative magnitudes similar to those reported for simple diaza crown ethers[11].

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† In formulae (6) and (7) the rectangle represents the porphyrin system and the elipse represents the aza crown ether.

Table 1

Association constants and fluorescence quenching for metal ion complexation by capped porphyrin (6)

M' salt	Ka/M^{-1} [a,c,d]	$I_{ML}\%$ [b,c,d]	Ka/M^{-1} [d,e]
$Cu(II)Cl_2$	3.6×10^4	86	
$Cu(II)(OAc)_2$	9.3×10^4	88	1.5×10^4
$Fe(III)Cl_3$	1.1×10^4	69	8.0×10^3
$Fe(II)SO_4$	4.2×10^4	90	4.1×10^3
$Mn(II)(OAc)_2$	2.2×10^3	83	4.5×10^2
$Ni(II)(OAc)_2$	1.4×10^3	94	
$Co(II)(OAc)_2$	7.2×10^2	83	

[a] Obtained by non-linear regression analysis of fluorescence quenching for different concentration of (6) and M' salt in methanol.

[b] Limiting intensity when all the ligand is bound.

[c] Data for (6, M=Zn).

[d] Excitation wavelength 540nm (M=Zn) and 500nm (M=Cu) and emission recorded from 557-700nm (M=Zn) and 525-700nm (M=Cu). Quenching at 567nm (M=Zn) and 531nm (M=Cu).

[e] Data for (6, M=Cu).

Table 2

Association constants for ammonium salt complexation by capped porphyrin (6, M=ZnII) and zinc porphyrin (8)

Guest salt	Ka/M^{-1} [a]
$^{+}NH_3(CH_2)NH_2\ ClO_4^{-}$	8.3×10^3 (253)
$^{+}NH_3(CH_2)NH_2\ ClO_4^{-}$	4.4×10^3 (154)
$^{+}NH_3(CH_2)NH_2\ ClO_4^{-}$	5.1×10^3 (<100)[b]
$^{+}NH_3(CH_2)_2{}^{+}NH_3\ 2ClO_4^{-}$	6.2×10^3 (<100)[b]
$^{+}NH_3(CH_2)_3{}^{+}NH_3\ 2ClO_4^{-}$	8.7×10^3 (<100)[b]
$^{+}NH_3CH_2CH_3\ ClO_4^{-}$	7.7×10^2 (<100)[b]

[a] Based upon change in absorbance at 578nm on addition of a methanol solution of the salt (0.001 to 0.5M) to a solution of the zinc porphyrin (2×10^{-5}M) in chloroform-methanol (9:1). The data in parenthesis refer to zinc porphyrin (8).

[b] No effect on spectrum on addition of 0.5M solution of guest salt.

Metal complexes may also be examined using FAB mass spectrometry[12]; in particular equimolar mixtures of the zinc porphyrin (6, M=ZnII) and CuII, FeII and FeIII triflate salts give peaks in the FAB mass spectrum (Xenon atom bombardment at 8kV, glycerol or 2,4-di-*t*-pentylphenol matrix) corresponding to the bimetal species $[6,(M=Zn).M']^+$ (M'=Cu,Fe). In the presence of an excess of $Zn(OAc)_2$ to the zinc porphyrin, a similar result is obtained $[6,(M=Zn).M']^+$ (M'=Zn). In addition to these bimetal complexes with the zinc porphyrin (6, M=ZnII) similar bimetal complexes have been observed by FAB mass spectrometry for the copper porphyrin (6, M=Cu) and the iron porphyrin [6, M=FeIII (OAc)] with CuII triflate. The zinc porphyrin (6, M=ZnII) was also examined as a host for alkylammonium cations, using changes in the absorption spectrum (450-600nm) in the presence of the added salt to detect complex formation and determine association constants. The results of this study (Table 2) indicate that association constants are similar for the mono- and di-perchlorate salts of the diamines $NH_2(CH_2)_nNH_2$ (n=2,3 and 4) and ethylammonium perchlorate. Thus, complexation probably involves attachment of the perchlorate counterion at the metal and of a cationic species at the crown ether [as in (7)], giving enhanced association constants as compared with the uncapped porphyrin (8). Further studies are in progress to determine the nature of this complexation.

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