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(25) The Pd–Pd distance along the chains is 5.21 Å and between the chains (nearest) is ca. 7.58 Å. Furthermore, metal atoms of different oxidation states can only be adjacent to one another, where there is disorder in the crystal due to chains slipping past each other. See ref 8.
(26) The nature of the second d–d transition will depend to a first approximation on the relative order of the d orbitals of the tetravalent atom. It has been established[27] that the empty orbital on Pd(II) in complexes such as *trans*-$[Pd^{II}(NH_3)_2Cl_2]$ is $d_{x^2-y^2}$. The pronounced *z*-axis compression suffered by the Pd(IV) complex under discussion should make d_{z^2} the highest in energy. The other unfilled d orbital on this d^6 atom may then be d_{yz} or $d_{x^2-y^2}$ (where y is the Pd–N direction). In either case symmetry and overlap considerations predict one other mixed-valence transition: $d_{yz} \rightarrow d_{yz}$ or $d_{z^2} \rightarrow d_{x^2-y^2}$, respectively. The latter transition will only take place if there is significant d_{z^2}–$d_{x^2-y^2}$ mixing (both have a_g symmetry in the D_{2h} symmetry point group) and should be at lower energy than $d_{z^2} \rightarrow d_{z^2}$.
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Structures of Simple Organometallic Ions Derived from Nuclear Magnetic Resonance Studies of the Oriented Species

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The ions CH_3Hg^+, $(CH_3)_3Sn^+$, and $(CH_3)_3Pb^+$ have been oriented in lyotropic nematic media and their proton nuclear magnetic resonance (NMR) spectra in the homogeneously oriented state have been analyzed in terms of scalar and dipole–dipole nuclear couplings. These couplings include those between protons and the 16.8% abundant mercury-199, 7.67% tin-117, 8.68% tin-119, and 21.11% lead-207. The metal–carbon bond lengths have been calculated from experimental data assuming a tetrahedral carbon and using a reference distance r_{C-H} of 1.096 ± 0.005 Å. Such a procedure reveals a systematic trend of shorter metal–carbon distances determined by the NMR method compared to the best recent electron diffraction results (on the order 3–5%). Relative comparisons between the NMR results for the ions reported here and the dimethyltin ion published previously are much more reliable and the magnitude for the decrease in metal–carbon bond length with charge on the metal atom and its coordination number is obtained. Special care has been used to eliminate error arising from the uncertainty in the scalar coupling between metal atom and protons which may depend on the state of solvation of these organometallic ions.

Introduction

The orientation of complex ions in nematic lyomesophases was recently achieved by several chemical techniques.[1,6] The nuclear magnetic resonance (NMR) spectra of these oriented ions are suitable for the study of their relative nuclear positions in fluid media by methods already established for small oriented molecules.[7,8] The present study is a report on the structures of the organometallic ions trimethyltin, trimethyllead, and methylmercury. Previous reports from these laboratories have been made with respect to the structures of dimethyltin[5] and dimethylthallium[3] ions. This present work completes a series of simple organometallic ions in which metal–carbon distances can be compared with considerable precision. The scattering of x rays by small carbon and hydrogen atoms in close proximity to heavy-metal atoms is a notoriously difficult problem and leads to an absence of data for hydrogen positions and data of low precision for carbon positions.[9] The diffraction of electrons in the gas phase is appropriate for the study of related molecular species but not ions. Nevertheless, comparison with related molecular species is an important aspect of this investigation. Unfortunately some of these related molecules were studied quite early in the history of the electron diffraction technique before the advent of high-speed computers. The original experimental data did not have the quality that later scientific technology brought to almost all modern experimental methods. References to these related studies will be made during comparative discussion.

Experimental Section

Sodium decyl sulfate from Mann Research Laboratories, Inc., was recrystallized from ethyl alcohol several times and dried under vacuum.

Methylmercury nitrate was prepared from methylmercury chloride (Alfa Inorganics) and silver nitrate (M & B Ltd.). A suspension of 2.5 g of methylmercury chloride in water was added slowly, while stirring, to a well-agitated solution of silver nitrate (1.698 g) in deionized water. Light was excluded during the reaction as much as possible. After filtering from the silver chloride formed, the solution of methylmercury nitrate was further treated with 0.2 g of methylmercury chloride in suspension to ensure complete reaction of the silver nitrate. Final filtration was followed by evaporation to dryness in a vacuum evaporator. The crystals of methylmercury nitrate were recrystallized twice from carbon tetrachloride to give a final yield of 1.9 g (68.5%). The proton magnetic resonance spectrum at high gains showed no observable impurities in aqueous solution.

Trimethyltin Nitrate. The chloride salt (Alfa Inorganics) was made up to 2.0 g/30 ml of deionized water. Dowex-1 resin (15 ml wet) was prepared in a column in the basic form. The solution of tri-

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methyltin chloride was passed through the column followed by water until the eluate was neutral. The trimethyltin hydroxide was exactly neutralized with dilute nitric acid. After evaporating to dryness the product crystals were recrystallized twice from a mixture of chloroform–carbon tetrachloride. The 1.83-g (80.7%) yield of pure product was identified and determined to be free of impurities by means of an NMR spectrum taken at the highest gain levels.

Trimethyllead Nitrate. This compound was prepared, identified, and purified in a manner similar to that for trimethyltin nitrate starting from the soluble acetate derivative.

Trimethyllead Decyl Sulfate. Sodium decyl sulfate (1.302 g) solution was passed through an acidified Dowex column for cation exchange. The eluent was in the form of decylsulfuric acid. An anion-exchange column was used to replace the acetate ion in trimethyllead acetate by hydroxide ions. The stoichiometric amounts of decylsulfuric acid and trimethyllead hydroxide were mixed in aqueous solution and evaporated to dryness under vacuum. The complex ion detergent formed was quite hygroscopic and therefore stored in a vacuum desiccator. Purity and identity of the product (78.8% yield) was determined from the NMR spectrum.

Compositions of Nematic Mesophases. Several nematic phases were prepared containing each ion and the following are typical compositions in weight percent of components, followed by mole fraction in parentheses: (a) sodium decyl sulfate 28.5% (0.0392), methylmercury nitrate 15.84% (0.0204), 1-decanol 3.47% (0.0079), D_2O 52.19% (0.9325); (b) sodium decyl sulfate 35.23% (0.0521), trimethyltin nitrate 10.69% (0.0182), 1-decanol 4.69% (0.0114), sodium nitrate 2.09% (0.0095), D_2O 47.3% (0.9088); (c) trimethyllead decyl sulfate 21.13% (0.0170), sodium decyl sulfate 22.41% (0.0340), 1-decanol 5.52% (0.0138), sodium nitrate 4.55% (0.0211), D_2O 46.39% (0.9141) or sodium nitrate 3.05% (0.0141), sodium decyl sulfate 35.13% (0.0531), 1-decanol 3.46% (0.046), D_2O 46.30% (0.9091), trimethyllead nitrate 12.06% (0.0151).

Proton magnetic resonance spectra were observed using a Varian T-60 spectrometer with a probe temperature of 33.1 °C. Sufficient time was allowed to elapse in the magnetic field of the spectrometer for uniform orientation to occur. This is indicated by sharp transitions at the extremes of the spectra. Spectra were calibrated using the side-band technique.

Results

Studies in Isotropic Media. The prerequisites for accurate determinations of the values of dipole–dipole couplings in oriented media are good measurements of the scalar spin–spin couplings. The measurement of spin–spin scalar couplings in aqueous media leaves open the possibility of a medium effect between the aqueous and lyotropic nematic phases. This has been overcome in our previous studies by measurement of scalar couplings in both aqueous and micellar solutions. These micellar solutions have compositions as close as possible to those of the lyotropic nematic phases. The solute ion in the concentrated micellar solution resides in an electrical double layer (edl) counterion environment which copies very closely the situation of the ion in the oriented lyomesophase. Table I gives a summary of the measurements in various isotropic environments for the ions under study in this work. The variation of these scalar couplings with the solvent is small but appreciable, as reported previously.[5,10] In choosing an appropriate magnitude for the scalar couplings, the values, which were derived from the micellar concentrations closest to those of the nematic phases, were used in analysis of the spectra from anisotropic media. The simple aqueous solutions do not in general reproduce the edl counterion environment sufficiently well. Previous determinations of the scalar couplings are also listed in Table I.

Studies in the Nematic Lyomesophases. (a) Methylmercury Ion. The spectra of the oriented methylmercury ion are specially simple. The dipole–dipole coupling between protons in the methyl group leads to a simple triplet with separations $^3/_2|D_{HH}|$ between transitions[8] and each component of the triplet is the center of a lower intensity doublet which can be assigned to the effect of 16.86% mercury-199 of spin $^1/_2$. The doublet separations are $|J_{HgH} + D_{HgH}|$ and require some choices of sign before they can be interpreted in terms of the required D_{HgH}. The low-field transition of the triplet and its low-intensity doublet are reproduced in Figure 1(a). The sign of the scalar coupling J_{HgH} has previously been determined by Anet and Sudmeier[11] for aqueous methylmercury nitrate and it is known to be absolutely negative. From three different nematic phases the values obtained for $|D_{HH}|$ were (I) ±279.5 ± 0.1, (II) ±223.3 ± 0.1, and (III) ±218.1 ± 0.1 Hz. Each of these phases was repeated with the decanol content omitted in order to form micellar solutions. The values of J_{HgH} were determined to be (I) −259.4 ± 0.1, (II) −259.8 ± 0.1, and (III) −259.1 ± 0.1 Hz with the absolute negative sign assigned.[11] With these values of the scalar coupling and the experimental determinations of $|D_{HgH} + J_{HgH}|$ the possible values of D_{HgH} become (I) +232.9 ± 0.2 or +26.6 ± 0.2, (II) +238.6 ± 0.2 or 21.2 ± 0.2, and (III) +238.4 ± 0.2 or +20.8 ± 0.2 Hz. The absolute sign of the dipolar coupling D_{HgH} is in all cases positive. The sign of D_{HH} can be shown to be absolutely negative.

Table I. Scalar Couplings in Aqueous and Micellar Solutions

Compd	Solvent	Range of J_{XII},[a] Hz	Concn range
Methylmercury nitrate	D_2O	257.8 ± 0.1 to 258.4 ± 0.1 258[c]	0.0153–0.0285 mole fraction
Methylmercury nitrate	Micellar	259.1 ± 0.1 to 259.8 ± 0.1	Micellar solutions with composition varied near (a)[b] but decanol removed
Trimethyltin nitrate	D_2O	66.8 ± 0.1, no range	0.0132–0.0221 mole fraction
Trimethyltin nitrate	Micellar	67.1 ± 0.1 to 68.9 ± 0.1	Phases (b)[b] with smaller water content
Trimethyllead nitrate	D_2O	76.4 ± 0.1, no range	0.0152–0.0247 mole fraction
Trimethyllead nitrate	Micellar	76.9 ± 0.1, no range	Phases (c)[b] with variation of water content

[a] J_{XII} = metal nucleus X to proton coupling; X = ^{199}Hg, ^{207}Pb, and the mean of ^{117}Sn and ^{119}Sn. [b] See Experimental Section. [c] Reference 11.

The equation[8]

$$\frac{D_{HgH}}{D_{HH}} = \frac{\gamma_{Hg}}{\gamma_H}\left(\frac{r_{HH}}{r_{HgH}}\right)^3\left[\left(\frac{r_{HH}}{r_{HgH}}\right)^2 - 2\right] \qquad (1)$$

leads to five roots for the ratios (r_{HH}/r_{HgH}) of internuclear distances. The distance r_{CH}, the carbon–hydrogen bond length, was taken as 1.096 ± 0.005 Å and an additional assumption of exact tetrahedral angles at the carbon was made. This necessitates a distance r_{HH} = 1.790 Å for proton–proton positions in the methyl group. Using this distance in eq 1 and the two possible values of the ratio (D_{HgH}/D_{HH}) gives ten possible roots for r_{HH} for each sample (I, II, and III) some of which are negative and thus have no meaning. The only physical meaningful roots in the three cases are (I) r_{HgH} = +2.528 ± 0.005 Å, (II) r_{HgH} = +2.530 ± 0.005 Å, and (III) r_{HgH} = +2.526 ± 0.005 Å. With the tetrahedral carbon implicit in the assumptions, the mercury–carbon distance in the ion becomes r_{HgC} = 1.94 ± 0.01 Å with the angle between the C_3 axis and the HgH direction being α = 24.12 ± 0.02°. The C_{3v} symmetry of the ion requires the ratio (D_{HgH}/D_{HH}) to be independent of the degree of orientation.[8] The experimental values for the three lyomesophases are (I) −0.0949 ± 0.0008, (II) −0.0949 ± 0.0009, and (III) −0.0953 ± 0.0009.

(b) Trimethyltin Ion. The dominant parameter in determining the spectra of oriented trimethyltin ion is the dipole–dipole coupling between protons in the methyl groups. Three groups of transitions with total relative intensity 1:2:1 are observed. The central features together with the low-field

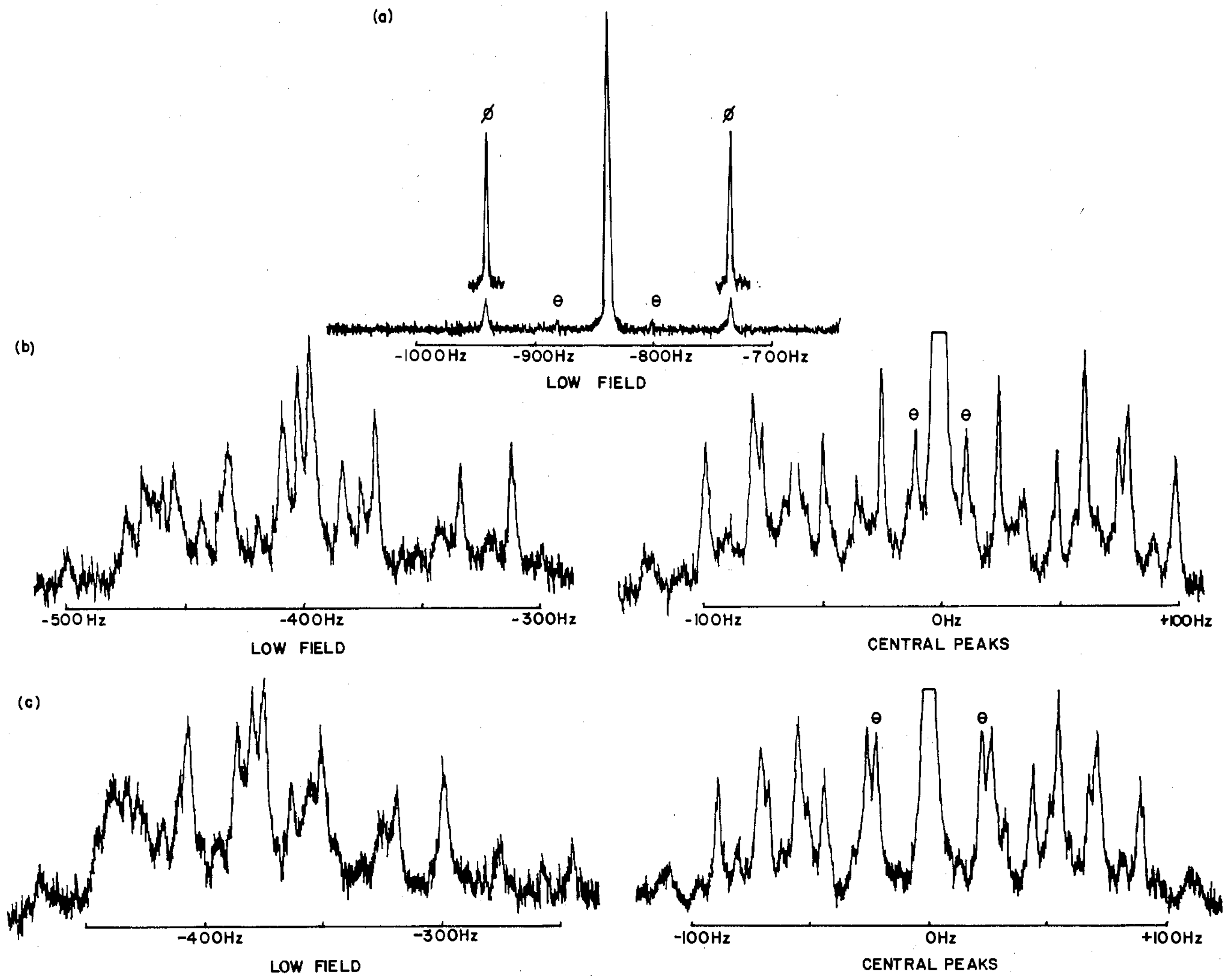

Figure 1. (a) Low-field transition for oriented methylmercury ion bounded by low-intensity mercury-199 satellites. The complete spectrum is a triplet each component of which has the low-intensity mercury satellites. (b) The central- and low-field transitions in the proton magnetic resonance spectrum of oriented trimethyltin ion in a nematic lyomesophase. The peaks marked θ are from the tin-117 and -119 satellites. (c) The central- and low-field transitions in the proton magnetic resonance spectrum of oriented trimethyllead ion in a nematic lyomesophase. The peaks marked θ are from the lead-205 satellites.

components are reproduced in Figure 1(b). The principal transitions observable belong to the $A_3A'_3A''_3$ type of nuclear spin system[8] but low-intensity satellite spectra have been identified from the additional spins of tin-117 and tin-119. The satellite spectra belong to an $A_3A'_3A''_3X$ system—two subspectra of the type $A_3A'_3A''_3$ separated by $|J_{SnH} + D_{SnH}|$.[8] Two mesophases were prepared with different orientations of the trimethyltin ion; these are designated IV and V. Five spectra of each sample were averaged and the positions of 149 transitions noted. The program UEA[12] was used to find the best iterated NMR parameters. For the two mesophases the results were as follows: (IV) $D_{H'H} = 268.34$ Hz (dipole–dipole coupling within methyl groups), $D_{HH} = -32.93$ Hz (intermethyl dipole–dipole coupling), and $J_{HH} = 0$ with an rms error of 0.102 Hz; (V) $D_{H'H} = 280.53$ Hz, $D_{HH} = -34.78$ Hz, and $J_{HH} = 0$ with an rms error of 0.380 Hz. The two subspectra of low intensity were identified from the most intense peaks and gave values $|D_{SnH} + J_{SnH}| = 21.6 \pm 0.1$ Hz and $|D_{SnH} + J_{SnH}| = 19.3 \pm 0.1$ Hz corresponding to IV and V, respectively. The value of $|J_{SnH}| = 68.9 \pm 0.1$ Hz was taken from the micellar solutions, whose compositions differed as little as possible from the mesophases. This leads to two possible values of D_{SnH} for each sample: (IV) $D_{SnH} = \pm 90.5 \pm 0.2$ or $\pm 47.3 \pm 0.2$ Hz; (V) $D_{SnH} = \pm 88.2 \pm 0.2$ or $\pm 49.6 \pm 0.2$ Hz. Taking a local point C_{3v} symmetry for the tin and proton positions on one methyl group, a computation similar to the one described above can be made for the trimethyltin ion. Taking a tetrahedral carbon and $r_{CH} = 1.096 \pm 0.005$ Å as before and finding the corresponding five roots of eq 1 for each possible value of $(D_{SnH}/D_{H'H})$, it is possible to extract the unique physically meaningful possibility. The internuclear distances obtained for the two samples are (IV) $r_{SnH} = 2.634 \pm 0.002$ and $r_{SnC} = 2.057 \pm 0.006$ Å and (V) $r_{SnH} = 2.630 \pm 0.002$ and $r_{SnC} = 2.053 \pm 0.006$ Å. The ratio (D_{SnH}/D_{HH}) which is invariant with changes in orientation becomes (IV) -0.1763 ± 0.0008 and (V) -0.1768 ± 0.0007.

(c) Trimethyllead Ion. Two oriented samples of the trimethyllead ion were prepared and are identified as VI and VII for reference purposes. The spectrum of the oriented ion is very similar to that of trimethyltin and an illustration of it appears as Figure 1(c). Using the same techniques for spectral analysis from 135 observed and measured transitions, a final iteration led to agreement between theoretical and experimental transitions with rms errors of 0.106 Hz for VI and 0.188 Hz for VII. The parameters obtained were as follows: (VI) $D_{H'H} = 252.95$ Hz, $D_{HH} = -29.67$ Hz, $J_{H'H} = 0.0$; (VII) $D_{H'H} = 313.94$ Hz, $D_{HH} = -36.99$ Hz, and $J_{H'H} = 0.0$. The satellite spectra from lead-207 gave values (VI) $|D_{PbH} + J_{PbH}| = 52.2 \pm 0.1$ Hz and (VII) $|D_{PbH} + J_{PbH}| = 46.2 \pm 0.1$ Hz. Selecting the value $|J_{PbH}| = 76.9 \pm 0.1$ Hz from micellar solutions leads to four possible values of D_{PbH} for each oriented sample. These become (VI) $D_{PbH} = \pm 129.1 \pm 0.2$ or ± 24.7

Table II. Metal–Carbon Bond Lengths

Compd	$r_{M\text{-}C}$, Å	Method[a]	Ref
$(CH_3)_2Hg$	2.20 ± 0.10	I	14
$(CH_3)_2Hg$	2.23 ± 0.04	I	15
$(CH_3)_2Hg$	2.052	II	16
$(CH_3)_2Hg$	2.083 ± 0.005	I	17
CH_3HgCl	2.061 ± 0.002	III	18
CH_3HgBr	2.074 ± 0.015	III	18
CH_3HgX (X = Cl, Br, I)	2.003 ± 0.005	II	19
CH_3Hg^+	1.94 ± 0.01	II	Present work
$(CH_3)_4Sn$	2.18 ± 0.03	I	14
$(CH_3)_4Sn$	2.143 ± 0.003	I	20
$(CH_3)_3SnCl$	2.19 ± 0.03	I	21
$(CH_3)_3SnBr$	2.17 ± 0.05	I	21
$(CH_3)_3SnCl$	2.106 ± 0.006	I	22
$(CH_3)_3Sn^+$	2.053 ± 0.006	II	Present work
$(CH_3)_2SnCl_2$	2.108 ± 0.007	I	22
$(CH_3)_2SnBr_2$	2.17 ± 0.05	I	21
$(CH_3)_2Sn^{2+}$	2.02 ± 0.02	II	5
$(CH_3)_4Pb$	2.29 ± 0.05	I	14
$(CH_3)_4Pb$	2.203 ± 0.010	I	23
$(CH_3)_4Pb$	2.238 ± 0.009	I	24
$(CH_3)_3Pb^+$	2.096 ± 0.008	II	Present work

[a] I, electron diffraction; II, oriented molecules or ions by NMR; III, microwave spectroscopy.

± 0.2 Hz and (VII) D_{PbH} = ±123.1 ± 0.2 or ±30.7 ± 0.2 Hz. With the assumption of a tetrahedral carbon with r_{CH} = 1.096 ± 0.005 Å, the solutions of a correspondent to eq 1 lead to one physically meaningful result: r_{PbH} = 2.670 ± 0.005 Å and r_{PbC} = 2.096 ± 0.008 Å.

Discussion

The present study is useful in comparing the metal–carbon distance obtained for several organometallic ions of the most simple kind and by the same technique. Vibrational corrections have not been included[8] nor the small change in shape of the ions in the uniaxial constraint of the nematic medium.[13] It is becoming clear that separation of vibrational effects and accounting for the intermolecular potential functions separately are not tractable problems at this point. The question raised recently[13] with respect to overall distortion of the oriented species in the intermolecular uniaxial force field indicates that the use of small degrees of orientation and correspondingly small values of dipole–dipole couplings is a source of error in structure determinations. The dipole–dipole couplings measured in the present study (the smallest ~20 Hz) are large enough to render this source of error small.

In Table II a comparison of the present structures with all previous determinations in related molecules in terms of the metal–carbon bond distance is made. Neglecting the early studies, which can be regarded as preliminary ones, the tin–carbon and mercury–carbon distances in the ions $(CH_3)_2Sn^{2+}$,[5] $(CH_3)_3Sn^+$, and CH_3Hg^+ are correctly placed in terms of the positive charge on the metal atom. Recent electron diffraction studies[17] appear to give a longer metal–carbon bond length than the NMR method[16] for the dimethylmercury molecule. The shortening of the metal–carbon bond length in the ions is clearly demonstrated in all cases, but the lack of the NMR method for the tetrahedral species $Sn(CH_3)_4$ and $Pb(CH_3)_4$ makes comparisons among the tin and lead results subject to different systematic errors between techniques. Considering only the comparisons of dimethylmercury and methylmercury ion by the NMR method, the results indicate a ~5% shortening of the C–Hg bond. The shortening of the Sn–C bond in passing from $(CH_3)_3Sn^+$ to $(CH_3)_2Sn^{2+}$ is barely discernible and might be expected to be smaller than the case of carbon–mercury bond since the change in charge on the central atom is accompanied by a higher coordination number in each case. The same trend of a larger bond length of Pb–C can be detected for the recent electron diffraction study compared to the present NMR result for $(CH_3)_3Pb^+$. Though the NMR method is not available for $(CH_3)_4Pb$, the change from 2.238 Å for the molecule to 2.096 Å for the ion $(CH_3)_3Pb^+$ clearly reflects the systematic trend of larger metal–carbon distances from electron diffraction studies. It appears that the systematic difference between the two techniques, estimated from the most recent studies, in the metal–carbon bond length is approximately 3–5%. The comparison in relative terms using the same technique is demonstrably much better and we can conclude that bond shortening in the metal–carbon bond with positive charge on the metal ion is well illustrated from the experimental results.

The previous study of the dimethyltin ion[5] demonstrated a considerable difference in J_{SnH} between aqueous, micellar, and liquid crystalline phases, which was attributed to different states of solvation in the electrical double layer. In this investigation both $(CH_3)_3Sn^+$ and $(CH_3)_3Pb^+$ showed a significant change in J_{XH} in passing from aqueous to micellar solution. The ions studied here all have but a single positive charge and solvation effects are likely to be much smaller.

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Registry No. CH_3Hg^+, 22967-92-6; $(CH_3)_3Sn^+$, 5089-96-3; $(CH_3)_3Pb^+$, 43628-90-6.

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