The mass spectrum of $(C_2H_5Si)_4Se_6$ was obtained by direct injection of a sample into an inlet system heated at just below 200°. Since the maximum observable *m/e* with our spectrometer is at about 675, the largest fragments observed were due to $(C_2H_5)_3Si_4Se_6$, the parent less an ethyl group. The most intense peaks were in the region of *m/e* 474–495, corresponding to $(C_2H_5Si)_3Se_4$.

$(CH_3Sn)_2S_3$.—Methyltrichlorostannane (4.4 g, 1.8 mmoles) was dissolved in 30 ml of acetone. A solution of 6.7 g (2.8 mmoles) of sodium sulfide enneahydrate in 12 ml of water was added dropwise, resulting in an exothermic reaction. After 0.5 hr, 50 ml of water was added, precipitating a white solid (1.6 g). After extraction with water for 2 hr to remove sodium sulfide, the water-insoluble product was vacuum dried over phosphoric anhydride for 4 days. *Anal.* Calcd for $C_2H_6Sn_2S_3$: C, 6.60; H, 1.65; S, 26.5; Sn, 65.3. Found: C, 6.96; H, 2.20; S, 26.6; Sn, 63.8.

$(CH_3Sn)_2S_3$ is a nonvolatile solid, which begins to decompose under vacuum at 200°. Cryoscopic molecular weight measurements in dimethyl sulfoxide yielded a value of 636 (calcd for $(CH_3Sn)_4S_6$, 727). The proton nmr spectrum [$(CD_3)_2SO$ solution] consists of a very sharp singlet at −1.0 ppm (referred to tetramethylsilane).

$(C_6H_5Sn)_2S_3$.—A solution of 10 g (33 mmoles) of phenyltrichlorostannane in 60 ml of acetone was added dropwise with stirring to a solution of 12 g (50 mmoles) of sodium sulfide enneahydrate in 18 ml of water. An exothermic reaction ensued with the production of a white precipitate. The mixture was stirred at room temperature for 3.5 hr, then filtered. The solid product was vacuum dried, then extracted with acetone in a Soxhlet apparatus. *Anal.* Calcd for $(C_6H_5Sn)_2S_3$: C, 29.5; H, 2.05; S, 19.7; Sn, 48.7. Found: C, 29.7, 29.0; H, 2.20, 2.15; S, 19.8, 19.4; Sn, 48.5, 47.8. Cryoscopic molecular weight measurements in dimethyl sulfoxide yielded 550 (calcd for $(C_6H_5Sn)_4S_6$, 731).

When heated under vacuum, $(C_6H_5Sn)_2S_3$ begins to decompose at 255°. The proton nmr spectrum in deuterated dimethyl sulfoxide consists of two broad peaks in the aromatic region, at −7.7 and −7.4 ppm (relative to tetramethylsilane) of relative intensity 2:3, respectively.

$(n\text{-}C_4H_9Sn)_2S_3$.—A solution of 28.2 g (100 mmoles) of *n*-butyltrichlorostannane in 50 ml of acetone was added slowly with stirring to a solution of 36.0 g (150 mmoles) of sodium sulfide enneahydrate in 75 ml of water. An exothermic reaction ensued with production of a white precipitate. The mixture was stirred at autogenous temperature for 2.5 hr and then filtered. The white solid was washed with three 25-ml portions of water, then dried over phosphoric anhydride under vacuum for 1 day, leaving 30 g of solid. The solid was extracted with acetone in a Soxhlet apparatus for 1 day, then dried further over phosphoric anhydride. *Anal.* Calcd for $(C_4H_9Sn)_2S_3$: C, 21.5; H, 4.05; Sn, 52.9; S, 21.5. Found: C, 21.7; H, 4.09; Sn, 50.7; S, 20.8. $(n\text{-}C_4H_9Sn)_2S_3$ melts with decomposition at 135–136° in an evacuated capillary tube and is soluble in dimethyl sulfoxide and slightly soluble in acetone. Cryoscopic molecular weight determination in dimethyl sulfoxide yielded 1070 (calcd for $(n\text{-}C_4H_9Sn)_4S_6$, 894).

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Lithium-7 Chemical Shifts of Lithium Perchlorate and Bromide in Various Solvents

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The Li^7 chemical shifts of dilute solutions of LiBr and $LiClO_4$ in water and eleven organic solvents were determined. The range of shifts observed (*ca.* 6 ppm) is nearly comparable to the total range reported for various compounds. These results do not appear to be dominated by any single solvent influence except possibly the effect of solvent anisotropy as determined by the geometry of the interaction between lithium ion and solvent molecules. Polar, dispersion, and coordination effects on the local shielding may also be important.

In spite of the rather promising characteristics of the Li^7 nucleus, high-resolution Li^7 magnetic resonance measurements have been limited in number. A few results have been reported on Li^7 chemical shifts of solutions of organolithium compounds,[1-4] lithium aluminum hydride,[3] and aqueous lithium chloride solutions.[5] Although the over-all range of shifts observed in previous work has been small, the prospect of probing the nature of lithium ion–solvent interactions by a study of Li^7 chemical shifts in several solvents appeared promising.

Experimental Section

Materials.—Lithium bromide was Reagent powder from Matheson Coleman and Bell, dried at 200–340° for 6 days at a pressure of 10^{-3} mm. Lithium perchlorate was anhydrous powder from G. Frederick Smith Chemical Co., Columbus, Ohio, dried at 190° for 6 days at a pressure of 10^{-3} mm. All of the solvents employed were Spectrograde materials from Matheson Coleman and Bell except dimethyl sulfoxide and triethylamine which were Reagent grade from the same company and were dried by passage through a column of molecular sieves (Linde 3A)

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in a closed system. Analysis to determine residual water contents in some of the solvents by the Karl Fischer method[6] revealed that the water content was below the limits of detection of the method ($<\sim 0.005$ *M*). The preparing and transferring of all but the aqueous solutions were carried out in a glove box under a dry nitrogen atmosphere.

Li^7 Magnetic Resonance Measurements.—The Li^7 nmr measurements were obtained at a frequency of 15.085 Mc/sec using a standard Varian HR-60 spectrometer. The sample container was similar to that previously described[7] for C^{13} measurements. Small corrections for bulk susceptibility differences between samples, made necessary because of imperfections in the geometry of the cell, were applied to the raw data. These adjustments were made on the basis of experimental results for this cell on the change in proton chemical shift between the water in the reference bulb and cyclohexane in solvents of different bulk susceptibility (acetone, cyclohexane itself, and tetrabromoethane) in the sample chamber. In no case did these corrections amount to more than 0.07 ppm. Chart calibration was accomplished with 50.5-cps side bands generated by a Hewlett-Packard 200CD audio oscillator and measured by a Hewlett-Packard 524C electronic counter. A sweep rate of about 2 cps/sec was employed, and at least five sweeps of both increasing and decreasing fields were observed for each sample. The precision of data is about ±0.05 ppm. A positive δ corresponds to a upfield chemical shift.

Results and Discussion

The Li^7 chemical shifts of dilute solutions of lithium bromide and of lithium perchlorate showing a total range of nearly 6 ppm are collected in Table I. The effect of the lithium salt concentration on the Li^7 shift was investigated for the solvent acetonitrile, and the results are collected in Table II. The position of the resonance line of lithium bromide seems to be nearly twice as sensitive to change in solution concentration as that of lithium perchlorate.

In order to assess the influence on the Li^7 shifts of residual water content in the solvents employed and to test the possibility of obtaining direct evidence pertaining to the solvation properties of the lithium ion, the shifts of dilute solutions of the salts in acetonitrile with Li^+/H_2O mole ratios varying from 0.1 to 100 were obtained. The data are presented in Table II. Appreciable effects of water on the chemical shifts are noted for even small water concentrations.

TABLE I

CHEMICAL SHIFTS OF $LiClO_4$ AND LiBr IN VARIOUS SOLVENTS[a]

Solvent	δ_{LiClO_4}[b]	δ_{LiBr}[c]
Acetonitrile	2.90	2.15
1,2-Dimethoxyethane	1.66	0.25
Dimethyl sulfoxide	1.29	1.29
Tetrahydrofuran	1.06	0
Triethylamine	1.00	
Methanol	0.85	0.86
Ethyl acetate	0.43	−0.56
Water	0	0
N,N-Dimethylacetamide	−0.25	0
N,N-Dimethylformamide	−0.32	−0.17
Acetone	−1.23	−1.07
Pyridine	−2.26	−3.02

[a] Parts per million with respect to 23% aqueous LiBr. A positive change in δ corresponds to an increase in shielding. [b] Concentration of $LiClO_4$: 7.5×10^{-2} *M*. [c] Concentration of LiBr: 8.6×10^{-2} *M*.

TABLE II

THE INFLUENCE OF SALT AND WATER CONCENTRATIONS ON THE Li^7 CHEMICAL SHIFTS OF $LiClO_4$ AND LiBr IN ACETONITRILE

δ_{LiClO_4}[a] (salt concn, *M*)	δ_{LiBr}[a] (salt concn, *M*)	δ_{LiClO_4}[a,b] (H_2O/Li mole ratio)	δ_{LiBr}[b,c] (H_2O/Li mole ratio)
2.92_7 (0.047)	2.09_5 (0.058)	2.90 (0.10)	
			1.61 (0.11_3)
2.89_0 (0.071)		2.83 (0.30_6)	
2.88_8 (0.100)	1.98_3 (0.115)		1.54 (0.51_3)
2.85_0 (0.189)	1.90_4 (0.230)	2.74 (0.55_5)	
			1.50 (1.02)
		2.60 (1.11)	
		2.36 (2.06)	
		2.16 (3.0_6)	
			1.24 (3.0_8)
		2.02 (4.0_6)	
		1.89 (5.0_6)	
			1.06 (5.1_4)
		1.72 (6.6_7)	
		1.70 (7.11)	
			0.88 (7.19)
		1.53 (9.11)	
			0.73 (9.25)
		1.39 (12.2)	
		1.22 (16.2)	
		1.06 (22.0)	
		0.94 (30.0)	
		0.83 (45.0)	
		0.62 (70.0)	
			0.11 (91.4)
		0.49 (100)	
		0.00 (555)	
			−0.13 (645)

[a] Ppm with respect to 23% aqueous LiBr. A positive change in δ corresponds to an increase in shielding. [b] Concentration of lithium salt: 8.6×10^{-2} *M*. [c] Ppm with respect to 29% aqueous LiBr. A positive change in δ corresponds to increase in shielding.

The approximately 6-ppm range of chemical shifts exhibited in Table I is nearly as large as the total range of Li^7 chemical shifts previously observed in various compounds and generally attributed to "structural influences." The small range of shifts is consistent with theoretical interpretations of Jameson and Gutowsky.[8] Certainly, this nearly equal sensitivity to "solvent" and "structural effects" will place severe limitations on applications of Li^7 magnetic resonance for structural studies or impose rigid requirements for duplicating the medium for which data are to be compared. Of course, it is not strictly valid to consider the present data in the category of solvent effects since solute–solvent interactions may in many cases constitute interactions which can properly be classified as bonding or structural. There is direct chemical evidence for the chemical interaction of lithium ion with solvent molecules. For example, trimethylammonium methylide is stabilized as the lithium bromide complex in ether and in tetrahydrofuran. However, when the solvent is changed to dimethoxyethane, the lithium is removed from coordination with carbon, and the complex breaks down into trimethylamine and polyethylene.[9,10] The ability

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of lithium ion to coordinate strongly with ligands is also implied by studies in which crystalline hydrates have been precipitated from solutions of lithium perchlorate in dimethylacetamide[11] and by conductance measurements which indicate that complex aggregates of lithium perchlorate are present in diethyl ether.[12] In addition, abundant spectroscopic data have been accumulated to substantiate the existence of strong solute–solvent interactions in solutions of lithium salts.[13–16]

Since it has been well established that complicating influences such as ion-pair and aggregate formation are less prevelant with perchlorate salts than with the corresponding bromides, we will focus our attention on the former in our discussion.

Effect of Different Solvents.—It is convenient to consider the total shielding constant σ of the lithium ion in a solution of lithium perchlorate in a particular solvent as the sum of σ_{gas} and σ_{sol}, the shielding constant of the isolated species in an infinitely dilute gas and the shielding contribution due to solvent, respectively. Buckingham, Schafer, and Schneider,[17] Lumbruso, Wu, and Dailey,[18] and Stephen,[19] as well as others,[20–23] have viewed the solvent effect σ_{sol} in proton shifts as a sum of contributions. They represent σ_{sol} as

$$\sigma_{sol} = \sigma_b + \sigma_a + \sigma_w + \sigma_E$$

where σ_b is the contribution to screening which is proportional to the bulk magnetic susceptibility of the medium, σ_a is due to anisotropy in magnetic susceptibility of solvent molecules, σ_w is due to van der Waals interactions between solute and solvent, and σ_E results from the polar effect on the electronic structure of the solute caused by the electric field due to the charge distribution in neighboring solvent molecules.

The quantity σ_b should not contribute to the solvent effects reported in this paper, as the sample cell was designed to minimize differences in this contribution[7,24] and small empirical corrections were applied to the raw data to eliminate them. The quantity σ_a which has received a great deal of theoretical and experimental attention in proton magnetic resonance work[17,19,20,23,25] is strictly a magnetic effect due to proximity and average orientation of anisotropic solvent molecules. The quantities σ_w and σ_E, which have also been studied both theoretically and experimentally,[17–22] may be considered to influence σ *via* their effects on σ_d and σ_p, the local diamagnetic and paramagnetic terms according to the partitioning of Ramsey's[26] theoretical expression for σ by Pople,[27] Saika and Slichter,[28] and McConnell.[29] Thus, dispersion and polar influences can effect both σ_d and σ_p by influencing the average radii of atomic orbitals centered upon the lithium atom since these quantities occur in the expressions for both terms.[8,28,29] They may also influence σ_p by altering the electronic energy levels of the solute,[30] thereby changing the excitation energies on which σ_p is dependent.

Inspection of Table I reveals no direct correlation with any of the molecular properties or functions of properties (such as $(\epsilon - 1)/(\epsilon + 1)$, ΔH_{vap}, etc.) to which σ_w and σ_E have been related theoretically in previous investigations.[17–22] This would seem to indicate that the observed shifts are not dominated by either of these terms and may result from appreciable contributions from all of the influences noted above. One pattern which seems to emerge from the $LiClO_4$ data and which may be of significance is the grouping of the carbonyl-containing solvents. A specific carbonyl influence resulting from coordination of lithium ion at the oxygen atom of the carbonyl group in an orientation placing the ion in the region of similar (probably negative) shielding associated with the magnetic anisotropy of that group might account for this similarity. Similar effects on proton shieldings in carbonyl compounds are well authenticated.[31,32] Analogous explanations can be advanced for the extremely high and low shieldings in the solvents acetonitrile and pyridine, respectively. The magnetic anisotropy of triply bonded systems is well established theoretically and experimentally.[31,33] A nucleus which is situated in a position colinear with the symmetry axis of such a system experiences an increase in shielding associated with its anisotropic magnetic susceptibility. If a lithium ion were coordinated with acetonitrile *via* interaction at the exposed sp lobe of the nitrogen atom, then it would be expected to experience an increase in shielding comparable to that of a proton in acetylene (estimated to be a few ppm).[33] Similarly, a lithium ion coordinated at an exposed sp^2 lobe on the nitrogen atom in pyridine would be expected to feel the same sort of deshielding influence of the aromatic ring current as the protons in benzene, *i.e.*, about 2 ppm.[31–33] These postulated influences, which may be classified as σ_a with the solute–solvent average mutual orientation dictated by coordination requirements, are consistent with the observed results. This is essentially the same as one of the effects discussed by Bothner-By.[23] A similar argu-

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ment has been employed to explain the abnormally large shielding of lithium in fluorenyllithium,[1] where the geometry of the coordination places the lithium atom in the region strongly shielded by ring currents. However, influence of σ_E and σ_W must also be important in this ionic system where the reaction field should be strong near the nucleus. It is interesting to note in this regard that the observed shifts bear a linear relationship to Kosower's solvent polarity parameter (Z) for the solvents acetonitrile, dimethyl sulfoxide, dimethylformamide, acetone, and pyridine[34] (the only nonhydroxylic solvents for which both types of data are available).

Effect of Water on Li+ Shifts in Acetonitrile.—The data of Table II demonstrate that the chemical shift of lithium ion in acetonitrile is most sensitive to changes in concentration of added water when the mole ratio n_{H_2O}/n_{Li^+} varies between 0.1 and about 20. Since the mole ratio n_{CH_3CN}/n_{Li^+} is 220 in each of these solutions, some preference of Li^+ for water compared to acetonitrile in the solvation sphere is indicated. An alternative interpretation consistent with an overwhelming preference for water in the inner solvation sphere would attribute the continuing change in shift at higher water concentrations to the gradual change in the medium external to the inner solvation sphere and to its influence on the latter and ultimately on Li^+, primarily through σ_E.

Effect of Salt Concentration.—Table II displays the small effect on the lithium chemical shift of a fourfold change in the concentration of lithium perchlorate and bromide in acetonitrile. While the changes in shift are small, they are outside the limits of experimental error and indicate that the residual influence of the anion exists even at salt concentrations of about 0.05 to 0.23 *M*. As might be expected, the sensitivity of shift to changes in salt concentration is more than twice as great for lithium bromide as for the perchlorate salt.

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Stoichiometry of the Reaction between Chromium(II) and the Chlorine Oxidants in Aqueous Perchloric Acid

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The stoichiometry of the reactions between excess chromium(II) and chlorate ion, chlorine dioxide, chlorite ion, hypochlorite ion, and chlorine in aqueous perchloric acid has been studied as a function of initial hydrogen ion and chloride ion concentration. In every case significant yields of the three possible chromium(III) products—$Cr(OH_2)_6^{3+}$, $(H_2O)_5CrCl^{2+}$, and a polynuclear chromium(III) species—were obtained. Extensive chlorine transfer to the chromium(III) was indicated by the large yields of $(H_2O)_5CrCl^{2+}$. An increase in both the hydrogen ion concentration and the initial chloride ion concentration increased the yields of the $(H_2O)_5CrCl^{2+}$ product. Increasing amounts of $Cr(OH_2)_6^{3+}$ were obtained with added chloride ion in the chlorate, chlorine dioxide, and chlorite reactions, but the yield was decreased in the hypochlorite and chlorine systems. Increasing yields of $Cr(OH_2)_6^{3+}$ were produced at higher hydrogen ion concentrations for all of the oxidizing agents except chlorine. Less polynuclear species was produced with all of the oxidizing agents if either the hydrogen ion or the initial chloride ion concentration was increased. At least one step in each of the reductions is inner-sphere since chlorine transfer to chromium is quite efficient. Reactive intermediates, in addition to known chlorine species, are involved, and the results are interpreted in terms of chromium–chlorine oxidant intermediates.

Introduction

The products formed when chromium(II) perchlorate is oxidized in aqueous perchloric acid depends on the nature of the oxidizing agent. Ardon and Plane[1] have suggested that with a one-electron oxidizing agent, a mononuclear chromium(III) species, usually either $Cr(OH_2)_6^{3+}$ or $(H_2O)_5CrX^{2+}$ (where X is a ligand derived from the oxidizing agent), is formed. With two-electron oxidizing agents, however, they proposed the formation of a binuclear chromium(III) species

$$\mathrm{Cr(II)} + 2e = \mathrm{Cr(IV)} \tag{1}$$

$$\mathrm{Cr(II)} + \mathrm{Cr(IV)} = \text{binuclear species} \tag{2}$$

Kolaczkowski and Plane[2] have shown that, when chromium(II) is oxidized by oxygen, a binuclear species $[Cr(H_2O)_4OH]_2^{4+}$ is the predominant product after 1 hr, but Thompson and Connick[3] found that this is *not* the product first formed.

The chlorine-containing oxidizing agents can be reduced by both one- and two-electron paths, and Ardon and Plane[1] have shown that when chromium(II) is treated with these oxidizing agents, both mononuclear and polynuclear chromium(III) products are formed. Chlorine dioxide, chlorite ion, hypochlorite ion, and chlorine are possible intermediates in the reduction of

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