COMMUNICATIONS

[6] Abbreviations used: biPhMe: 2,2'-bis(1-methylindazolyl)phenylmethoxy-
metallacyclic; EtHg, N,N,N'-tris(2-pyridylmethyl)amine; Mezinc: 1,4,7-tri- 
4,1,4,7-triazacyclohexane; tmen: N,N,N',N'-tetramethylhexadecamidene; tsp: 
tris(2-pyridylmethyl)amine.

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[10] a) R. L. Rardin, A. Bino, P. Poguvinich, W. B. Tolman, S. Liu, S. J. Lipard, 
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[11] X-ray diffraction studies were carried out at 172 K on an Enraf-Nonius diffrac-
tometer on a crystal with dimensions 0.50 x 0.45 x 0.30 mm and the following 
crystallographic parameters: space group, P65 (no. 173); a = b = 13.129(5), 
c = 25.41(3) À; V = 3974(4) À³; Z = 2. 9733 reflections were measured and 
combined to give 3144 (Rm = 0.063) unique reflections. All calculations were 
performed by using 2077 reflections (l > 3.00Å) with 306 parameters (data/
parameter = 6. 79) to afford R = 0.050 and Rw = 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 cita-
tion.


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J. Am. Chem. Soc. 1991, 113, 3039-3044; b) M. P. Hendrich, E. Mönke, B. G. Fox, 

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[17] Interestingly, when exposed to O2, 1 converts to a (3,4-oxo)diiron species with 
an NMR spectrum identical to that of the previously reported 
[Fe2O2(C6H4)(bpfi)](ClO4) (S. Ménage, L. Que, Jr., New. J. Chem. 1991, 
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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.[13] It has been proposed that the type of aggregate 
structure depends on the shape of the amphiphile, as character-
ized 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. Vesic-
ular structures are also formed by two-headed single-chain sur-
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%).

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

As can be seen in Figure 1, the application of both the freeze-
fraction 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 sub-
sequent encapsulation experiments[10] with the fluorescent dye 
etthidium bromide.[11] Conductivity measurements revealed that 
the critical aggregation concentration (CAC) of 2 is 2 x 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 dif-
fraction. The diffraction patterns displayed a clear periodicity 
of 53 Å up to the 10th order reflection.

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Research (NWO).

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\cite{1, 2} 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 carboxyl 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.\cite{12, 13} In chloroform, resorcinol and resorcinol derivative 3 form a 1:1 inclusion complex with 2; the corresponding association constants are $K = 3400$ and $500 \text{ M}^{-1}$, respectively. These values are similar to those measured for guest 3 with 1b ($K = 2600$ and 700 $\text{ M}^{-1}$, respectively). In water, under the CAC of 2, compound 3 is bound in a 1:1 host–guest ratio with an association constant of $K = 3 \times 10^5 \text{ M}^{-1}$. 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\cite{13} with nonionic 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 $K = 4 \times 10^5 \text{ M}^{-1}$. 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 accelerate this end the synthesis of chiral derivatives of 2 is currently in progress.

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\[8\] A. J. P. Martin, E. J. M. diverse.\cite{10} In these complexes a maximum of two SO$_2$ ligands in a trans configuration are found, as shown by X-ray structure analysis.\cite{11} In SO$_2$-bound bridging ligands are also known, for example S- or SO$_2$-bound bridging ligands are also known, and the coordination numbers vary between 4 and 6. In these examples the coordination number varies between 4 and 6.

The chemical structure of NiSO$_4$ is given in Fig. 2. The unit cell contains one Ni atom, five SO$_2$ ligands, and one SO$_2$ ligand.

**Synthesis and Structure of \[\text{Ni} (\text{SO}_2)_2 (\text{AsF}_5)_2\] and \[\text{Fe} (\text{SO}_2)_4 (\text{AsF}_5)_2\]**

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The chemistry of SO$_2$ as a ligand has been studied in detail. The coordination behavior of this atom molecule is remarkably versatile: Six different bonding modes are known;\cite{11} this figure does not take into account predictions based on organometallic reactions.\cite{111} Vibrational spectra and/or stability criteria allow predictions to be made on the nature of the metal–ligand linkage;\cite{111} 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$_2$ binding ligands are also known. Only three complexes (Ni$^{II}$ and Mn$^{II}$ chemistry)\cite{14} 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$_5$ in liquid SO$_2$ yields NiSO$_2$(AsF$_5$)$_2$.\cite{12} Accounts in the literature regarding the nature of the Ni–ligand bond and the number of coordinated SO$_2$ molecules differ. Passmore and Desjardins\cite{13} have suggested...