89. Anion Selectivity of Metalloporphyrins in Membranes

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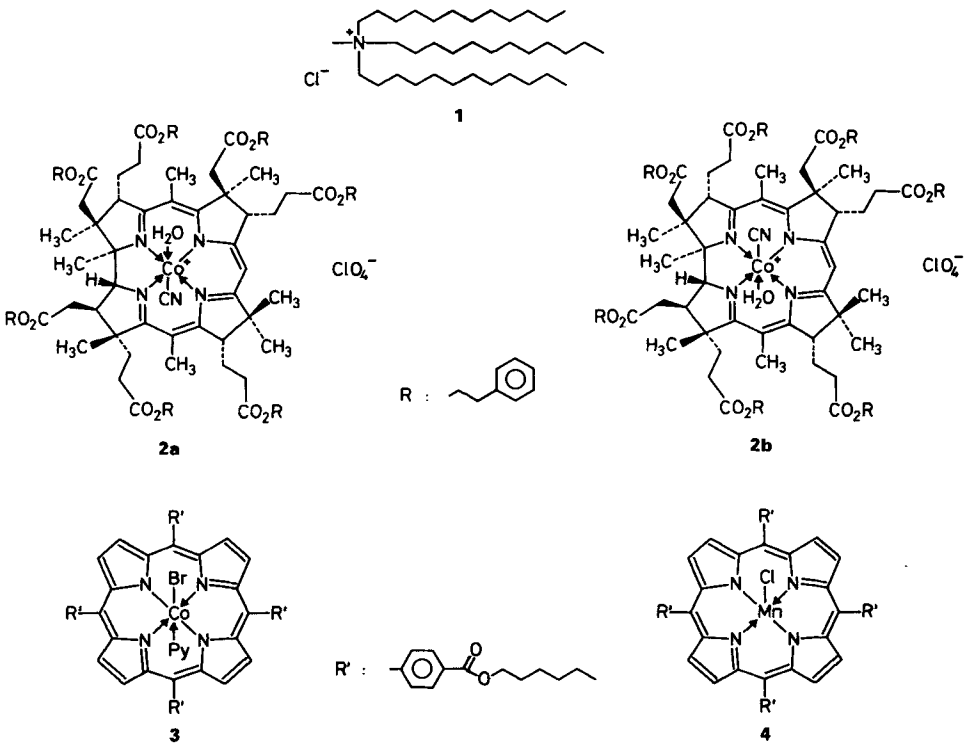
Lipophilic Co(III) and Mn(III) complexes of 5,10,15,20-tetrakis[4-(hexyloxycarbonyl)phenyl]porphyrin act as positively charged carriers for anions and induce anion selectivities in membranes clearly deviating from the sequence of classical anion exchangers. Different anion selectivities are observed for the Co(III) and Mn(III) porphyrins.

Introduction. – Certain derivatives of vitamin B_{12} such as **2a** and **2b** were shown to behave as positively charged carriers for anions which induce an anion selectivity sequence in membranes clearly deviating from that of classical anion exchangers such as tridodecyl(methyl)ammonium chloride (**1**; so-called *Hofmeister* series [1]) [2–4]. So far, such a selectivity behaviour has only been observed for systems with a Co(III) center complexed by a corrin-ring system [2], which is known to exhibit exceptionally fast exchange kinetics for axial ligands at a Co(III) ion [5] [6]. A cleavage of the corrin-ring system led to a loss in anion selectivity [2], presumably due to a slow-down of the exchange kinetics for the axial ligands.

We hoped to expand the application of (transition) metal complexes as anion-selective charged carriers in membranes by exploiting the structurally related and more versatile metalloporphyrins. To our knowledge, these compounds have not yet found use as selective anion carriers in membranes (see, however, the finding that hemin acts as anion exchanger in collodion membrane electrodes [7]). Indeed, fast-exchange kinetics for axial ligands seems to be typical also for certain metalloporphyrins, *e.g.* with similar rates in Co(III) porphyrins and in vitamin-B_{12} derivatives [8].

An extended study on a series of commercially available metalloporphyrins such as 5,10,15,20-tetraphenyl- and octaethylporphyrins indicated their usefulness as anion carriers in membranes [9]. Lack of EMF stability and lifetime of membrane electrodes with these carriers induced us to investigate more lipophilic porphyrins. Here we report on the synthesis and characterization in membranes of the Co(III) and Mn(III) complexes of such a suitable porphyrin.

Results and Discussion. – Based on our experience with the corrinoid Co(III) complexes derived from vitamin B_{12} [2–4], we expected the tetrahexyl ester of the commercially available 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin to be suitably lipophilic for the solvent polymeric membranes used. Esterification of this porphyrin and incorporation of the metal ions by the 'acetylacetonate method' [10] to give the crystalline



complexes **3** and **4** proceeded cleanly. The porphyrins **3** and **4**, and their metal-free precursor were fully characterized spectroscopically.

Anion selectivities were measured potentiometrically using solvent polymeric membranes with the plasticizer decane-1,10-diyl-diglutarate-bis(1-butyl-pentyl)ester *(Fig.)*. Selectivity factors describing the preference by the membrane for an interfering ion X^- relative to Cl^- have been determined by the separate-solution method [11]. The classical anion exchanger tridodecyl(methyl)ammonium chloride (**1**) induces a selectivity sequence in membranes corresponding to the *Hofmeister* series (*Column 1* in the *Fig.*). In contrast, the plasticized PVC membrane without an anion-selective component (blank membrane) exhibits insignificant anion selectivity (*Column 5* in the *Fig.*). Membranes based on a *ca.* 2:1 mixture **2** composed of the two isomeric corrinoid Co(III) complexes **2a** and **2b** show selectivities that clearly deviate from those of membranes with the lipophilic quaternary ammonium salt **1**. Indeed, highly selective NO_2^- electrodes have been realized on the basis of such Co(III) corrins [3] [4]. The lipophilic Co(III) porphyrin **3** yields an anion selectivity in membranes resembling that of the Co(III) corrin mixture **2** (with a pronounced deviation for I^-; *cf. Columns 2* and *3* in the *Fig.*). Replacement of Co(III) at the porphyrin center by Mn(III) yielding **4**, leads to very different membrane selectivities *(Column 4* in the *Fig.)*.

The data in the *Fig.* indicate that the Co(III) and Mn(III) porphyrins **3** and **4** behave as anion-selective ionophores [2]. This behaviour is corroborated by the electrode re-

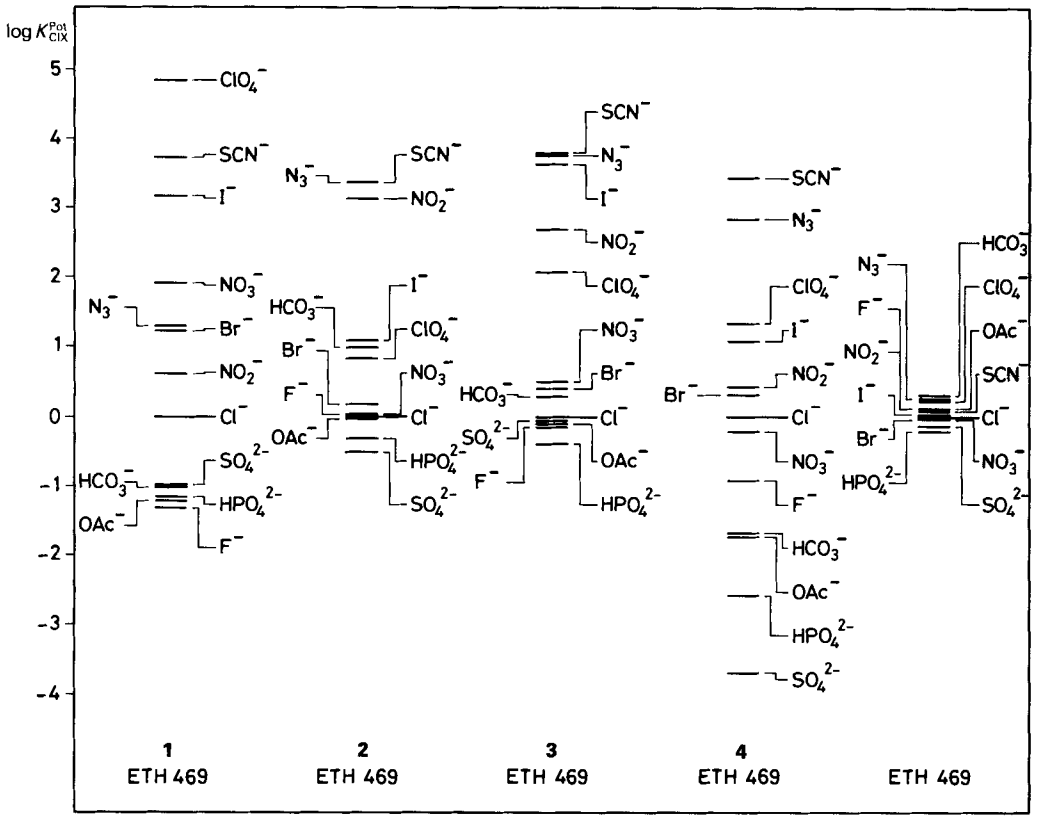


Fig. *Selectivity factors, log* K^{Pot}_{ClX}, *for solvent polymeric membranes with decane-1,10-diyl-diglutarate-bis-(1-butylpentyl)ester (ETH 469) as plasticizer.* A ligand-free membrane (last column) is compared with membranes containing the different components **1**–**4** (separate-solution method, *Tris*/H_2SO_4-buffered solutions of 0.1M sodium salts, pH 7.40 ± 0.05). Three electrodes of the same type have been characterized. The standard deviation of the selectivity factors (log K^{Pot}_{ClX} units) is ±0.1 for the preferred and ±0.2 for the rejected anions, respectively.

Table. *Slopes of the Linear Range of Electrode Functions for Various Anions.* Values in brackets indicate range of linear regression (log *a* units).

Anion	Ion-selective component[a])			
	1	**2**	**3**	**4**
ClO_4^-	− 56.8 ± 0.8%	− 44.9 ± 2.8%	− 35.3 ± 6.0%	− 50.4 ± 3.0%
	(− 4.1 to − 1.0)	(− 4.1 to − 1.0)	(− 3.1 to − 1.0)	(− 5.1 to − 1.0)
SCN^-	− 55.3 ± 1.9%		− 56.3 ± 11.9%	− 56.0 ± 1.2%
	(− 4.1 to − 1.0)		(− 3.6 to − 2.5)	(− 4.1 to − 1.0)
NO_2^-	− 46.2 ± 1.2%	− 56.9 ± 2.3%	− 42.3 ± 6.5%	
	(− 4.1 to − 1.0)	(− 4.5 to − 1.0)	(− 3.6 to − 2.0)	
Cl^-				− 42.1 ± 6.3%
				(− 3.6 to − 1.0)

[a]) Membrane compositions, see *Exper. Part.*

sponse functions summarized in the *Table*. For the most preferred ions (*e.g.* SCN^-, NO_2^-), the slope of the electrode response is close to the theoretical value (−58.2 mV). Due to a sigmoid electrode response function, some other ions exhibit a sub-*Nernstian* slope of the electrode response function even over a short activity range.

These data demonstrate the usefulness of lipophilic metalloporphyrins as components for anion-selective sensors[1]). They confirm our observation with commercially available, but less lipophilic metalloporphyrins [9]: Different porphyrin-bound metal centers lead to different selectivities deviating from the selectivity sequence of classical anion exchangers. In analogy to the situation encountered with the lipophilic Co(III) corrins [2–4], the relevant contribution of the metalloporphyrins to the anion selectivity of the membrane is presumably the tendency of the metal center to coordinate the anion[2]).

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Experimental Part

General. Chemicals and solvents: *o*-nitrophenyl octyl ether (*o*-NPOE; *Fluka, puriss. p.a.*, for ion-selective electrodes); *m*-nitrobenzyl alcohol (NOBA); decane-1,10-diyl-diglutarate-bis(1-butylpentyl)ester (ETH 469; *Fluka, p.a.*, for ion-selective electrodes); tridodecyl(methyl)ammonium chloride *(Polysciences Inc.)*; poly(vinyl chloride) (PVC; *Fluka, purum p.a.*, for ion-selective electrodes); 2-amino-2-hydroxymethyl-1,3-propanediol *(Tris; Fluka, puriss. p.a.)*; 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin *(Strem Chemicals Inc.)*; *p*-toluenesulfonic acid *(Fluka, puriss. p.a.)*; 1-hexanol (*Fluka, puriss.*, distilled); manganese(II) acetylacetonate *(Fluka, techn.)*; cobalt(II) acetylacetonate *(Fluka, purum)*, hydrobromic acid (48%; *Fluka, puriss. p.a.*); CH_2Cl_2, MeOH, AcOEt, THF, pyridine, and Et_2O (all *Fluka, puriss. p.a.*); CH_2Cl_2 and THF were filtered through aluminium oxide before use (aluminium oxide: *Woelm B.* Akt. I); H_2SO_4, conc. *(Merck, p.a.)*. TLC: silica-gel plates (*Merck*, Art. 5735). EMF *measurements:* deionized H_2O, doubly distilled from quartz vessels; sodium salts of high purity were used throughout *(Merck, p.a.*, except for $NaNO_2$: *Merck, 'reinst'*; NaSCN: *Fisher Scientific Co.)*. UV/VIS: *Perkin-Elmer PE 555* or *Uvikon 810*; λ_{max} (log ε) in nm. IR: *Perkin-Elmer PE 125*; in $CHCl_3$; cm^{-1}, relative intensities. ^{1}H-NMR: *Bruker WM-300*; in $CDCl_3$; 300.14 MHz; TMS internal reference, chemical shifts in ppm with δ(TMS) = 0; coupling constant J in Hz. Fast-atom-bombardment (FAB) MS: *Kratos AEI MS-50* fitted with *M*-scan FAB-system; Ar bombardment at 8–10 kV; *m/z* (relative intensities).

EMF Measurements. The solvent polymeric membranes were prepared according to [13] using 1% *(w/w)* of ligand, 66% *(w/w)* of ETH 469 (respectively 67% *(w/w)* of ETH 469 for membranes without ligand) and 33% *(w/w)* of PVC. Cell assemblies of the following type were used: Hg; Hg_2Cl_2, KCl (satd.) | 1M LiOAc | sample soln. || membrane || inner filling soln., AgCl; Ag. The inner filling soln. was 0.01M NaCl except for liquid-membrane electrodes containing ligands **2** or **3** where 0.01M $NaNO_2$ was added. For details on the membrane preparation and evaluation of the EMF measurement, see [13]. The EMF measuring equipment is specified in [3]. Changes in the liquid-junction potential and the activity coefficients were calculated with parameters given in [14–16]. The selectivity factors, $K^{Pot}_{Cl,X}$, were obtained by the separate-solution method [11] in 0.1M solns. of the corresponding Na salts. The solns. were buffered using 0.01M *Tris* adjusted to pH 7.40 ± 0.05 with conc. H_2SO_4. The electrode functions were measured in unbuffered solns. When not in use, the electrodes were stored in 0.01M *Tris*. All measurements were performed at 20 ± 0.5°.

5,10,15,20-Tetrakis[4-(hexyloxycarbonyl)phenyl]porphyrin (**5**). A soln. of 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (500 mg, 0.63 mmol) and TsOH (1.6 g, 9.3 mmol) in 1-hexanol (20 ml) was heated to 120° for 7 h under N_2. TLC then indicated complete esterification. The alcohol was removed at 40–50°/0.05 Torr, and the residue was dissolved in CH_2Cl_2 (100 ml) and shaken first 3 times with 100 ml of neutral 1M phosphate buffer, then

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[1]) It is of interest in this context, that recently a sensor for salicylate was found based on chloro[5,10,15,20-tetraphenylporphinato]manganese(III) [12].

[2]) This is supported by preliminary UV/VIS studies [9].

with 100 ml of H_2O. The org. phase was filtered (paper filter) and concentrated to *ca.* 3 ml. Addition of *ca.* 100 ml of MeOH led to the precipitation of the product, that was washed with small amounts of MeOH and dried (r.t./10^{-3} Torr, 2 h) to give 530 mg (74.3%) of **5** as a violet powder (uniform by TLC). The raw product was dissolved in 100 ml of hot AcOEt. Overnight, a first crop of 190 mg of red-violet crystals separated out. The mother liquour was concentrated and yielded a second crop of crystalline **5** (210 mg). After drying (r.t./10^{-3} Torr, 16 h), 400 mg (56.1%) of crystalline **5** was obtained. Material from the second crop was used for the subsequent analysis. M.p. > 250°. UV/VIS (CH_2Cl_2, $c = 2.31 \cdot 10^{-6}$ mol/dm^3): 400 (sh, 4.95), 419 (5.68), 450 (3.98), 514 (4.29), 549 (3.92), 588 (3.71), 644 (3.52). IR (4%): 3310*w*, 1934*w*, 1815*w*, 1710*s*, 1607*s*, 1556*m*, 1466*m*, 1404*m*, 1308*m*, 1271*s*, *etc.* ^{1}H-NMR: −2.78 (*s*, 2 H, NH); 0.96 (*t*, $J = 7$, 12 H, CH_3); 1.43 (*m*, *ca.* 16 H, CH_2); 1.58 (*m*, *ca.* 8 H, CH_2); 1.92 (*quint.*, $J = 7$, 8 H, CH_2CH_2O); 4.51 (*t*, $J = 7$, 8 H, CH_2O); 8.29 (*d*, $J = 8$, 8 H); 8.45 (*d*, $J = 8$, 8 H); 8.82 (*s*, 8 H, H of pyrrol). FAB-MS (NOBA): 1145 (11), 1144 (23), 1143 (62), 1142 (37), 1140 (42), 1131 (12), 1130 (14), 1129 (25), 1128 (75), 1127 (100, $(M + 1)^+$), 1126 (80), 1125 (36), 1124 (25), 1045 (6), 1044 (14), 1043 (22), 1042 (17), 1041 (6), 1040 (4), 1039 (3), 1001 (6), 999 (10), 998 (24). Anal. calc. for $C_{72}H_{78}N_4O_8$ (1127.43): C 76.70, H 6.97, N 4.97; found: C 76.66, H 7.14, N 5.09.

Bromo(pyridine){5,10,15,20-tetrakis[4-(hexyloxycarbonyl)phenyl]porphyrinato}cobalt(III) (**3**). The above porphyrin **5** (50 mg, 0.044 mmol) and Co(II) acetylacetonate (56.5 mg, 0.22 mmol) were dissolved in 5 g of 1-hexanol. The mixture was heated to 120° for 3.5 h under N_2. TLC and UV/VIS then showed complete incorporation of Co(II). Then, 5 ml of CH_2Cl_2 were added, and the mixture was filtered through a short column with 1 g of aluminium oxide (*ca.* 10 ml of CH_2Cl_2 were used to wash out the product). CH_2Cl_2 (at r.t.) and 1-hexanol (at 40–50°) were removed at reduced pressure, and the residue was dissolved in 10 ml of pyridine. After addition of 0.5 ml of HBr (48%), the mixture was heated at 100° for 1 h. To the cold mixture, 50 ml of CH_2Cl_2 were added followed by 50 ml of H_2O. The mixture was shaken and the org. phase separated. After shaking it two more times with *ca.* 50 ml of H_2O, the CH_2Cl_2 phase was filtered through a paper filter and concentrated to *ca.* 1 ml. The raw product was then precipitated by addition of *ca.* 50 ml of hexane to give 50 mg (83.8%) of **3** as a violet powder (uniform by TLC). The precipitate was dissolved in *ca.* 20 ml of Et_2O/hexane 1:1. After 3 days, 20 mg of dark violet crystals of **3** separated out, which were recrystallized once more from the same mixture to give after drying (r.t. 10^{-3} Torr, 16 h) a sample of 16 mg of crystalline **3**, that was used for the subsequent analysis. M.p. > 250° (in the dark at 124–126°). UV/VIS (CH_2Cl_2, $c = 1.34 \cdot 10^{-5}$ mol/dm^3): 322 (4.43), 441 (5.24), 520 (sh, 3.71), 556 (4.12) 595 (3.82). UV/VIS (pyridine, $c = 8.13 \cdot 10^{-6}$ mol/dm^3): 338 (4.33), 438 (5.44), 552 (4.15), 590 (sh, 3.81). IR (4%): 1935*w*, 1814*w*, 1711*s*, 1607*s*, 1468*m*, 1447*m*, 1404*m*, 1386*m*, 1350*m*, 1308*m*, 1274*s*, *etc.* ^{1}H-NMR: 0.86 (*m*, 2 H, *o*-H of pyridine); 0.95 (*t*, $J = 7$, 12 H, CH_3); 1.42 (*m*, *ca.* 16 H, CH_2); 1.56 (*m*, *ca.* 8 H, CH_2); 1.90 (*quint.*, $J = 7$, 8 H, CH_2CH_2O), 4.49 (*t*, $J = 7$, 8 H, CH_2O); 5.00 (*m*, 2 H, *m*-H of pyridine); 6.00 (*m*, 1 H, *p*-H of pyridine), 8.16 (*d*, $J = 7$, 8 H); 8.38 (*d*, $J = 8$, 8 H); 8.96 (*s*, 8 H, H of pyrrol). FAB-MS (*o*-NPOE): 1267 (1), 1266 (4), 1265 (6), 1264 (9), 1263 (8), 1262 (10, $M^+ - Br$), 1187 (9), 1186 (22), 1185 (63), 1184 (100, $(M + 1 - Br - py)^+$), 1183 (96), 1182 (23), 1181 (16), 1101 (11), 1100 (18), 1099 (19), 1098 (3), 1097 (3), 1057 (5), 1056 (11), 1055 (21), 1054 (15).

Chloro{5,10,15,20-tetrakis[4-(hexyloxycarbonyl)phenyl]porphyrinato}manganese(III) (**4**). The porphyrin **5** (50 mg, 0.044 mmol) and Mn(II) acetylacetonate (55.7 mg, 0.22 mmol) were dissolved in 3 g of 1-hexanol. The mixture was heated under N_2 for 1.5 h to 120° when TLC and UV/VIS indicated complete incorporation of Mn(II). The mixture was diluted with 5 ml of THF and filtered through a short column of (*ca.* 1 g) aluminium oxide (washing with *ca.* 10 ml of THF). Solvents were removed under reduced pressure as before. The residue was taken up in 20 ml of CH_2Cl_2 and shaken vigorously with 20 ml of sat. aq. NaCl soln. The org. phase was filtered and dried (r.t. 10^{-3} Torr, 16 h) to give 51 mg (94.6%) of **4**, uniform by TLC. The raw product was dissolved in 3 ml of hot AcOEt, and the open flask was placed into a jar containing 20 ml of hexane. The closed vessel was allowed to stand in the dark for 3 months. Olive-green crystals separated out that were washed with hexane and dried (r.t. 10^{-3} Torr, 16 h) to yield 25 mg (46.4%) of pure **4**. M.p. 228–229°. UV/VIS (CH_2Cl_2, $c = 6.56 \cdot 10^{-6}$ mol/dm^3): 280 (4.39), 324 (sh, 4.47), 348 (sh, 4.68), 374 (4.81), 400 (4.72), 448 (sh, 4.20), 477 (5.12), 530 (3.76), 582 (4.03), 617 (4.05). IR (4%): 1948*w*, 1824*w*, 1712*s*, 1610*s*, 1568*w*, 1468*m*, 1403*m*, 1386*m*, 1340*m*, 1308*s*, 1273*s*, *etc.* FAB-MS (*o*-NPOE): 1217 (5), 1216 (8), 1215 (14), 1214 (13, M^+), 1182 (13), 1181 (36), 1180 (87), 1179 (100, $M^+ - Cl$), 1178 (13), 1177 (10), 1098 (4), 1097 (4), 1096 (6), 1095 (6), 1052 (9), 1051 (18), 1050 (19). Anal. calc. for $C_{72}H_{76}ClMnN_4O_8$: C 71.13, H 6.30, N 4.61; anal. calc. for $C_{72}H_{76}ClMnN_4O_8 + 1\ H_2O$: C 70.09, H 6.37, N 4.54; found: C 70.07, H 6.14, N 4.29.

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