Interestingly, it was recently reported that $Co_2(CO)_8$ cleaves sulfur from thioamides to give the cluster compounds $(\mu_3\text{-S})(\mu\text{-}R^1C{=}NR^2)Co_3(CO)_7$, R^1 = Me, Ph; $R^2 = C_6H_{11}$, but since no intermediates were observed, the state of aggregation of the cluster that existed when the desulfurization occurred is not known.[16]

The desulfurization of organic molecules is a reaction of interest regarding the purification of fossil fuels.[17] Recently, organometallic complexes have attracted attention as desulfurization agents.[18]

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Supplementary Material Available: Complete tables of fractional atomic coordinates, bond distances and angles are available for all three structures (12 pages). Ordering information is given on any current masthead page.

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Fully Functionalized Thiol Vesicles: Structure and Esterolytic Properties

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Exceptional attention has focused on synthetic surfactant vesicles because of their ability to model biological membranes and their potential use as "chemical machines"; i.e., highly organized reagent assemblies designed to perform specific chemical tasks.[2,3] Electron microscopy has been an essential tool in the structural characterization of vesicles but is limited to the examination of "fixed" specimens. Accordingly, spectroscopic[4] or chemically reactive[5] reporter molecules have been designed to probe vesicular microenvironments. Several probes have detected substantial molecular ordering in vesicles, particularly in multilamellar types.

The existence of ordered, stable, membrane-enclosed vesicles, offering unique microenvironments, invites vigorous exploitation;

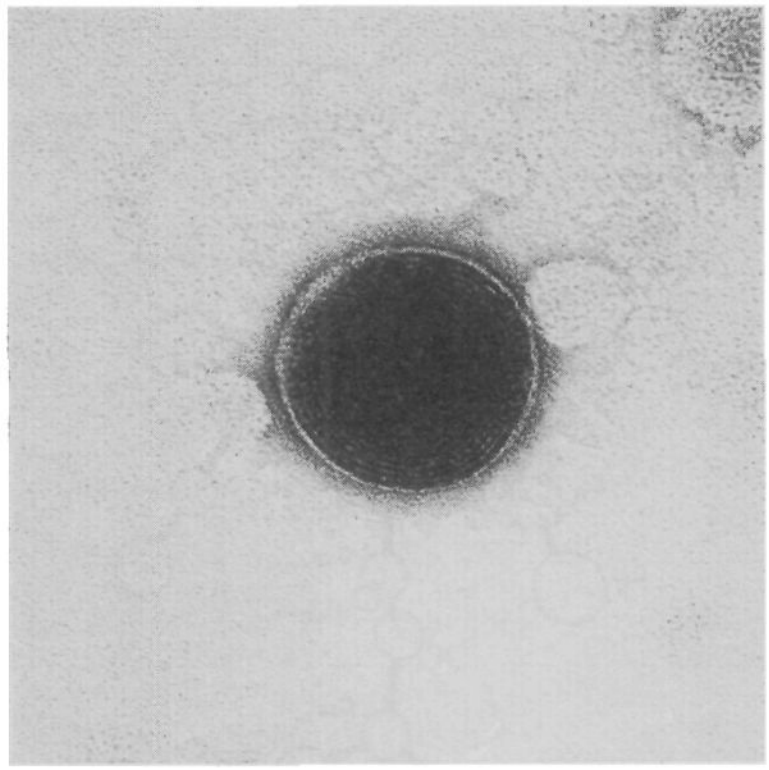

Figure 1. Electron micrograph of vesicular **1** on a Formvar carbon-coated copper grid; magnification, ×230000.

for example, the extension of micellar chemistry[6] to vesicles: the bimolecular cleavage of active esters in alkylammonium ion vesicles,[7] unimolecular decarboxylation,[8] and various photochemical reactions.[9] Of special interest is the formation of vesicles from amino acid derivatives, where the incorporated chirality and functionality permit innate and induced circular dichroism[10] and chiral chemical discrimination.[11]

Our concern centers on *functionalized* vesicles as organic reagents and bioorganic models.[2a,12] Very little has been done in this area. The cleavage of *p*-nitrophenyl esters is catalyzed by hydrophobic imidazole[7] or thiol[13] reagents when both substrate and reagent are noncovalently bound to $R_2N^+Me_2$ vesicles, but the vesicles themselves are not functionalized. Perhaps the sole chemical utilization of synthetic functional vesicles is the enantioselective cleavage of activated phenylalanine esters by vesicles constructed from a histidine-derived surfactant.[11b]

We now report (a) the synthesis of *N*,*N*-dihexadecyl-*N*-(β-mercaptoethyl)-*N*-methylammonium chloride (**1**), (b) the subsequent preparation and characterization of *fully functionalized* thiol vesicles of **1**, and (c) some chemical properties of these vesicles, including distinguishable "inner" and "outer" reactions. The esterolytic reactivity of vesicular **1** is also compared to that of *micellar* **2**[14] and vesicle-bound heptanethiol.[13]

$(n\text{-}C_{16}H_{33})_2N^+(CH_3)CH_2CH_2SH,Cl^-$
1

$n\text{-}C_{16}H_{33}N^+(CH_3)_2CH_2CH_2SH,Cl^-$
2

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The synthesis of **1** parallels that of **2**[14a,b] and is outlined in Scheme I. Cetyl bromide quaternization of amino alcohol **3**[15]

Scheme I

$$\underset{\mathbf{3}}{\mathrm{RNMeCH_2CH_2OH}} \xrightarrow[\text{reflux, 21 h, 81\%}]{\text{RBr, EtOH}}$$

$$\underset{\mathbf{4}}{\mathrm{R_2N^+MeCH_2CH_2OH,\ Br^-}} \xrightarrow[\text{pyr, } CH_2Cl_2\text{, 1 h, 23 °C}]{Tf_2O}$$

$$\underset{\mathbf{5}}{\mathrm{R_2N^+MeCH_2CH_2OTf,\ OTf^-}}$$

$$\xrightarrow[\text{16 h, 23 °C, 82\%}]{CH_3COS^-Na^+} \underset{\mathbf{6},\ X = OTf \quad \mathbf{7},\ X = Cl}{\mathrm{R_2N^+MeCH_2CH_2SCOCH_3,\ X^-}} \xrightarrow[\text{75\% aqueous EtOH, reflux } (N_2)\text{, 3 h, 81\%}]{\text{3N HCl,}} \mathbf{1}$$

$$R = n\text{-}C_{16}H_{33}$$

gave the dihexadecylcholine derivative **4** which was converted to its triflate derivative **5**. Without isolation, **5** was reacted with (pH 7.5) aqueous sodium thioacetate[16] affording surfactant **6** which was ion exchanged [Dowex 1-X8 (Cl^-), 80% aqueous EtOH, 75 °C, 80% yield] to its water-soluble chloride form (**7**). Deprotection of **7** with O_2-free aqueous ethanolic HCl followed by lyophilization and recrystallization (EtOAc) afforded **1**[17] with quantitative SH activity toward Ellman's reagent.[18]

Vesicles of **1** were typically created by injecting[13,19] 0.25 mL of $\sim 10^{-3}$ M ethanolic solutions into 3 mL of various aqueous solutions held at ~60 °C during injection. Vesicle formation was verified in three ways. (1) Figure 1 is an electron micrograph of vesicular **1** (prepared by injection into 2% aqueous uranyl acetate) showing a closed, single-compartment, multilamellar vesicle. Several similar structures were observed with diameters of 1000–1300 Å and bilayer widths of 30–40 Å, markedly resembling vesicles prepared from nonfunctional ammonium ions.[3a,c] The bilayer width is appropriate for two fully extended C_{16} chains.[4c] ((2) Differential scanning calorimetry[20] of 0.015 M vesicular **1** in 0.02 M, pH 7.5, aqueous Tris buffer revealed a reversible gel to liquid crystalline phase transition with $\Delta H = 2.4$ kcal/mol, $T_c = 35.25$ °C, a van't Hoff enthalpy of 450 kcal/mol, and a cooperativity of 190 molecules of **1**. These transitions are similar to those of vesicular dipalmitoylphosphatidylcholine.[21] (3) Gel filtration of 2×10^{-3} M vesicular **1**, prepared in 0.1 M aqueous 6-carboxyfluorescein, was done on a Sephadex G-25-80 column by using 0.01 M aqueous Tris buffer (pH 7.4, 0.1 M in KCl) as eluant. Elution of vesicle-entrapped dye was detectable in the column void volume as a 110-fold enhancement in fluorescence intensity at 520 nm upon lysing the vesicular eluant with ethanol. The gel filtration result is consistent with vesicles of size ~1000 Å (excluded by Sephadex), which contain high concentrations of dye with self-quenching fluorescence.[4c,13,22]

Examination of positively stained electron micrographs at lower magnification revealed only intact spherical objects. In addition, many independently prepared vesicle solutions displayed no noticeable turbidity and good reproducibility in kinetic experiments (see below). Taken together with the strong probability that the "cmc" of **1** is less than that of its unfunctionalized analogue, 8×10^{-6} M,[8] it is likely that **1** is overwhelmingly present as intact vesicles. It is thus highly likely that all observed properties of our solutions can be attributed to intact vesicles.

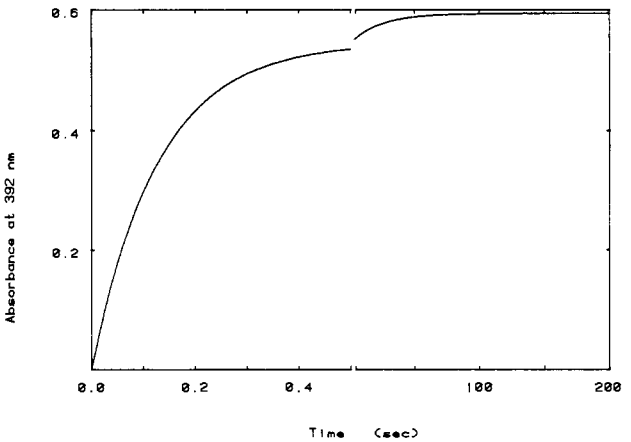

Figure 2. Cleavage by 1.80×10^{-3} M vesicular **1** (method A) of 2×10^{-5} M PNPA. Absorbance at 392 nm (released *p*-nitrophenylate ion) is plotted against time. The first 91% of the reaction occurs with $k_\psi = 3.97$ s^{-1}, the subsequent 9% of reaction with $k_\psi = 0.00434$ s^{-1}. Note that the time axis is discontinuous.

Table I. Rate Constants for the Reactions of Vesicular 1 and PNPA[a]

10^3[1], M[b]	method[c]	$k_\psi{}^{f,d}$ s^{-1}	$k_\psi{}^{s,e}$ s^{-1}	$k_\psi{}^{s,f}$ %
0.213	A	0.53 ± 0.01	0.076[g]	10
0.227	B	0.44 ± 0.02	0.038 ± 0.003	8.6
0.427	A	1.27 ± 0.05	0.058[g]	5.8
0.450	B	1.06 ± 0.02	0.072 ± 0.001	4.1
0.818	A	$1.95 \pm 0.06_4$	*h*	*h*
0.900	B	$1.42 \pm 0.00_2$	0.072 ± 0.002	5.1
1.44	B	2.98 ± 0.06	0.045 ± 0.001	5.7
1.57	A	3.0 ± 0.1	0.052[g]	8.6
1.80	B	4.0 ± 0.1	0.043 ± 0.00	8.6
3.13	A	4.2 ± 0.1	*h*	*h*
3.60	B	4.9 ± 0.1	0.032 ± 0.001	8.1
4.24	A	3.4 ± 0.3	*h*	*h*
6.14	A	2.39 ± 0.03	*h*	*h*
6.43	A	1.86 ± 0.03	0.033[g]	5.5

[a] Conditions: 0.01 M Tris buffer, pH 7.5 ± 0.3, containing 4.2 vol·% ethanol and 0.2 vol·% CH_3CN, $\mu = 0.01 \pm 0.0025$, 25 °C, [PNPA] = 2–4 × 10^{-5} M. [b] Final concentration after stopped-flow mixing. [c] Method of vesicle-substrate preparation; see text. [d] Rate constant of faster reaction; errors refer to average deviations of 3 runs, unless otherwise noted by a subscript. [e] Rate constant of slower reaction; errors are average deviations of 2 runs, unless otherwise noted. [f] Percent of total reaction occurring at slower rate. [g] Single run. [h] Not determined.

Two experimental methods were used to explore the esterolytic reactivity of vesicular **1** toward *p*-nitrophenyl acetate (PNPA). In *coinjection* (*method A*), a solution of **1** and PNPA in $EtOH/CH_3CN$ was injected into 10^{-2} M aqueous HCl at 55 °C, affording vesicular **1** with *entrapped* and externally bound PNPA. Preformed vesicular **1**/PNPA was then combined with 10^{-2} M aqueous Tris buffer (7.2×10^{-3} M in KOH and 3×10^{-3} M in KCl) in the stopped-flow spectrometer, initiating esterolysis at a final pH of 7.55. In *subsequent injection* (*method B*), vesicles of **1** were first formed by ethanolic injection at 60 °C into an aqueous solution which was 9.1×10^{-3} M in H^+, 1.69×10^{-3} M in K^+, and 2.6×10^{-2} M in Cl^-. Vesicular **1** was subsequently reacted with 8×10^{-5} M PNPA in 0.02 M Tris buffer (final pH 7.60) in the stopped-flow instrument. PNPA is not initially entrapped by vesicular **1** in method B. The kinetics of all esterolysis reactions were followed by monitoring the release of *p*-nitrophenylate ion at 392 nm[23] and 25 ± 0.2 °C.

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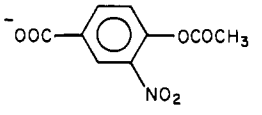
The kinetic runs were *biphasic*, each consisting of two sequential pseudo-first-order reactions, a "fast" process (k_ψ^f) accounting for 90–96% of PNPA cleavage and a "slow" reaction (k_ψ^s) accounting for the remainder. A typical result appears in Figure 2. Rate constants ($r > 0.999$) for both reactions were readily determined by standard methods and are recorded as a function of [**1**] in Table I. For reasons discussed below, we identify k_ψ^f with reactions occurring on the outer surface of vesicular **1** and k_ψ^s with reactions occurring *within* vesicular **1**. Both k_ψ^f and k_ψ^s are relatively independent of experimental kinetic method (A or B), but *only* k_ψ^f meaningfully responds to variation of [**1**] and does so in a manner reminiscent of the behavior of heptanethiol + $R_2N^+Me_2$ vesicles.[13]

Vesicular [**1**] shows $k_\psi^{f,max} = 4.9\ s^{-1}$ at [**1**] = 3.6×10^{-3} M. Plotting $1/k_\psi^f$ vs. $1/$[**1**] (using data for which [**1**] $\leq 3.6 \times 10^{-3}$ M) in the Lineweaver Burk analysis commonly employed for micellar reactions[6] gives $k_v = 9.8 \pm 0.3\ s^{-1}$ and $K/N = 276 \pm 2\ M^{-1}$, where k_v represents the rate constant for cleavage of externally bound PNPA. Assuming an aggregation number $N \sim 14\,000$,[24] the binding of PNPA to vesicular **1** is characterized by $K \sim 3.9 \times 10^6\ M^{-1}$. In PNPA cleavage, vesicular **1** is superficially comparable to micellar **2**, for which $k_\psi^{max} = 2.16\ s^{-1}$ (pH 7) or $9.71\ s^{-1}$ (pH 8), but **2** requires higher concentrations ($\sim$0.02 M) to reach optimal efficiency. Assuming $N \sim 70$[14a] for micellar **2**, $K \sim 2400\ M^{-1}$ for binding PNPA,[14a] about 1600 times less than K for vesicular **1**. Defining k_{cat} as $k_\psi^{max}/$[surfactant], $k_{cat} = 1360$ L/mol·s for vesicular **1** and $\sim$300 L/mol·s for micellar **2** under roughly comparable conditions. Vesicular **1** and heptanethiol/$R_2N^+Me_2$ (R = 85% *n*-C_{18}, 15% *n*-C_{16}) vesicles[13] are kinetically comparable in terms of k_{cat} for PNPA cleavage.[25]

Most intriguing is the observation of "outside" and "inside" thiolytic PNPA cleavages by vesicular **1**. This kinetic dichotomy persists with *p*-nitrophenyl hexanoate, and we believe that both substrates migrate across the outer bilayer of vesicular **1** at rates at least comparable to that of cleavage.[26] Due to the multilamellar nature of vesicular **1**, there are more binding sites on the interior lamellae than on the exterior surface. It is thus possible that the overall rate of substrate diffusion into the vesicles exceeds the overall rate of substrate exit so that biphasic kinetics attend substrate thiolysis whether the **1**/substrate systems are constructed by coinjection or subsequent injection methods.

Ionic substrates, however, cannot as easily cross vesicular membranes;[3c] anionic substrates in particular should be bound to one or the other side of a cationic bilayer. Accordingly, the anionic PNPA analogue, 4-acetoxy-3-nitrobenzoate, **8**,[27] was cleaved by 1.03×10^{-3} M vesicular **1** at pH 8.1. Vesicular **1**



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prepared by coinjection, where **8** can bind to both interior and exterior surfaces of the vesicles, displayed biphasic kinetics for cleavage of **8** (method A), with k_ψ^f (96% of reaction) = $2.5\ s^{-1}$ and $k_\psi^s = 0.099\ s^{-1}$. Vesicular **1**, prepared by method B and *subsequently* reacted with **8**, displayed only monophasic kinetics ($\geq$99% of reaction) with $k_\psi^f = 2.4\ s^{-1}$.[28] Note that k_ψ^f is identical under both conditions and comparable to the analogous k_ψ^f value for PNPA (Table I).

These results offer strong support for associating the biphasic esterolytic reactions with internal and external vesicular thiol groups. These may differ in reactivity for a variety of reasons. We second Fendler's observation that "functionalized surfactant vesicles hold the key to new types of highly relevant and. . .fascinating chemistry".[2a] We are vigorously exploring the chemistry of **1** and related functional vesicles.

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(24) This value can be estimated for dihexadecyldimethylammonium bromide vesicles from data in ref 8.

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Iron and Ruthenium Carbonyl Catalyzed Reductive Carbonylation of Nitro Compounds by Sodium Methoxide. A Significant Effect of the Metal on the Reaction Course

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Metal carbonyl induced reduction and reductive carbonylation reactions are important processes of considerable industrial interest. The nitro functionality has played a major role in this chemistry. One of us has recently demonstrated that nitro compounds could be reduced to amines by the clusters triiron[2] or triruthenium[3] dodecacarbonyl under gentle conditions using phase-transfer catalysis. Although the same products were obtained by using either of the metal carbonyls, there were significant reactivity differences depending on the atmosphere used (nitrogen or carbon monoxide).

Under the phase-transfer conditions, the initial reaction in the organic phase likely involves either conversion of $M_3(CO)_{12}$ to $M_3(CO)_{11}^{-2}$ by the quaternary ammonium hydroxide[2] or attack by hydroxide ion at a metal carbonyl carbon to give the anion **1** bearing a hydroxycarbonyl ligand.[4] The latter type of complex is analogous to species obtained from the phase-transfer catalyzed

$$M_3(CO)_{12} + R_4N^+OH^- \rightarrow \underset{\mathbf{1}}{R_4N^+M_3(CO)_{11}COOH^-} \xrightarrow[-CO_2]{} \underset{\mathbf{2}}{R_4N^+HM_3(CO)_{11}^-}$$

reaction of group 6 metal carbonyls with hydroxide ion.[5] Loss of carbon dioxide from **1** would generate the trinuclear metal hydride **2** which is the key species in the iron reaction and may or may not be so in the case of ruthenium (species of higher nuclearity are also possible with ruthenium).[6]

Let us consider the consequences of using methoxide instead of hydroxide ion in the iron and ruthenium carbonyl catalyzed reactions of nitro compounds. If $M_3(CO)_{11}^{2-}$ was still generated, then one would observe little that had not already been noted in

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