Molecular Golf Balls: Vesicles from Bowl-Shaped Host Molecules**

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Synthetic molecules containing a hydrophilic head group and one or two hydrophobic tails are known to form a great variety of supramolecular structures such as micelles, multilayers, rods, and vesicles.1-11 It has been proposed that the type of aggregate structure depends on the shape of the amphiphile, as characterized by the so-called “packing parameter”.12 Recent studies, however, indicate that other factors are important. For example, single-tail surfactants with a large rigid segment13 or surfactants with a hyperextended chain14 form vesicles instead of micelles, as predicted by the shape–structure concept. Vesicular structures are also formed by two-headed single-chain surfactants, for instance the lariat ether bolaamphiphiles.15 We report here that bowl-shaped host 2, which has two tails, two head groups, and a rigid cleft, forms vesicles upon dispersal in water.

Amphiphile 2 was synthesized in two steps (Scheme 1): first 1a16 was treated with hexadecylamine in acetonitrile under Finkelstein conditions17 (60%) and subsequently the product was methylated with methyl tosylate in toluene (80%).

When 2 (10 mmol) was dissolved in methanol (50 mL) and injected in water (3 mL), vesicles were formed, as could be deduced from electron microscopy.

As can be seen in Figure 1, the application of both the freeze-fracture and the negative staining technique show the presence of spherical vesicles with a diameter of approximately 4000 Å. These aggregates have a closed structure, as deduced from subsequent encapsulation experiments18 with the fluorescent dye ethidium bromide.19 Conductivity measurements revealed that the critical aggregation concentration (CAC) of 2 is 2 \times 10^{-5} \text{m}.

A vesicle dispersion of the amphiphile was dried on a glass plate (Figure 1a) and negative staining technique (magnification 9000 x) (b). The two methods of preparation permit a comparison of the vesicle structure. The freeze-fracture and the negative staining technique show the presence of vesicles with a diameter of approximately 4000 Å. A vesicle dispersion of the amphiphile was dried on a glass plate (Figure 1a) and negative staining technique (magnification 9000 x) (b). The two methods of preparation permit a comparison of the vesicle structure. The freeze-fracture and the negative staining technique show the presence of vesicles with a diameter of approximately 4000 Å.
Based on these data, we propose that the vesicles have a structure similar to that of a golf ball (Fig. 2). The thickness of the bilayer is 53 Å, which corresponds to two fully extended hexadecylamine chains. The host amphiphiles are aligned with their concave binding moieties facing the aqueous phases.

We previously showed that molecular clips such as 1b can bind aromatic substrates in chloroform, for example resorcinol and its derivative 3. Binding occurs by π-stacking interactions with the two aromatic "walls" of 1b and by hydrogen bonding with the urea carbonyl groups, as determined by IR and H NMR spectroscopy.

The binding properties of 2 were determined in chloroform and water by NMR and UV/Vis titration experiments. In chloroform, resorcinol and resorcinol derivative 3 form 1:1 inclusion complexes with 2; the corresponding association constants are \( K = 3400 \) and 500 m\(^{-1}\) respectively. These values are similar to those measured for these guests with 1b (\( K = 2600 \) and 700 m\(^{-1}\)) respectively. In water, under the CAC of 2, compound 3 is bound in a 1:1 host–guest ratio with an association constant of \( K = 3 \times 10^5 \) m\(^{-1}\). This value is very high when compared to that in chloroform, but is of the same order of magnitude as that found for amphiphilic cyclophanes with non-ionic guests. Titration experiments with 2 in concentrations above the CAC indicated that only 50 % of the molecular bowls are capable of binding a guest molecule. In a separate experiment we checked with electron microscopy that the vesicle structure is not destroyed by guest binding. The titration curve could only be fitted by assuming that half of the host molecules are occupied by guests.

In summary, we have shown that molecular objects with high binding affinities can be formed from rigid host molecules that have two tails and two ammonium groups. Further studies are aimed at stabilizing the aggregates by polymerization. Application of the polymerized structures can be conceived in the field of chromatographic separation of organic molecules. To conclude, the end synthesis of chiral derivatives of 2 is currently in progress.

**COMMUNICATIONS**

**Synthesis and Structure of**

\[ \text{[Ni(SO}_2\text{)}_6\text{(AsF}_3\text{)}_2\] **and** \[ \text{[Fe(SO}_2\text{)}_4\text{(FAsF}_5\text{)}_2\]**

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The chemistry of SO\(_2\) as a ligand has been studied in great detail. The coordination behavior of this atom molecule is remarkably versatile: Six different bonding modes are known; this figure does not take into account insertion products obtained from organometallic reactions. Vibrational spectra and/or stability criteria allow predictions to be made on the nature of the metal–ligand linkage, these predictions are often, but not always, correct. The most common modes of coordination for SO\(_2\) ligands in transition metal chemistry are \( \eta^2 \)-S and \( \eta^2 \)-SO\(_2\) however, examples of \( \eta^1 \)-SO-bound bridging ligands are also known. Only three complexes of Ni\(^{11}\) and Mn\(^{11}\) chemistry in which the SO\(_2\) ligands are exclusively O-bound, as determined by X-ray structure analysis, have been reported to date. In these complexes a maximum of two SO\(_2\) ligands in a trans arrangement are attached to a six-coordinate metal center. The oxidation of Ni powder with AsF\(_3\) in liquid SO\(_2\) yields Ni[SO\(_2\)]\(_3\)(AsF\(_3\))\(_2\). Accounts in the literature regarding the nature of the Ni–ligand bond and the number \( n \) of coordinated SO\(_2\) molecules differ. Passmore and Desjardins have suggested...