The platination of oligonucleotides by *trans*-DDP has been shown to produce intrastrand 1,3-(N7,N7) cross-links with d(GpTpG),[14] d(GpCpG),[15] d(GpApG),[16] and a 1,3-(N1,N7) cross-link with d(ApGpG).[17] Monoadducts and interstrand cross-links were mainly formed in the reaction with double-stranded DNA;[18] *trans*-DDP was considered unable to form 1,2-intrastrand d(GpG) or d(ApG) adducts as a result of its structure.[17] Thus, the stable adduct **M2** represents a new and unprecedented chelation geometry for a *trans* platinum complex. Although the chelation process is relatively slow, the N3-Pt-N7 structure may be of biological relevance since A-N3 is readily exposed to platination in the minor groove. The involvement of the N3 atom of adenine as an alkylation site[19] and in the cleavage reaction of hammerhead ribozyme has recently been demonstrated.[20] This study is presently being extended to other ribo- and deoxy-dinucleotides.

Experimental Section

trans-EE was synthesized according to a literature procedure.[12] r(ApG) was purchased from Sigma. *trans-EE* (2.3 mg, 5.6 μmol) was added to 5 mL of a 1 mM solution of r(ApG) (5 μmol, pH 4.0) at room temperature in the dark. Samples were collected for HPLC detection at various time intervals. Samples were lyophilized and dissolved in D_2O (0.5 mL) and the ROESY NMR spectra (mixing time 300 ms, 3 mM sample, pH 3.9, $T=280$ K) were recorded on a Bruker DRX 600 instrument. The pH values were measured on a Philips PW 9420 pH meter. HPLC was performed on a Waters 626 LC instrument using Millennium 32 software and a reverse-phase Waters Symmetry C8 column with gradient elution (0–50% methanol in 50 mM $NaClO_4$ at a flow rate of 0.8 mL min^{-1}).

Received: December 5, 2000 [Z16227]

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[1] *Cisplatin* (Ed.: B. Lippert), Helvetica Chimica Acta/VCH, Zurich, **1999**.

[2] "Metallopharmaceuticals I": G. Natile, M Coluccia in *Topics in Biological Inorganic Chemistry*, *Vol. 1* (Eds.: M. J. Clarke, P. J. Sadler), Springer, Berlin, **1999**, pp. 73–98.

[3] M. Coluccia, A. Nassi, F. Loseto, A. Boccarelli, M. A. Mariggiò, D. Giordano, F. P. Intini, P. Caputo, G. Natile, *J. Med. Chem.* **1993**, *36*, 510–512.

[4] N. Farrell in *Metal Ions in Biological Systems*, *Vol. 32* (Eds.: A. Sigel, H. Sigel), Marcel Dekker, New York, **1996**, pp. 603–639.

[5] L. R. Kelland, C. F. J. Barnard, I. G. Evans, B. A. Murrer, B. R. C. Theobald, S. B. Wyer, P. M. Goddard, M. Jones, M. Valenti, A. Bryant, P. M. Rogers, K. R. Harrap, *J. Med. Chem.* **1995**, *38*, 3016–3024.

[6] M. Coluccia, A. Boccarelli, M. A. Mariggiò, N. Cardellicchio, P. Caputo, F. P. Intini, G. Natile, *Chem. Biol. Interact.* **1995**, *98*, 251–266.

[7] B. Andersen, N. Margiotta, M. Coluccia, G. Natile, E. Sletten, *Metal-Based Drugs* **2000**, *7*, 23–32.

[8] Y. Liu, M. F. Sivo, G. Natile, E. Sletten, *Metal-Based Drugs* **2000**, *7*, 169–176.

[9] B. Van Hemelryck, J.-P. Girault, G. Chottard, P. Valadon, A. Laoui, J.-C. Chottard, *Inorg. Chem.* **1987**, *26*, 787–795.

[10] C. Meiser, B. Song, E. Freisinger, M. Peilert, H. Sigel, B. Lippert, *Chem. Eur. J.* **1997**, *3*, 388–398.

[11] BIOSYM User Guide for Insight II (version 2.3.5), Discover (version 2.9.5) and NMR Refine (version 2.3).

[12] R. Cini, P. Caputo, F. P. Intini, G. Natile, *Inorg. Chem.* **1995**, *34*, 1130–1137.

[13] A. Albinati, P. S. Pregosin, F. Wombacher, *Inorg. Chem.* **1990**, 29, 1812–1817.

[14] J. L. van der Veer, G. J. Ligtvoet, H. van den Elst, J. Reedijk, *J. Am. Chem. Soc.* **1986**, *108*, 3860–3862.

[15] D. Gibson, S. J. Lippard, *Inorg. Chem.* **1987**, *26*, 2275–2279.

[16] A. C. Lepre, L. Chassot, C. E. Costello, S. J. Lippard, *Biochemistry* **1990**, *29*, 811–823.

[17] A. C. Lepre, K. G. Strothkamp, S. J. Lippard, *Biochemistry* **1987**, *26*, 5651–5657.

[18] M. Boudvillain, R. Dalbies, C. Aussourd, M. Leng, *Nucleic Acids Res.* **1995**, *23*, 2381–2388.

[19] M. A. Warpehoski, D. E. Harper, *J. Am. Chem. Soc.* **1995**, *117*, 2951–2952.

[20] S. Bevers, G. Xiang, L. W. McLaughlin, *Biochemistry* **1996**, *35*, 6483–6490.

Molecular Modulation of Surfactant Aggregation in Water: Effect of the Incorporation of Multiple Headgroups on Micellar Properties[**]

Jayanta Haldar, Vinod K. Aswal, Prem S. Goyal, and Santanu Bhattacharya[*]

Surfactant molecules self-organize in water,[1] often producing nearly spherical aggregates called micelles in dilute solutions, and lyotropic mesophases at higher concentrations. The polar headgroups of these aggregates lie near the bulk aqueous phase, whereas the hydrocarbon chains extend inwardly to avoid unfavorable water contacts. Electrostatic interactions between the headgroups determine their relative positions and separations in an aggregate. The correlation of the molecular structure of various surfactants with the aggregate type produced upon self-assembly is important as surfactant solutions are useful in a number of household, industrial, and scientific applications.[2]

Molecular design of surfactants of widely varying architectures offers an excellent opportunity for tailoring surfactant aggregation behavior and the resulting complex fluid properties. For instance, dimeric or oligomeric surfactants that consist of two or more conventional surfactant units connected at the headgroup by a suitable spacer are attracting attention because of the number of unusual properties that they manifest.[3]

In ionic micelles, surfactant molecules such as cetyltrimethylammonium bromide (CTAB) also ionize in aqueous solution and the corresponding micelles are aggregates of

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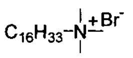
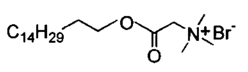
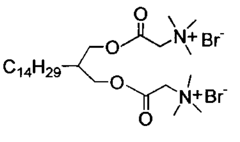
[**] This work was supported by a grant from the Inter University Consortium. S. B. is the Swarnajayanti Fellow of the Department of Science and Technology.



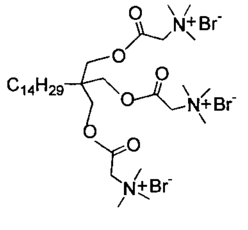
CTAB



1 ($h = 1$)



2 ($h = 2$)



3 ($h = 3$)

the resulting CTA$^+$ ions. However, the ionization is far from complete on a micellar surface. The Br$^-$ counterions, tend to stay near the CTA$^+$ micellar surface. The shape, size, fractional charge of the micelle, and the inter-micellar interaction depend on the distribution and nature of these counterions.[4]

It was however, not clear whether a surfactant will form micelles, if several charged headgroups are incorporated on one end of a single hydrocarbon chain of the surfactant molecule. This is because with every increase in the number of charges, the micellar surface demands a progressively smaller aggregation number, which is not consistent with the micellar volume that has to be filled. In such a situation does the surfactant behave like a salt, for example NaCl, where the surfactant is fully ionized (as is NaCl into Na$^+$ and Cl$^-$ ions) and there is no aggregation of cations? To address this fundamental question, we have synthesized a novel class of cationic surfactants with multiple headgroups and herein we show for the first time that they indeed form micelles.

The newly designed surfactants **2** and **3** are intriguing, since for a given hydrophobic part, the cationic headgroup charges (h) are increased two or three times over that of the reference surfactant, which bears a single cationic headgroup (**1**, $h = 1$). The critical micelle concentration (cmc) for each surfactant was determined at 25 °C by plotting the values of the pyrene fluorescence intensity ratio I_3/I_1, against the surfactant concentration.[5] For each surfactant reproducible breaks were observed indicating the onset of micellization. The cmc values obtained using this procedure were ~1.0 mM (**1**), 3.5 mM (**2**), 3.7 mM (**3**), and the value obtained using the same method for CTAB (0.8 mM) was consistent with the cmc value reported.[5]

To investigate the aggregate microstructures of these surfactants in water we used small angle neutron scattering (SANS), a noninvasive technique that provides information on colloidal particles of a length of 10–1000 Å. SANS has been used to obtain structural details about complex fluids of diverse origin. These include micellar solutions,[6a] microemulsions,[6b] polymers,[6c] proteins,[6d] materials,[6e] and biological samples.[6f] Since neutrons have an irregular variation of scattering length for various elements, the contrast between the particle and the matrix can be easily varied to enhance the signal. Thus SANS is an ideal technique to obtain information about the micellar shape, size, aggregation number, charge on the micelle, the extent of hydration, and the inter-micelle interaction.[7, 8] SANS experiments involve measurement of differential scattering cross section ($d\Sigma/d\Omega$) as a function of wave vector transfer Q.

SANS distributions from micellar solutions of the surfactants CTAB and **1**–**3** at a fixed surfactant concentration and temperature are shown in Figure 1. All the distributions show well-defined peaks characteristic of suspensions of charged particles.[6a] The SANS distribution from a suspension of charged particles or a micellar solution is determined by the product of two terms, namely, the intra-particle structure factor $P(Q)$ and the inter-particle structure factor $S(Q)$. $P(Q)$ depends on the shape and size of the particle, $S(Q)$ on the inter-particle distance and the inter-particle interaction potential. The peak in the SANS distribution is the consequence of a corresponding peak in the inter-particle structure factor $S(Q)$. Usually this peak occurs at $Q_m \approx 2\pi/d$, where d is the average distance between micelles and Q_m is the value of Q at the maximum of the peak. Since Q_m was found to vary with the number of headgroups (h), one can conclude that inter-micelle distance and hence the number density (n) of micelles is not the same for the above surfactant solutions even when they have identical surfactant concentrations. This also suggests that the aggregation number (N) (the number of molecules that form a micelle) of the micelles varies with the number of headgroups. The actual value of N was determined by analyzing the data using the method of Hayter and Penfold.[7] In addition, this analysis provided information about the micellar dimensions and the fractional charge ($\alpha = Z/N$, where Z is charge on the micelle).

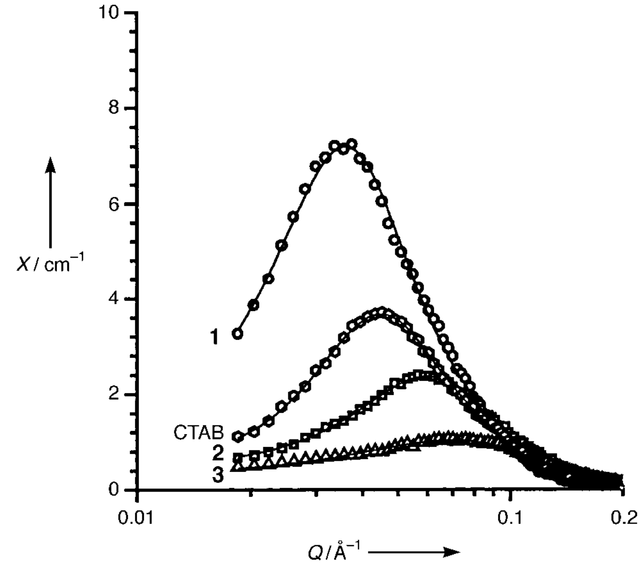


Figure 1. SANS distributions of micellar solutions of CTAB and the newly synthesized surfactants **1**–**3** at a concentration of 50 mM and 40 °C. Q = wave vector transfer; X = cross section.

These results demonstrate that micelles are indeed formed from all the surfactants tested here irrespective of the number of headgroups (h). The aggregation number (N) decreases with an increase in h. This is understandable as with larger headgroup sizes and enhanced electrostatic repulsion, as in the cases with $h = 2$ and $h = 3$, greater micellar surfaces are required and fewer surfactant molecules can be accommodated in a single micellar aggregate.

Compared with the surfactant **1** ($h=1$), CTAB micelles have a considerably lower aggregation number ($N=135$ vs 244, Table 1) at the same concentration and temperature, even though the CTAB micelles also have a single Me_3N^+ headgroup per hydrocarbon chain. It is possible that the surfactant **1** is more tightly associated in the micellar aggregate because of the presence of an ester linkage [-OC(O)-] between the Me_3N^+ headgroups and the hydrocarbon chain. The presence of this linkage facilitates intermonomer association through dipolar interactions. Furthermore since these ester linkages are located near the "Stern-layer" region[9] of the micelles, strong hydrogen bonding interactions among the surfactant molecules can occur through interfacially associated water molecules.[10]

Table 1. Micellar parameters of the surfactants CTAB and **1**–**3**.[a]

Surfactant	N[b]	α	Semi-minor axis $b=c$ [Å]	Semi-major axis a [Å]	a/b
1	244	0.08	24.5	66.9	2.73
2	48	0.23	17.3	36.2	2.10
3	20	0.27	14.5	27.3	1.88
CTAB	135	0.14	22.0	37.3	1.70

[a] All the SANS spectra were performed at 40°C using 50 mM micellar solutions. [b] The aggregation number, N, is calculated from the relation $N=\pi a b^2/3v$ where, a = semi-major axis, b = semi-minor axis and v = volume of the surfactant monomer (Tanford's equation (C. Tanford, *J. Phys. Chem.* **1972**, *76*, 3020–3024)).

The drop in the aggregation number (N) on an increase in the number of headgroups (Table 1) is expected as with each rise in the number of cationic headgroups the charge repulsion between the headgroups becomes more pronounced. To accommodate these unfavorable electrostatic consequences the hydrocarbon chains in the micelles of multiheaded surfactants take up severely bent conformations (Figure 2) leading to the formation of an increasingly "disorganized" collection of surfactant molecules in the resulting micellar aggregate. In such "porous" aggregates, the hydrophobic core of micelles has a more aqueous environment. By comparison, in micelles of surfactants bearing a single charge on the headgroup the hydrocarbon chains are considerably more extended, and the terminal CH_3 group buried deeply in the core. Noteworthy is that at the surfactant concentration of 50 mM, micelles are prolate ellipsoidal ($a \neq b=c$) in all the samples including CTAB. The semi-major axis (a) and the semi-minor axis (b) are given in Table 1; both a and b and the axial ratio a/b decrease when h is increased.

Fractional charge (α) is a measure of the dissociation of the counterion of surfactant molecules present in the micelle. Analysis of the SANS data (Table 1) gives a fractional charge of 0.08 for the surfactant with single headgroup ($h=1$). This means that only 8% of the counterions (Br^-) are dissociated from the micelle of this surfactant leaving the remaining 92% bound.

The data in Table 1 also show that α increases with the number of headgroups on the surfactant. This is not surprising if the equilibrium dissociation constant increases linearly with the number of cationic headgroups per surfactant molecule, then one could expect, $\alpha_2=2\alpha_1$, and $\alpha_3=3\alpha_1$ where α_1, α_2, α_3 represent fractional charges on the single-, double-, and triple-headed surfactant respectively. However, from Table 1, we see that $\alpha_2>2\alpha_1$, suggesting far greater dissociation of the counterions in the case of micelles of a double-headed surfactant than would be expected merely from doubling the number of headgroups of the single-headed surfactant. Double-headed surfactants require more room at the headgroup level than that needed for the packing of two single-headed surfactants in a micelle. This is because the positive charges located on each of the two heads of **2** tend to stay as far apart as possible as a result of electrostatic repulsion. In addition, with an increase in charge, the headgroup hydration increases facilitating greater ionization.

Although the Me_3N^+ units on the triple-headed surfactant **3** tend to stay as far apart as possible, the intermolecular repulsion between individual surfactants in the micelle increase steeply. As a consequence, the aggregation number of these micelles is considerably lower than that in **2**. To alleviate the headgroup level repulsion and to fill up the micellar volume, the hydrocarbon chains in these micelles take up bent conformations. While increased charge facilitates hydration, the hydrocarbon chain coiling regulates the extent of the increase in the fractional charge (α_3).

Additives such as KBr[11] (0.1M) or sodium salicylate (Na-Sal)[12a–f] (0.01M) induce pronounced micellar growth of CTAB (0.1M) leading to marked increases in the viscosity of the resulting micellar solutions. This has been attributed to the transition from spherical to rod-like morphology.[12e] While surfactant **1** also showed similar behavior in the presence of Na-Sal (0.01M) or KBr (0.1M), such changes in viscosity could not be brought about with the micelles of either **2** or **3** even with very high concentrations of the above additives. This prompted us to examine rheological properties of each surfactant solution[12a–d] in the presence of Na-Sal at a chosen Na-Sal-to-surfactant ratio of 25 mM Na-Sal and 50 mM surfactant (see Experimental Section).

Soon after mixing the samples, CTAB-Na-Sal/W or **1**-Na-Sal/W (where W = water) developed into thick, viscous masses. Oscillatory shear experiments were conducted at a torque ramp from 0.001 to 100 Pa to find the stress where these materials were in the linear response region. Shear stress of 1.5 Pa and 1.0 Pa was used for solutions of CTAB and **1**, respectively, Figure 3. In both figures, the curves describing G′ and G″ cross as the frequency increases, indicating that these materials are more elastic than viscous at higher

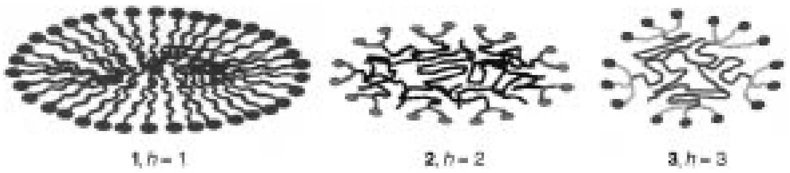


Figure 2. Schematic representation of multiheaded surfactant micelles where chain coiling is required to alleviate inter-surfactant headgroup repulsion within the aggregate.

frequencies. In Figure 3a, G′ reaches a plateau and G″ first has a maximum, then a minimum, and finally increases with increasing frequency. In contrast in Figure 3b, both G′ and G″ curves continue to slope upward with increasing frequency.

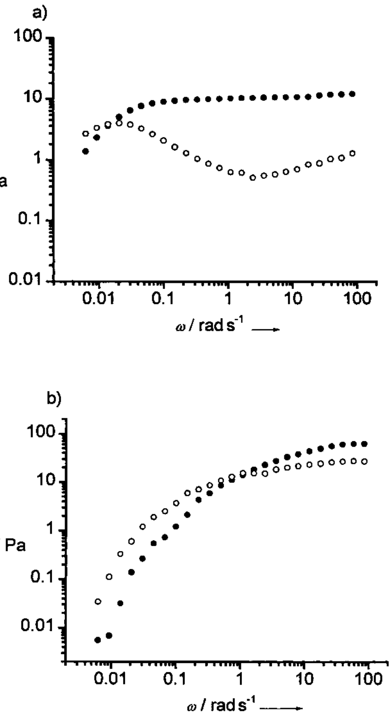


Figure 3. The dependence of storage moduli, G′ (●) and loss moduli, G″ (○) as a function of shear rate for a solution containing 50 mM surfactant and 25 mM Na-Sal. a) CTAB; and b) **1** ($h = 1$).

In the case of mixtures of solutions containing Na-Sal and either **2** or **3** which remained as *free-flowing* solutions, the oscillatory shear experiments were attempted at several different stress values from 0.003 Pa to 10 Pa. However, it was not possible to perform oscillatory shear experiments with **2**-Na-Sal/W or **3**-Na-Sal/W as the viscosity of these samples did not change significantly from that of the surfactant solutions alone. This observation indicates that these samples were inelastic although they might be a little more viscous than water and suggests that there is no significant change in the micellar structure of **2** and **3** in the presence of Na-Sal. This result clearly shows that the number of headgroups on the surfactant molecule could significantly modulate the organic-salt-induced micellar growth.

In summary we have observed some unusual effects associated with the micellar aggregation properties of surfactants with two or three cationic headgroups. We find for the first time that the hydrocarbon chains in the micelles from surfactants bearing multicharged headgroups are highly folded. The maximum number of charged headgroups that can be attached onto a single hydrocarbon chain so that micelle formation is still feasible remains to be examined. The counterion distributions around the micelles from surfactants with multiple headgroups also need to be elucidated.

Experimental Section

Synthesis: The compounds **1** ($h = 1$), **2** ($h = 2$), and **3** ($h = 3$) were synthesized by esterification of 1-hexadecanol, 2-hydroxymethyl-hexadecanol or 2,2-dihydroxymethyl-hexadecanol, respectively, with 1.1, 2.2, and 3.3 equivalents of 2-bromoacetyl bromide in the presence of Et_3N and a catalytic amount of 4-dimethylaminopyridine (DMAP) in CH_2Cl_2/THF (1/1). After purification, the respective bromoacetylated products were quaternized with NMe_3 in dry acetone in screw-top pressure tube. Pure surfactants **1** (yield 98%), and **2** (87%) were obtained upon repeated recrystallizations from $CHCl_3$/*n*-hexane, and $CHCl_3$/EtOAc respectively. **3** (65%) was purified by repetitive precipitation from $CHCl_3$/EtOAc/*n*-hexane mixture. **2** and **3** were found to be extremely hygroscopic.

Selected spectroscopic and analytical data for the new surfactants: **1**: IR (KBr): $\tilde{\nu} = 1751\ cm^{-1}$ (C=O); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (t, 3H, CH_3), 1.25 (s, 26H, 13 × CH_2), 1.63–1.70 (m, 2H, CH_2CH_2O), 3.67 (s, 9H, 3 × N^+CH_3), 4.18 (t, 2H, CH_2O), 4.99 (s, 2H, CH_2N^+); ESI-MS (HP1100LC-MSD): [M^+] $(C_{21}H_{44}NO_2)^+$: calcd: 342.3, found: 342.2; elemental analysis (%) for $C_{21}H_{44}NO_2Br$ calcd: C 59.7, H 10.5, N 3.31; found: C 59.54, H 10.63, N 2.95. **2**: IR (KBr): $\tilde{\nu} = 1749\ cm^{-1}$ (C=O); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (t, 3H, CH_3), 1.26 (s, 26H, 13 × CH_2), 2.12–2.18 (m, 1H, $CHCH_2O$), 3.62 (s, 18H, 6 × N^+CH_3), 4.03 (dd, 2H_a, 2 × $CHCH_aH_bO$), 4.44 (dd, 2H_b, 2 × $CHCH_aH_bO$), 5.50 (*s*, 4H, 2 × CH_2N^+); ESI-MS (HP1100LC-MSD): [M^{2+}] $(C_{27}H_{56}N_2O_4)^{2+}Br^-$ (78.91): calcd: 551.3, found: 551.3, [M^{2+}] $(C_{27}H_{56}N_2O_4)^{2+}Br^-$ (80.91): calcd: 553.3, found: 553.4. [M^{2+}]/2: calcd: 236.2, found: 236.1; elemental analysis (%) for $C_{27}H_{56}N_2O_4Br_2 \cdot H_2O$: calcd: C 49.85, H 8.99, N 4.3; found: C 49.53, H 8.97, N 3.9. **3**: IR (KBr): $\tilde{\nu} = 1751\ cm^{-1}$ (C=O); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (t, 3H, CH_3), 1.26 (s, 26H, 13 × CH_2), 3.36 (*s*, 27H, 9 × N^+CH_3), 4.25 (s, 6H, 3 × CH_2O), 5.57 (s, 6H, 3 × CH_2N^+); ESI-MS (HP1100LC-MSD): [M^{3+}] $(C_{33}H_{68}N_3O_6)^{3+}2Br^-$ (78.91): calcd: 760.3, found: 760.3, [M^{3+}] $(C_{33}H_{68}N_3O_6)^{3+}Br^-$ (78.91) Br^- (80.91): calcd: 762.3, found: 762.4, [M^{3+}]2Br^- (80.91): calcd: 764.3, found: 764.3, [M^{3+}]Br^- (78.91)/2: calcd: 340.7, found: 340.7, [M^{3+}]Br^- (80.91)/2: calcd: 341.7, found: 341.6, M^{3+}/3: calcd: 200.8, found: 200.9; elemental analysis (%) for $C_{33}H_{68}N_3O_6Br_3 \cdot H_2O$: calcd: C 46.05, H 8.2, N 4.88; found: C 45.67, H 8.05, N 4.43.

CMC Measurements: In a Hitachi model F-4500 fluorescence spectrometer, steady-state fluorescence emission ($\lambda_{ex} = 310$ nm) because of pyrene doped in micellar solutions was measured at 25 °C. The cmc values were determined from the plots of the concentrations of the respective surfactant versus the ratio (I_3/I_1) of the intensities of the third (I_3) and the first (I_1) vibronic peaks in the emission spectra.

SANS Measurements: Neutron-scattering experiments were performed at 40 °C on a 1.85 m (sample to detector distance) SANS spectrometer equipped with a linear position-sensitive detector, (LPSD) at the Dhruva reactor, Trombay, India. To provide a good contrast between the micelle and the solvent, surfactant solutions (50 mM) were prepared in D_2O. The spectrometer made use of a BeO filter as the monochromator. The mean wavelength (λ) of the incident neutron beam is 5.2 Å. The wave vector transfer Q ($= 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle) in SANS spectrometers is small, typically in the range 0.001 to 1.0 Å^{-1}. The Q range of the instrument is 0.018–0.32 Å^{-1}. To obtain low Q values, the SANS instrument used large wavelength (~5 Å) neutrons and small scattering angles (~0.5–10°). The data were corrected for detector background sensitivity, empty cell scattering and sample transmission factors. The D_2O intensity was subtracted from that of the sample. The corrected intensities were normalized to absolute cross-section units. The experimental points were fitted using nonlinear least-squares routine. The SANS distributions have been analyzed by Hayter-Penfold method.[7] The original model, which was valid for spherical micelles, has subsequently been modified for other aggregation shapes.

Rheological Measurements: The sample solutions for rheological measurements were mixtures of aqueous solutions of surfactant and sodium salicylate (Na-Sal). Solutions were prepared by adding water to weighed quantities of the respective surfactant and Na-Sal and the mixture was heated > 50 °C to ensure complete dissolution. The final concentrations of surfactant and Na-Sal were 50 mM and 25 mM respectively. All the solutions were left standing for 1 day at ambient temperature to reach equilibrium. The rheological properties of the above mixtures were measured with a Rheolist TA Instrument (model AR1000, cone and plate geometry with a truncation gap of 53 μm). The radius of the cone was 20 mm, and the angle between the cone and plate was 2°. The experiments were performed at 35 °C for the single-headed surfactant **1** and at 25 °C for CTAB, **2**, and **3**. Both the steady shear (flow-step) and oscillatory shear (stress control) measurements were performed and the measurements were taken over a frequency sweep range of 0.001 to 100 s^{-1}. The rheometer has a built-in computer which converts the torque measurements into either G′ (the storage modulus) and G″ (the loss modulus) in oscillatory shear experiments or viscosity in flow-step measurements.

Received: August 16, 2000
Revised: January 2, 2001 [Z15649]

[1] F. M. Menger, J. S. Keiper, *Angew. Chem.* **2000**, *122*, 1980–1996; *Angew. Chem. Int. Ed.* **2000**, *39*, 1906–1920.
[2] J. M. Schnur, *Science* **1993**, *262*, 1669–1676.
[3] a) R. Zana, Y. Talmon, *Nature* **1993**, *362*, 228–230; b) S. Bhattacharya, S. De, *Chem. Eur. J.* **1999**, *5*, 2335–2347.
[4] R. Oda, I. Huc, M. Schmutz, S. J. Candau, F. C. Mackintosh, *Nature* **1999**, *399*, 566–569.
[5] K. Kalyanasundaram, J. K. Thomas, *J. Am. Chem. Soc.* **1977**, *99*, 2039–2044.
[6] a) S. De, V. K. Aswal, P. S. Goyal, S. Bhattacharya, *J. Phys. Chem.* **1996**, *100*, 11664–11671; b) M. Dreja, W. P. Hintzen, H. Mays, B. Tieke, *Langmuir* **1999**, *15*, 391–399; c) J. S. Higgins, H. C. Benoit, *Polymers and Neutron Scattering*, Clarendon Press, Oxford, **1994**; d) V. Receveur, D. Durand, M. Desmadril, P. Calmettes, *FEBS Lett.* **1998**, *426*, 57–61; e) G. Kostorz in *Neutron Scattering, Vol. 15* (Ed.: G. Kostorz), Academic Press, New York, **1979**, pp. 227–289; f) J. Trewhella, S. C. Gallagher, J. K. Kruegu, J. Zhao, *Sci. Prog. Oxford* **1998**, *81*, 101–122.
[7] J. B. Hayter, J. Penfold, *Colloid Polym. Sci.* **1983**, *261*, 1022–1030.
[8] S. H. Chen, T. L. Lin in *Methods of Experimental Physics, Vol. 23B* (Eds.: D. L. Price, S. K. Skold), Academic Press, New York, **1987**, pp. 489–542.
[9] J. H. Fendler, *Membrane Mimetic Chemistry*, Wiley, New York, **1982**.
[10] S. Bhattacharya, S. Haldar, *Langmuir* **1995**, *11*, 4748–4757.
[11] V. K. Aswal, P. S. Goyal, *Phys. Rev. E* **2000**, *61*, 2947–2953.
[12] a) T. Shikata, H. Hirata, T. Kotaka, *Langmuir* **1987**, *3*, 1081–1086; b) M. Löbl, H. Thurn, H. Hoffmann, *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 1102–1106; c) H. Rehage, H. Hoffmann, *J. Phys. Chem.* **1988**, *92*, 4712–4719; d) H. Rehage, H. Hoffmann, *Mol. Phys.* **1991**, *74*, 933–973; e) T. M. Clausen, P. K. Vinson, J. R. Minter, H. T. Davis, Y. Talmon, W. G. Miller, *J. Phys. Chem.* **1992**, *96*, 474–484; f) V. K. Aswal, P. S. Goyal, P. Thiyagarajan, *J. Phys. Chem. B* **1998**, *102*, 2469–2473.

$R^*_4Tl_3Cl$ and $R^*_6Tl_6Cl_2$ ($R^* = SitBu_3$)—The First Compounds with Larger Clusters Containing Covalently Linked Thallium Atoms[**]

Nils Wiberg,* Thomas Blank, Hans-Wolfram Lerner, Dieter Fenske und Gerald Linti

Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 60th birthday

Many compounds of the compositions TlR_3 and TlR (R = inorganic, organic group) exist with thallium in the oxidation states +III and +I,[1] (the Tl–R bonds in the former compounds are more covalent in nature, those in the latter more electrovalent), whereas very few compounds of the composition TlR_2 with thallium in the oxidation state +II are known to date. They form dimers $R_2Tl{-}TlR_2$ with a covalent Tl–Tl bond (Tl–Tl 2.914 ($R = Si(SiMe_3)_3$),[2] 2.966 ($R = SitBu_3$),[3] 2.881 Å ($R = SitBu_2Ph$)[4]). A few Tl^I compounds also have Tl–Tl bonds; however, as weak interactions with Tl–Tl distances > 3.3 Å these vary significantly from the strong interactions in the three reported dithallanes with Tl–Tl distances < 3.0 Å (e.g. $(PhCH_2)_5C_5Tl \cdots TlC_5(CH_2Ph)_5$: Tl–Tl 3.632 Å;[5] $[(Me_3Si)_3CTl]_4$: Tl–Tl 3.322 and 3.627 Å;[6] $\{MeSi[N(Tl)tBu]_3\}_2$ has a Tl–Tl distance in the intermediate range (3.146 Å) and in addition several very weak Tl–Tl interactions;[7] in $\{MeC[CH_2N(Tl)SiMe_3]_3\}_2$ and other Tl^I amides Tl–Tl interactions exclusively occur with very large Tl–Tl distances (> 3.6 Å)[8]). Thallium cluster compounds containing more than two covalently linked thallium atoms were hitherto unknown.

We obtained compounds of this type, namely the trithallane $R^*_4Tl_3Cl$ (**1**) and the hexathallane $R^*_6Tl_6Cl_2$ (**2**), in the attempt to synthesize sterically overloaded disupersilylthallium chloride R^*_2TlCl (R^* = supersilyl = $SitBu_3$) analogously to the preparation of R^*_2ECl (E = Al, Ga, In)[9] from the trihalide ECl_3 and two molar equivalents of supersilylsodium NaR^* in tetrahydrofuran (THF). Treatment of $TlCl_3$ in THF at −78 °C with NaR^* in the molar ratio 1:2 leads to the slow (several hours) formation of a red-brown reaction solution as well as a

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[+] Crystal structure analyses

[**] Compounds of Silicon, Part 143. Supersilyl Compounds of Boron and Its Homologues, Part 12. This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. Part 42: N. Wiberg, W. Niedermayer, *J. Organomet. Chem.* **2001**, in press; Part 11. M. Kehrwald, W. Köstler, A. Rodig, G. Linti, T. Blank, N. Wiberg, *Organometallics* **2001**, in press.

1433-7851/01/4007-1232 $ 17.50+.50/0