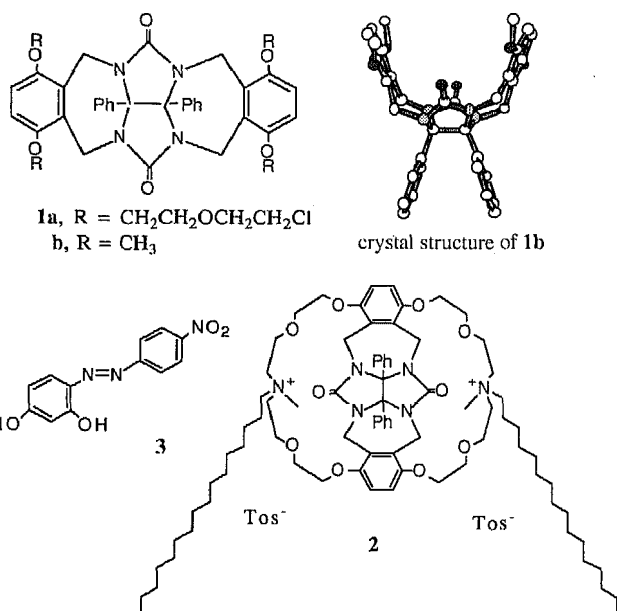


- [6] Abbreviations used: biPhMe: 2,2'-bis(1-methylimidazolyl)phenylmethoxy-methane; Hbpg: *N,N*-bis(2-pyridylmethyl)glycine; Me₃tacn: 1,4,7-trimethyl-1,4,7-triazacyclononane; tmen: *N,N,N',N'*-tetramethylethylenediamine; tpa: tris(2-pyridylmethyl)amine.
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- [11] X-ray diffraction studies were carried out at 172 K on an Enraf-Nonius diffractometer on a crystal with dimensions 0.50 × 0.45 × 0.30 mm and the following crystallographic parameters: space group, *P6₃*, (no. 173); *a* = *b* = 13.129(5), *c* = 25.413(7) Å; *V* = 3794(4) Å³; *Z* = 2. 9733 reflections were measured and combined to give 3144 (*R_{int}* = 0.063) unique reflections. All calculations were performed by using 2077 reflections (*I* > 3.00 σ(*I*)) with 306 parameters (data/parameter = 6.79) to afford *R* = 0.050 and *R_w* = 0.067. The Texsan-Texray Structure Analysis Package from Molecular Structure Corporation (1985) was used. Further details of the crystal structure investigation are available on request from the Director of Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (UK), on quoting the full journal citation.
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- [17] Interestingly, when exposed to O₂, **1** converts to a (μ-oxo)diiron species with an NMR spectrum identical to that of the previously reported [Fe₂O(O₂CC₆H₅)(bpg)₂](ClO₄) (S. Ménage, L. Que, Jr., *New J. Chem.* **1991**, *15*, 431–438).

factants, for instance the lariat ether bolaamphiphiles.^[6] 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**^[7] was synthesized in two steps (Scheme 1): first **1a**^[8] was treated with hexadecylamine in acetonitrile under Finkelstein conditions^[9] (60%) and subsequently the product was methylated with methyl tosylate in toluene (80%).



Scheme 1.

When **2** (10 mmol) was dissolved in methanol (50 μL) 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

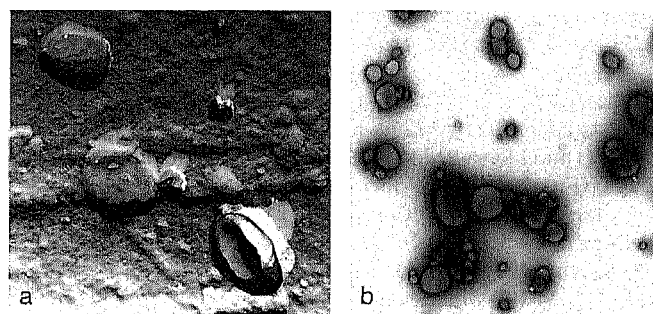


Fig. 1. Electron micrographs of a 0.02 M dispersion of **2**. Freeze-fracture (magnification 28000 ×) (a) and negative staining technique (magnification 9000 ×) (b).

of spherical vesicles with a diameter of approximately 4000 Å. These aggregates have a closed structure, as deduced from subsequent encapsulation experiments^[11] with the fluorescent dye ethidium bromide.^[10] Conductivity measurements revealed that the critical aggregation concentration (CAC) of **2** is 2×10^{-5} M. A vesicle dispersion of the amphiphile was dried on a glass plate in vacuo to give a cast film which was examined by X-ray diffraction. The diffraction patterns displayed a clear periodicity of 53 Å up to the 10th order reflection.

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] 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".^[2] Recent studies, however, indicate that other factors are important. For example, single-tail surfactants with a large rigid segment^[3,4] or surfactants with a hyperextended chain^[5] form vesicles instead of micelles, as predicted by the shape–structure concept. Vesicular structures are also formed by two-headed single-chain sur-

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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.

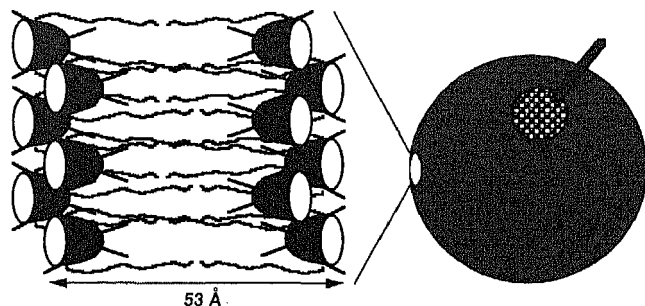


Fig. 2. Schematic representation of a vesicle formed by **2**.

We previously showed^[11] that molecular clips such as **1b** can bind aromatic substrates in chloroform, for example resorcinol and its derivative **3**. Binding occurs by π - π stacking interactions with the two aromatic "walls" of **1b** and by hydrogen bonding with the urea carbonyl groups, as determined by IR and ¹H NMR spectroscopy.

The binding properties of **2** were determined in chloroform and water by NMR and UV/Vis titration experiments.^[12] In chloroform, resorcinol and resorcinol derivative **3** form 1:1 inclusion complexes with **2**; the corresponding association constants are $K_a = 3400$ and 500 M^{-1} , respectively. These values are similar to those measured for these guests with **1b** ($K_a = 2600$ 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 $K_a = 3 \times 10^5 \text{ M}^{-1}$. 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^[13] 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 involved in the binding process. In this case, we obtained a good correlation for a 1:1 complex with a binding constant of $K_a = 4 \times 10^5 \text{ M}^{-1}$. This result suggests that only the dimples on the outer surface of the molecular golf balls are accessible to guest molecules and that the inner part of the aggregates cannot be reached.

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 this end the synthesis of chiral derivatives of **2** is currently in progress.

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Synthesis and Structure of [Ni(SO₂)₆](AsF₆)₂ and [Fe(SO₂)₄(FAsF₅)₂]**

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The chemistry of SO₂ as a ligand^[1] and solvent^[2] has been studied in great detail. The coordination behavior of this three-atom molecule is remarkably versatile: Six different bonding modes are known;^[1] this figure does not take into account insertion products obtained from organometallic reactions.^[3] Vibrational spectra and/or stability criteria allow predictions to be made on the nature of the metal-ligand linkage;^[1] these predictions are often, but not always, correct.

The most common modes of coordination for SO₂ ligands in transition metal chemistry are η^1 -S and side-on η^2 -SO; however, examples of S- or SO-bound bridging ligands are also known. Only three complexes (Ni^{II} and Mn^{II} chemistry^[4–7]) in which the SO₂ ligands are exclusively O-bound, as determined by X-ray structure analysis, have been reported to date. In these complexes a maximum of two SO₂ ligands in a *trans* arrangement are attached to a six-coordinate metal center.

The oxidation of Ni powder with AsF₅ in liquid SO₂ yields [Ni(SO₂)₆](AsF₆)₂.^[8] Accounts in the literature regarding the nature of the Ni-ligand bond and the number *n* of coordinated SO₂ molecules differ. Passmore and Desjardins^[8] have suggest-

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