COMMUNICATIONS

Siemens 3.0 T feld-axial transceiver. The signal intensity of the water peak was not affected by the inclusion of the sample. The measurements were performed at 85 °C. Since the carbon atom side is partly disordered, it is not possible to distinguish between H₂O and NH₃⁺ centers. The overall number of both species groups found in lattice positions is 320 per formula unit; however, it must be assumed that some of these units are so disordered that they are not detectable by difference Fourier syntheses. Thus, for instance, a relevant lattice positions could be localized in the vicinity of the center of the cavity of the cluster. Results of model calculations revealed that a further 50–70 positions that should be occupied by 1,4-dioxane units are present. Elemental analyses, red fluxations, and the determination of the NH₂⁺ content by the Kjeldahl method yield the quoted formula. As a result of the quite characteristic bond valence sums, the positions of protonation could be unequivocally located. The calculated values lie between 0.15 and 0.45 for the 70 doubly protonated and between 1.1 and 1.3 for the 28 singly protonated oxygen atoms. This corresponds to what is expected from our experience with a number of other relevant cluster anions. Furthermore, significantly lowered bond valence sums (average 5.66) for 70 NO₃ atoms without H₂O ligands, which lie in the equatorial plane or above and below it on the periphery of the four-legged anion, show that the 4d (and likewise the 5e) centers without consideration of the [4M(NO₃)]⁺⁺ units are predominantly localized here. This correlates with the degree of reduction corresponding to the molecular formula, which was also determined by mass spectrometric redox titrations (see ref. [13]). (Calculation of bond valence sums according to J. D. Brown in Structure and Bonding in Crystals, Vol. 4, (eds.: M. O'Keeffe, A. Navrotsky), Academic Press, New York, 1981, p. 1.) Part of the [MoO₃]₃⁺(H₂O)₃⁺ and the [MoO₃]₃⁺(H₂O)₃⁺ octahedron (e.g., bridging, term = terminal) is disordered in such a way that the rare O₂⁻ and H₂O ligands exchange their positions in each case unequivocally recognized in the individual octahedron through two Mo positions with symmetrical “distances” between 0.7 and 0.8 Å. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the deposition number CSD-510358.

1. Characterization of 4: some characteristic IR bands (KBr disc prepared under argon): ν(NO) = 1610 (m, br, ν(NH)) and ν(ν(NH)) = 1404 (m, δ(NH)), 957 (m, ν(NH)), 812 (s), 740 (s), 656 (s), 551 (s). Characteristic resonances Raman bands (ν(OH)) = 3350 cm⁻¹ and ν(OH) = 3664 cm⁻¹; 2. Characteristic resonances Raman bands (ν(OH)) = 3350 cm⁻¹ and ν(OH) = 3664 cm⁻¹; 3. Characteristic resonances Raman bands (ν(OH)) = 3350 cm⁻¹ and ν(OH) = 3664 cm⁻¹; 4. Characteristic resonances Raman bands (ν(OH)) = 3350 cm⁻¹ and ν(OH) = 3664 cm⁻¹; 5. Characteristic resonances Raman bands (ν(OH)) = 3350 cm⁻¹ and ν(OH) = 3664 cm⁻¹; 6. Characteristic resonances Raman bands (ν(OH)) = 3350 cm⁻¹ and ν(OH) = 3664 cm⁻¹; 7. Characteristic resonances Raman bands (ν(OH)) = 3350 cm⁻¹ and ν(OH) = 3664 cm⁻¹; 8. Characteristic resonances Raman bands (ν(OH)) = 3350 cm⁻¹ and ν(OH) = 3664 cm⁻¹.

A Self-Assembled Bifunctional Receptor

Dmitry M. Rudkevich,* Alexander N. Shvyanyuk, Zbigniew Brzozka, Willem Verboom, and David N. Reinholdz

Molecular self-assemble is an important part of life processes and biological systems. It results in a wide variety of complex structures such as double-stranded DNA, viral protein coatings, lipid membranes, and globular proteins. Self-assembling processes have also found applications in the design of nanostructures such as inorganic clusters, tubes and channels, monolayers, and hydrogen-bonded networks. The functions of such complexes alkali metal cations with a high selectivity for Na⁺. This calixarene was prepared in 78% yield from the corresponding triester monocarboxylic acid chloride and 2-amino-6-(hexanamido)pyridine. The anion receptor porphyrin 2 was obtained in 49% overall yield by reaction of thymine with the appropriate bromoacetamidophosphonyl in DMSO in the presence of K₂CO₃ as a base, followed by metatation with Zn(OAc)₂·2H₂O. The Zn center in porphyrin 2 is expected to bind anions in apotic solution. For the assembly through hydrogen bonding, compounds 1 and 2 are functionalized with complementary dianamidopyridine and thymine units, respectively.

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Calix[4]arene 1 strongly complexes Na$^+$ in CDCl$_3$, [D$_2$]MeCN, and [D$_2$]toluene solutions; from dilution experiments in [D$_2$]MeCN with NaN$_3$ an association constant ($K_{\text{un}}$) of $5.0 \times 10^8$ mol$^{-1}$ was found. Calixarene 1 could be converted easily to the corresponding lipophilic complexes (1·Na$^+$)ClO$_4^-$, (1·Na$^+$)I$^-$, and (1·Na$^+$)SCN$^-$ by stirring a CH$_2$Cl$_2$ solution of 1 with saturated aqueous solutions of the appropriate sodium salts for three to five hours. With the more hydrophilic salts NaF and NaNH$_2$PO$_4$, no complexes could be obtained.

Surprisingly, the diamidopyridine fragment in free 1 does not form hydrogen-bonded aggregates with complementary molecules such as N-butylthymine. In the $^1$H NMR spectra no characteristic shifts$^{[1][2]}$ of CO(NH) signals were observed upon addition of N-butylthymine to CDCl$_3$, [D$_2$]MeCN, or [D$_2$]toluene solutions of 1. The diamidopyridine moiety in 1 is apparently involved in intramolecular hydrogen bonding with the ethyl carbonate groups, because the CO(NH)NH signals of 1 are shifted roughly $\Delta \delta = 0.3$ and 0.8 downfield in comparison with those of the (1·Na$^+$)ClO$_4^-$ complex in CDCl$_3$ and [D$_2$]MeCN, respectively. The Na$^+$ complexes of 1, in which the carboxyls from the ester groups and the amide group are coordinated to the cation, do form hydrogen bonds with complementary molecules as indicated by the downfield shifts for the diamidopyridine CO(NH) protons of approximately $\Delta \delta = 0.5$–0.6 in CDCl$_3$, [D$_2$]MeCN, and [D$_2$]toluene upon addition of N-butylthymine to a solution of the (1·Na$^+$)ClO$_4^-$ complex. From dilution experiments in [D$_2$]toluene $K_{\text{un}}$ values of $1.5 \times 10^9$ mol$^{-1}$ ($- \Delta G = 17.8$ kJ mol$^{-1}$) and $1.7 \times 10^9$ mol$^{-1}$ ($- \Delta G = 18.1$ kJ mol$^{-1}$) were calculated for (1·Na$^+$)ClO$_4^-$ and (1·Na$^+$)SCN$^-$, respectively.$^{[14][15]}$ This provides an interesting possibility of "switching on" the hydrogen bonding ability of 1 by complexation with Na$^+$ ions.$^{[16]}$ It means that anion receptor 2 can in principle be assembled with (1·Na$^+$)ClO$_4^-$ or (1·Na$^+$)SCN$^-$ complexes through a diamidopyridine–thymine interaction. UV/Vis experiments with porphyrin 2 show that it complexes $1^-$ and SCN$^-$ ions (introduced as tetrabutylammonium salts) in apolar solvents (CH$_2$Cl$_2$ and toluene). A bathochromic shift of the Soret band of 8–10 nm was found upon addition of Bu$_4$N$^+$ and Bu$_4$N$^+$SCN$^-$ to a toluene solution of 2, which is in agreement with the data published for simple tetracyanoporphyrins.$^{[11]}$ This binding is not strong; from dilution experiments a $K_{\text{un}}$ value of roughly 10 mol$^{-1}$ ($- \Delta G = 5.6$ kJ mol$^{-1}$) was calculated for both $1^-$ and SCN$^-$ ions in toluene. No indication for complexation of the ClO$_4^-$ ion was observed. Addition of free calix[4]arene 1 to a toluene solution of porphyrin 2 did not change the anion binding properties of 2; $K_{\text{un}}$ values of roughly 10 mol$^{-1}$ for the complexation of $1^-$ and SCN$^-$ ions were found. Interactions between the hydrogen bonding sites of 1 and 2 were not observed in the $^1$H NMR spectra upon mixing.

The final assembly experiment was carried out between (1·Na$^+$)SCN$^-$ and 2.$^{[17]}$ Addition of porphyrin 2 to a [D$_2$]toluene solution of (1·Na$^+$)SCN$^-$ resulted in a pronounced thymine–diamidopyridine interaction. From the $^1$H NMR chemical shifts of the CO(NH) signals a $K_{\text{un}}$ value of $2.8 \times 10^9$ mol$^{-1}$ ($- \Delta G = 24.9$ kJ mol$^{-1}$) for (1·Na$^+$)(2·SCN$^-$) was calculated. This is significantly higher than those of the interactions in (1·Na$^+$)·N-butylthymine·SCN$^-$ and Bu$_4$N$^+$(2·SCN$^-$) separately. A Job plot confirmed the 1:1 stoichiometry of the complex (Fig. 1).$^{[18][19]}$ The (1·Na$^+$)(2·SCN$^-$) assembly in toluene was also confirmed by UV/Vis spectroscopy; the Soret band displayed a bathochromic shift of 8 nm thus reflecting the Zn·SCN$^-$ interaction (Fig. 2). From these experiments a $K_{\text{un}}$ value of $2.5 \times 10^8$ mol$^{-1}$ was calculated, indicating strong anion binding.

![Diagram](image)

**Fig. 1.** Titration of 1 mmol of (1·Na$^+$)SCN$^-$ with 1 mmol of 2 in [D$_2$]toluene with formation of the assembly (1·Na$^+$)(2·SCN$^-$). Job plot.

These results prove the formation of the noncovalently organized bifunctional receptor system (1·Na$^+$)(2·SCN$^-$) (Fig. 3).$^{[20]}$ The Na$^+$ ion is complexed by calixarene 1, the SCN$^-$ ion coordinates to the Zn-porphyrin 2, and these cation and anion receptors are connected through hydrogen-bonded aggregation. The (significant) enhancement of the hydrogen bonding as well as the anion complexation points to a cooperative...
COMMUNICATIONS

Fig. 2. Complexation of (1-Na')SCN⁻ with 2 in toluene. The assembly was monitored by UV/Vis spectroscopy between 390 and 450 nm (E = extinction). 


Fig. 3. Energy-minimized structure of the complex (1-Na')(2-SCN⁻). 1 = green, 2 = cyan, 3 = yellow, N = red, C = blue, H = white.

Keywords: hydrogen bonding; molecular recognition; self-assembly.

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Communications

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