9-H), 3.22 (m, 2H, 3-H, 8-H), 3.84 (t, 8H, OCH_2), 4.46 (d, ^3J = 9.9 Hz, 2H, 2-H, 7-H), 6.68 (m, 8H, aryl-H), 6.91 (m, 4H, aryl-H), 6.93 (s, 2H, 5-H, 10-H), 7.08 (m, 4H, aryl-H); ^{13}C NMR (100 MHz, $CDCl_3$). δ = 14.0 (CH_3), 22.6/25.7/29.2/31.6 (CH_2), 39.0 (C-4, C-9), 47.0 (C-3, C-8), 52.0 (C-2, C-7), 67.9 (OCH_2), 114.2/114.4/125.9/128.4/129.4/(aryl-CH), 130.3/132.3/133.8/135.0/157.7/158.2 (C_q). Several signals are doubled, which confirms the formation of diastereoisomers.

[9] **10b**: M.p. 137 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.81 (m, 2H, 4-H, 9-H), 3.05 (m, 2H, 4-H, 9-H), 3.20 (m, 2H, 3-H, 8-H), 3.72 (4s, 12H, OCH_3), 4.316 (d, ^3J = 8.35 Hz, 2H, 2-H, 7-H)/4.318 (d, ^3J = 8.37 Hz, 2H, 2-H, 7-H), 6.98 (s, 2H, 5-H, 10-H)/6.99 (s, 2H, 5-H, 10-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.69 (C-4, C-9)/31.74 (C-4, C-9), 42.4 (C-3, C-8)/42.5 (C-3, C-8), 43.6 (C-2, C-7)/43.7 (C-2, C-7), 52.5/52.9 (OCH_3), 127.2 (aryl-CH), 128.8/128.8/133.7/134.0 (C_q), 171.2/171.3/172.8/172.8 (CO).

[10] **10c**: M.p. 94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (m, 12H, CH_3), 2.81 (m, 2H, 4-H, 9-H), 3.04 (m, 2H, 4-H, 9-H), 3.15 (m, 2H, 3-H, 8-H), 4.10 (m, 8H, OCH_2), 4.29 (d, ^3J = 8.4 Hz, 2H, 2-H, 7-H), 6.98 (s, 2H, 5-H, 10-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3), 31.8 (C-4, C-9), 42.5 (C-3, C-8), 43.9 (C-2, C-7), 61.4/61.9 (OCH_2), 127.1 (aryl-CH), 128.8/133.9 (C_q), 172.4/172.4 (CO). Several signals are doubled.

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[12] These symmetries require a rapid inversion of the thiopyran rings, as observed at room temperature in the NMR spectra.

[13] **10d**: M.p. 179 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.62 (s, 4H, 4-H), 3.79 (s, 6H, OCH_3), 3.84 (s, 6H, OCH_3), 7.23 (s, 2H, 5-H, 10-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.2 (C-4, C-9), 52.7/53.2 (OCH_3), 125.9 (C-5, C-10), 127.5/130.5/131.7/131.7 (C-2, C-3, C-4a, C-5a, C-7, C-8, C-9a, C-10a), 164.8/165.0 (CO).

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A Difunctional Receptor for the Simultaneous Complexation of Anions and Cations; Recognition of KH_2PO_4

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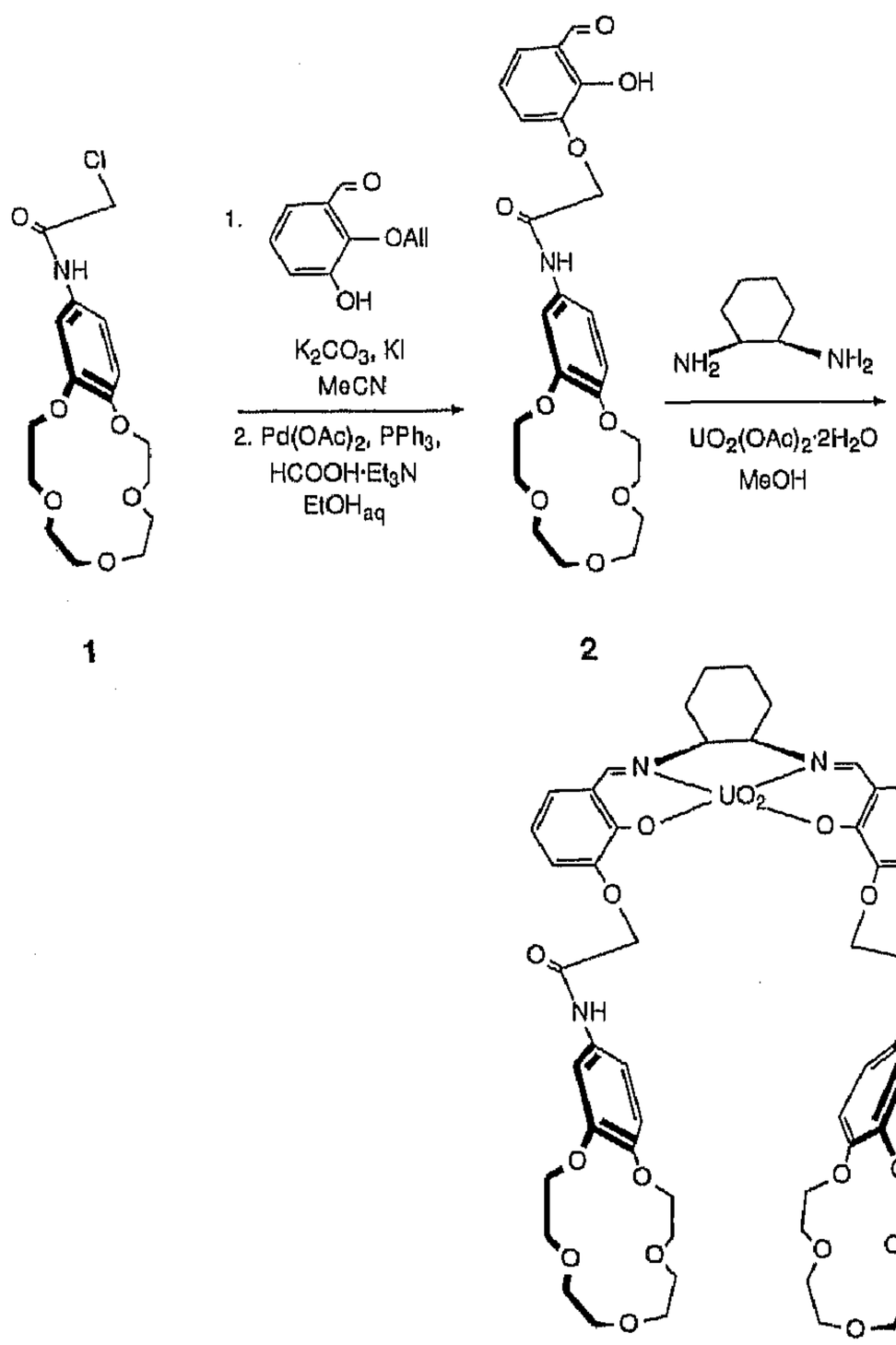
The design and synthesis of neutral macrocyclic receptors that selectively complex cations in apolar solvents rests on their ability to arrange their nucleophilic binding sites (Lewis-basic oxygen atoms of crown ethers etc.) in an array complementary to the cation.[1] Similarly macrocyclic and acyclic ligands that contain Lewis-acidic binding sites like boron, silicon, tin, and mercury centers complex anions, but the selectivity is not simply introduced.[2] Recently Reetz et al.[3] reported on a heterotopic receptor which, in addition to a crown ether moiety for complexation of K^+ ions, contains a σ-bonded Lewis-acidic boron center that is able to form a tetracoordinated adduct with anions and binds F^- ions selectively.

Recently we showed that neutral metalloclefts and metallomacrocycles containing both immobilized Lewis-acidic UO_2^+ centers and amido units as additional binding sites are excellent receptors for anions with a high selectivity for dihydrogen phosphate $H_2PO_4^-$.[4] We now describe the synthesis and complexation properties of a difunctional neutral receptor which contains binding sites for both *cations* and *anions* is therefore able to complex both species simultaneously in apolar solvents.[5]

The synthesis of the difunctional receptor **3** is summarized in Scheme 1. Reaction of (4-aminobenzo)[15]crown-5[6] with chloroacetyl chloride and K_2CO_3 in EtOAc/H_2O gave the corresponding [4-(chloroacetamido)benzo][15]crown-5 (**1**) in 85% yield. Aldehyde **2** was obtained by alkylation of 2-(2-allyloxy)-3-hydroxybenzaldehyde[7] with **1**, followed by palladium-catalyzed deallylation in 69% overall yield. Subsequent reaction of **2** with *cis*-1,2-diaminocyclohexane and $UO_2(OAc)_2 \cdot 2H_2O$ afforded the difunctional receptor **3** in 76% yield.



Scheme 1. All = allyl.

The complexation of the difunctional receptor **3** with cations and with anions was investigated by ^{1}H NMR spectroscopy, cyclic voltammetry, fast atom bombardment mass spectrometry (FAB-MS), and liquid–liquid extraction experiments. We first studied the complexation of tetrabutylammonium dihydrogen phosphate and potassium picrate, because UO_2-containing clefts complex $H_2PO_4^-$ [4] and bis(benzo[15]crown-5) ethers bind K^+ with a high degree of selectivity.[8]

In dilution experiments[9] with solutions of **3** and $Bu_4N^+H_2PO_4^-$ in [D_6]DMSO the ^{1}H NMR signals of the HC=N groups of both the free and complexed ligand were observed at δ = 9.51 and 9.46, respectively. From this experiment an association constant K_{ass} of $1.1 \times 10^3\ M^{-1}$ was calculated. The contribution of the $C(O)NH \cdots H_2PO_4^-$ hydrogen bond to the overall anion complexation can clearly be observed in the

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^{1}H NMR spectrum even in [D_6]DMSO as a solvent, since the N–H signals of the free and complexed **3** appear at $\delta = 10.47$ and 11.21, respectively.

Complexation of K^+ ions by receptor **3** was studied by picrate (Pic) extraction[8] experiments. For the 1:1 complex $3 \cdot K^+Pic^-$ a value of lg $K_{ex} = 5.3$ was obtained in chloroform.[10]

The complexation of K^+ and $H_2PO_4^-$ ions by **3** was also investigated by cyclic voltammetry in DMSO with 2% H_2O and with tetrabutylammonium tetraphenylborate as a supporting electrolyte. Addition of Bu_4N^+ $H_2PO_4^-$ to a solution of **3** causes a clear shift of both cathodic and anodic peaks toward more negative potentials. This effect is accompanied by a systematic increase in the peak separation, from 85 to 100 mV, and by a decrease of the normalized peak heights. These results suggest that a labile, redox-inactive complex is formed with $H_2PO_4^-$. Assuming the formation of a 1:1 complex, a K_{ass} value of 1.3×10^3 M^{-1} for $H_2PO_4^-$ is obtained, which is in a good agreement with the ^{1}H NMR measurements.

Upon addition of potassium tetraphenylborate to a solution of receptor **3** in DMSO the electrochemical behavior did not change, probably since the crown ether moieties in **3** are situated rather far from the redox-active UO_2 center. However, an indirect procedure for the determination of complexation constants[11] based on competition between Tl^+ and K^+ ions gave a K_{ass} value of 1.0×10^2 M^{-1} for K^+.

Finally, we used FAB-MS, an established technique for investigation of complexes in which cations[12] and anions are bound noncovalently.[4, 13] In the FAB^+ mass spectrum (*m*-nitrobenzyl alcohol as matrix) of the 1:1 complex[14] of receptor **3** and KH_2PO_4, prepared by mixing the host and guest in acetonitrile with 10% water and evaporating the solvent, an intense peak corresponding to $[3 + K^+]^+$ was observed. The corresponding FAB^- mass spectrum of the same sample yielded an intense peak for $[3 + H_2PO_4^-]^-$, while a signal for $[3 + H_2PO_4^- + K^+]^-$ is also present, which clearly proves the complexation of the salt.

Previously in our laboratory cation carrier assisted transport of *lipophilic* potassium salts was studied.[15] Now preliminary investigations have shown a significant transport of KH_2PO_4 as a *hydrophilic* potassium salt through a supported liquid membrane with receptor **3**.

In conclusion, we have demonstrated that the combination of binding sites for both cations and anions in a neutral receptor molecule leads to hosts with unique, multifunctional complexation behavior.

Experimental Procedure

A solution of aldehyde **2** (1.3 mmol) and *cis*-1,2-cyclohexanediamine [16] (0.65 mmol) in MeOH (100 mL) was refluxed for 1 h. Subsequently a solution of $UO_2(OAc)_2 \cdot 2H_2O$ (0.65 mmol) in MeOH (10 mL) was added and refluxing was continued for 1 h. After cooling, the precipitate that formed was filtered off and washed with MeOH (2×10 mL) to give **3** as a red solid in 76% yield. M.p. 185–187 °C; IR (KBr) $\tilde{\nu} = 1685, 1617, 904$ cm^{-1}; ^{1}H NMR ([D_6]DMSO): $\delta = 10.47$ (s, 2H, NH), 9.51 (s, 2H, HC=N), 7.47, 7.31 (2 d, $^3J_{HH} = 7.8$ Hz, 4H, arom.), 7.20–6.70 (m, 8H, arom.), 4.95 (s, 4H, $CH_2C(O)$), 4.75–4.65 (m, 2H, cyclohexylene), 4.70–4.00 (m, 32H, OCH_2), 2.40–1.70 (m, 8H, cyclohexylene); ^{13}C NMR ([D_6]DMSO): $\delta = 167.8$ (d, HC=N), 167.3 (s, C=O), 159.7, 149.5, 148.4, 144.7, 132.1 (5 s, arom.), 128.6 (d, arom.), 124.5 (s, arom.), 122.0, 116.2, 114.0, 112.0, 106.3 (5 d, arom.), 71.0 (t, $CH_2C(O)$), 70.5 (d, cyclohexylene), 69.8, 69.6, 68.7, 68.1 (4 t, OCH_2), 27.3, 21.5 (2 t, cyclohexylene); FAB-MS (NBA matrix): *m/z* 947.0 [$(M + H)^+$, calcd. 947.3]; correct C,H,N analysis.

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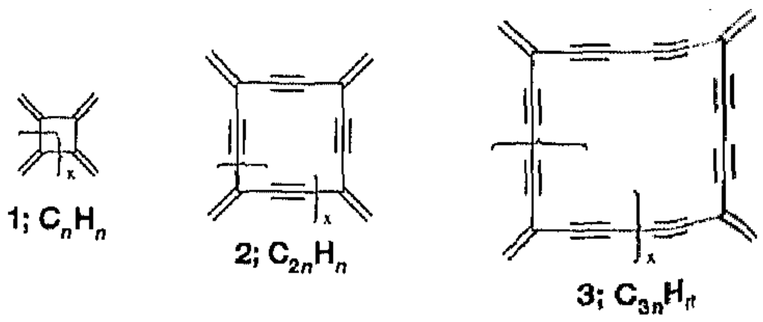
Expanded Radialenes: A Novel Class of Cross-Conjugated Macrocycles**

Armen M. Boldi and François Diederich*

Dedicated to Professor Donald J. Cram on the occasion of his 75th birthday

Radialenes (**1**) are a homologous series of all-*exo*-methylenecycloalkanes of molecular formula C_nH_n (for a recent review see ref. [1]). Upon insertion of acetylene or diacetylene moieties between each pair of vicinal *exo*-methylene units in the cyclic framework, the carbon-rich, hitherto unknown homologous se-



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