second red-brown band. The solution was evaporated to dryness and recrystallized from benzene–hexane to yield 0.05 g (1.5%) of π-cyclopentadienyltriphenylphosphinerhodium diiodide (**6**).

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Registry No. **2c**, 50276-27-2; **3a**, 50276-28-3; **3b**, 50276-29-4; **3c**, 50430-95-0; **4**, 12203-93-9; **5**, 34922-92-4; **6**, 12131-90-7; **7**, 32660-88-1; **8**, 50276-32-9; **1c**, 12192-96-0; **2a**, 12078-24-9; **2b**, 12078-27-2; PPh$_3$, 603-35-0.

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Studies of Membrane Processes. II. Participation of the Dimethyltin Ion in an Electrical Double Layer

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In two recent communications[2] from this laboratory, we have shown that the structure of complex ions can be investigated in lyotropic nematic phases. The thermotropic nematic phases, which are generally useful media for ordering molecular solutes, are not suitable for ionic compounds because of their general organic nature. Lyotropic nematic phases on the other hand[3-7] are much more sensitive to molecular solutes and undergo transitions to isotropic or lamellar phases at relatively low concentrations of solute. The study of small oriented solute molecules by nuclear magnetic resonance (nmr) spectroscopy is well established[8] and leads in general to structural data in terms of internuclear distance ratios. While X-ray and neutron diffraction have been the only useful tools to determine the structures of ions so far, it is evident that the nmr method of oriented ionic species becomes available and has the advantage that the nuclear positions in ionic structure are determined in an aqueous environment.[2] This report is the first determination of relative atomic positions in an aqueous ion. The dimethyltin ion reported here requires either a ^{13}C nmr spectrum or sensitivity enhancement of the proton spectrum of the ^{13}C-containing ions to determine relative positions of all atoms. Since we are not equipped for this work, the structural information is limited to proton and tin positions.

The thermotropic phase imposes orientation on solute molecules from the uniaxial and parallel alignment to the magnetic field of the molecular tumbling in the nematic solvent. The nature of the lyotropic middle nematic soap phase is quite different. The optic axis of superlattice structures of cylindrical arrangements is perpendicular to the magnetic field in highly and homogeneously aligned samples.[9] The cylinders are composed of hydrophobic hydrocarbon chains in the interior with ionic head groups at the interface and an aqueous counterion environment filling the interior space between varied packing of the cylinders.[10] The complex ion which achieves orientation in the phase does so in an exchange process in the interface region of the oriented electrical double layer. The proposed exchange process in the interstitial water of the nematic phase and with the electrical double-layer interface can be regarded chemically as somewhat analogous to ion-pair formation at the interface and a free-ion environment in the water. The fact that the negative detergent counterions are highly ordered results in transfers of this order to the positive ion during the lifetime in the double layer.

Experimental Section

Spectra were recorded with both a Perkin-Elmer R10 spectrometer at 33.3° and 60 MHz and a Varian T-60 with probe temperature 33.0°. Dimethyltin decyl sulfate was synthesized by ion-exchange methods from sodium decyl sulfate. Dowex 50 H^+ (13 ml) was washed with a dilute aqueous solution (5.5 g/100 ml of water) of dimethyltin dichloride until the eluent was neutral. The column was then washed with 200 ml of water. Sodium decyl sulfate solution (2.6 g/50 ml of water) was then slowly passed down the column followed by 100 ml of distilled water. The eluted solution was evaporated to dryness in a vacuum desiccator. The product was used without further purification to avoid complexation of the dimethyltin ions with organic donor molecules.[11]

The composition of the middle soap phase was 40 wt % dimethyltin decyl sulfate, 50% D_2O, 4% sodium sulfate, and 6% decanol.[2] All nmr spectra were calibrated by the audio side band technique and measured on a frequency counter.

Results

A study of the spectrum of the dimethyltin ion in aqueous solutions was considered necessary because previous work shows the scalar spin–spin coupling $^{2}J_{\text{H-Sn}}$ to be solvent and concentration dependent.[11] Concentrations of dimethyltin dinitrate (prepared by ion exchange) were made up in water so as to cover the region of concentration of the ion in the aqueous part of the nematic phase (1.5–3.0 mol %). The values of J obtained for these solutions were as follows: 1.5 mol %, $J = 102.5 \pm 0.1$ Hz (weighted mean value of J for the tin-117 and tin-119 isotopes); 1.9 mol %, $J = 102.5 \pm 0.1$ Hz; 2.2 mol %, $J = 102.8 \pm 0.1$ Hz; 3.0 mol %, $J = 102.6 \pm 0.1$ Hz. Each determination is the result of eight calibrations of different spectra of each tin satellite. The values are satisfactorily independent of concentration. The environment of an isotropic aqueous solution is sufficiently different from the aqueous part of the nematic phase to warrant a further check on J. Isotropic concentrated micellar[10] solutions of dimethyltin decyl sulfate were prepared in water containing sodium sulfate but omitting the decanol to avoid mesophase formation. The proportions of compounds by weight were

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Table I. Comparison of the Structural Parameters for Dimethyltin Ion with Other Molecular Species of Similar Symmetry with Freely Rotating Methyl Groups[a]

	I	II	III	IV	V
D_{12}/D_{11}	−0.0820 ± 0.0002	−0.0787 ± 0.0001	−0.0802 ± 0.0009	−0.0344 ± 0.0002	−0.0263 ± 0.0002
β	21.348 ± 0.0002	22.036	21.712	41.08	49.83
ρ,* Å	1.033 ± 0.005	1.033 ± 0.005	1.033 ± 0.005	1.033 ± 0.005	1.033 ± 0.005
ξ_0, Å	4.77 ± 0.03	4.84 ± 0.03	4.81 ± 0.03	6.62 ± 0.03	7.29 ± 0.03
$\sqrt{\langle R^2 \rangle}$	4.99 ± 0.01	5.06 ± 0.01	5.03 ± 0.01	6.77 ± 0.01	7.43 ± 0.02
$\langle\theta\rangle$, deg	17.0 ± 1.0	16.7 ± 1.0	16.8 ± 1.0	12.4 ± 1.0	11.3 ± 1.0
δ, deg	23.4 ± 0.2	23.0 ± 0.2	23.2 ± 0.2	17.3 ± 0.2	15.8 ± 0.2
r, Å	2.60 ± 0.02	2.63 ± 0.02	2.61 ± 0.02	3.46 ± 0.02	3.78 ± 0.02

[a] The first column refers to structural parameters identified in Figure 2. The asterisk signifies that the value of ρ is assumed in all cases. The Roman numerals at the heads of columns refer to the following molecules with literature references given: I, dimethyltin ion (present work); II, dimethylmercury;[20] III, dimethylacetylene;[13] IV, 2,3,5,6-tetrachloroxylene;[21] V, 2,4-dimethylhexadiine.[12] "r" is the distance from methyl protons to the center of symmetry of the molecule.

as close as possible to those in the phase. The weighted mean of the value of $^2J_{\text{H-Sn}}$ was 106.9 ± 0.1 Hz. The weighted mean coupling is obtained by taking into account the relative natural abundances of tin-117 and tin-119 which give two proton satellite spectra with small separations. In the phase, separate satellites for the tin isotopes were not observable.

Figure 1 illustrates the spectrum of oriented dimethyltin ion in the lyotropic nematic phase. The main peaks are split into a 1:2:1 triplet and these have several components. The center peaks (a) of total relative intensity 2 are symmetrically arranged while at +428 Hz the upper resonance (b) of relative intensity 1 is not a symmetric arrangement of transitions. The spectrum is typical for an $A_3A'_3$ spectrum and has been fully described before.[12,13] Three parameters determine the spectrum: the intra- and intermethyl proton-proton dipolar couplings D_{11} and D_{12} and the intermethyl scalar coupling J_{12}. The spectrum was analyzed using a modified UEA program[14] by selecting 15 observable transitions averaged over five spectra to give on the final iteration a fit to these transitions with an rms error of ±0.27 Hz. The derived values were D_{11} = 285.37 ± 0.03 Hz, D_{12} = −23.40 ± 0.09 Hz, and J_{12} = −0.1 ± 0.1 Hz. The spectrum is sensitive to the relative signs of D_{11} and D_{12}.

In Figure 1 the spectrum of the tin satellites can only be identified for a few transitions, because of signal to noise problems with the instrumentation available. If we consider the two tin isotopes of spin $^1/_2$, tin-117 and tin-119, as giving only one satellite transition instead of two because of the small magnitude of H-Sn couplings, then sufficient transitions of the $A_3A'_3$ part of the $A_3A'_3X$ spectrum can be measured. The separation of the two $A_3A'_3$ subspectra are determined by $|D_{\text{SnH}} + J_{\text{SnH}}|$. From careful examination of 20 spectra the value $|D_{\text{SnH}} + J_{\text{SnH}}|$ = 55.1 ± 0.4 Hz was computed. Some of the tin satellites are denoted in Figure 1a by circles above them.

Discussion

Changes in Environment between Isotropic Aqueous and Lyotropic Nematic Phases. Ion-pair formation in isotropic aqueous solutions does have some effect on chemical shifts which vary with concentration.[15] The magnitude of change in the chemical shift derived from ion pairs with changes in concentration depends a great deal on the sensitivity of the nuclear spin studied to electronic distributions in the ions but also on the extent of ion pairs formed. The extreme cases are proton-containing ions and thallium ions;[16,17] the latter are extremely sensitive and have a tendency to ion pair. Dimethyltin is studied by proton resonance methods here so we expect the chemical shifts to be a very insensitive measure of the difference in solvent environment between water and the lyotropic phase.

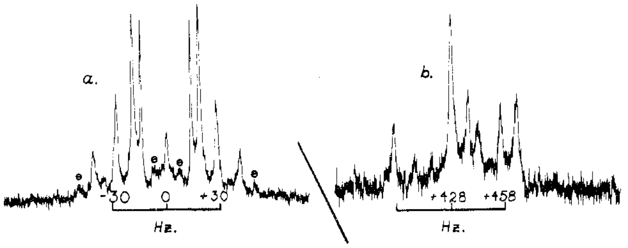

Figure 1. The nmr spectrum of the dimethyltin ion in the lyotropic nematic phase described in the text. The central group of transitions of total relative intensity 2 is shown as part a of the figure on the left, while the upfield components of total relative intensity 1 are shown on the right. The gain of the spectrometer was increased to display part b since the line widths are somewhat broader and the intensities lower. The slight increases in line width of the outer transitions (b) are associated with very small deviations from homogeneous orientation throughout the phase. The $A_3A'_3$ part of the $A_3A'_3X$ spectrum derived from ions with tin-117 and tin-119 spin $^1/_2$ nuclei of natural abundance 7.67 and 8.68% can be seen in averaged form for some of the strongest transitions. Because the tin atom is at the center of symmetry of the ion, the $A_3A'_3$ spectrum is split into two subspectra separated by $|J_{\text{SnH}} + D_{\text{SnH}}|$.

In rare cases there is a change in scalar coupling within the ion as concentration in water is varied[11,18,19] and this has been investigated by Hunter and Reeves[11] for the dimethyltin ion in water. The dimethyltin ion thus provides a sensitive probe for the change in solvent conditions from water to the lyotropic phase. The changes in $^2J_{\text{Sn-H}}$ with concentration in water for $(CH_3)_2Sn^{2+}$ as the dichloride in the region from 8 mol % to infinite dilution are between 97 and 112 Hz.[11] In 50:50 acetone-water over the same range the coupling constant varies from 93 to 105 Hz at infinite dilution (extrapolated). These changes are associated with the final stages of dissociation of the electrolyte $(CH_3)_2SnCl_2$ and some formation of solvated acetone or water complexes at infinite dilution.[11] The coupling constant measured here of 102.6 ± 0.2 Hz for the nitrate between 1.5 and 3 mol % concentrations in water and the value 106.9 Hz in the con-

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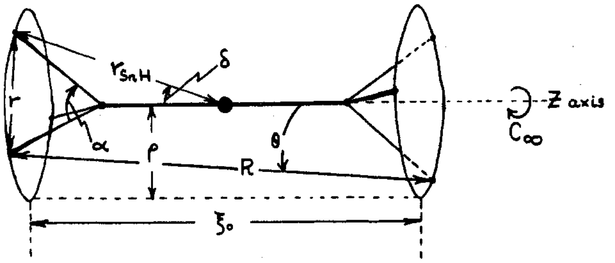

Figure 2. Geometric parameters appropriate for a discussion of the structure of the dimethyltin ion. On the nmr time scale the C–Sn–C bond direction is a C_∞ axis, denoted as the *z* axis. The methyl protons protons rotate freely on two circles displaced a distance ξ_0. The intramethyl proton–proton distance is "*r*." The instantaneous value of the intermethyl proton–proton distances is designated as "*R*;" this axis makes an angle θ with the *z* axis. "ρ" is the radius of the two circles swept out by the rotating methyl protons. "r_{SnH}" is the tin–proton distance and this vector makes an angle δ with the *z* axis. The H–C–H angles are given the symbol "α."

centrated micellar solution both lie in the expected range but indicate considerably different solvation of the dimethyltin ion. In what follows we shall be able to derive the actual value of the scalar coupling ${}^2J_{Sn-H}$ in the lyotropic nematic phase from analysis of the spectra in structural terms.

Analysis of Structural Details. The dimethyltin ion is known to be linear and Figure 2 depicts the geometric parameters necessary for discussion. Saupe[12] has treated a similar case and we shall adopt the same notation. Assuming that the methyl groups rotate freely and independently, the ratio of D_{12} to D_{11} is given by

$$\frac{D_{12}}{D_{11}} = \frac{-3\sqrt{3}}{\pi} \int_0^{2\pi} \frac{[(\beta - 1) + \cos\phi]}{[(\beta + 2) - 2\cos\phi]^{5/2}}\, d\phi \qquad (1)$$

for this particular linear arrangement.[12] ϕ is the relative rotational angle between the two methyl groups and $\beta = 3\xi_0{}^2/r^2 = \xi_0{}^2/\rho^2$. For free rotation, the value of $\beta = 21.348 \pm 0.002$ was obtained from the experimental values of D_{12} and D_{11} by use of a small computer program. If we now assume that $\rho = 1.033$ Å (from a tetrahedral carbon and a C–H bond distance of 1.097 Å) the value $\sqrt{\langle R^2\rangle}$ becomes 4.99 ± 0.01 Å (taking all errors from the present experiment).

It is possible, since the tin atom is a center of symmetry, to compute the partially averaged dipole–dipole coupling constant D_{SnH}[20]

$$D_{SnH} = \frac{-3\sqrt{3}\gamma_{Sn}D_{11}}{\gamma_H} \sin^3\delta(2 - 3\sin^2\delta) \qquad (2)$$

γ_{Sn} and γ_H are the mean magnetogyric ratios of tin-117 and tin-119 to that of the proton, respectively. The value of D_{SnH} obtained from (2) is 51.8 ± 0.1 Hz. The separation of the two experimental $A_3A'_3$ subspectra gave the value $|D_{SnH} + J_{SnH}| = 55.1 \pm 0.4$ Hz. The only acceptable value of $|J_{SnH}|$ becomes 106.9 ± 0.5 Hz which is that obtained from the micellar solution. By this argument we have been able to show that the solvent environment, from the point of view of the dimethyltin ion, in the lyotropic phase is essentially the same as that of the concentrated micellar solution. Aqueous dimethyltin nitrate has a significantly different solvation at the same concentrations. This result has significance for the study of sonicated membranes. It appears, at least from the point of view of the free ions, that sonicated vesicles dispersed in water provide the same ionic environment as in the original membrane. It is assumed that sonicated vesicles correspond to micellar solutions and the original superstructure of the membrane corresponds to the nematic phase.

Comparison of Data for the Dimethyltin Ion with Previous Determinations on Similar Structures. Englert[20] has investigated the structure of dimethylmercury in a thermotropic solvent. This is also a linear species. In Table I we have collected the structural data in the literature[12,13,20,21] for all related structures determined by nmr spectra of oriented molecules and compared them with those for dimethyltin. A similar assumption that $\rho = 1.033$ Å has been made in all cases and eq 1 was used to compute β under the conditions of free and independent rotation of the two methyl groups. It is interesting to note that the covalent radii of tin and mercury are in the right order and that the acetylenic group -C≡C- is intermediate in size.

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Transition Metal Complexes as Ligands. The Dioxodithiotungstate Ion $WO_2S_2{}^{2-}$ [1]

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Recently, we reported novel transition metal complexes with the tetrathiotungstate ($WS_4{}^{2-}$)[2,3] and monooxotrithiotungstate ($WOS_3{}^{2-}$)[4a] ions as ligands (see also the review of Diemann and Mueller, where the chemistry of closed-shell transition metal chalkogen compounds has been reported,[4b] and the third edition of Cotton and Wilkinson[4c]). Since these bidentate ligands, in contrast to the thiosulfate[5] ion, coordinate only through sulfur, we have extended our studies to see whether this is also true for the dioxodithiotungstate ($WO_2S_2{}^{2-}$) ion and report here these results.

Experimental Section

General Information. Electronic absorption measurements were made on the chloroform or acetonitrile solutions of the compounds using a Perkin-Elmer EPS-3T recording spectrometer. Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer Model 180 recording spectrometer.

Carbon, hydrogen, and sulfur were determined microanalytically and phosphorus was determined as ammonium molybdatophosphate

Materials. $(NH_4)_2WO_2S_2$ was prepared as previously described.[6]

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