TABLE V

VIBRATIONAL FREQUENCIES OF Al–H IN $AlH_yX_{3-y}\cdot 2(THF)$ COMPLEXES[a]

Compound	Vibrational frequencies, cm^{-1}							
AlH_2Cl	1836 m	1755 s			805 vs	776 s, sh 712 s		
AlH_2Br	1842 w, sh	1772 s			807 s	776 m, sh 718 s		
AlH_2I		1782 m, sh 1737 s			800 w	737 m 722 m		
AlD_2Cl			1340 s 1300 vs				600 vs	559 s 528 s
AlD_2I[b]			1340 s, sh 1305 vs					597 vs 538 s 514 m
$AlDCl_2$			1338 s	1298 vs			600 vs	
$AlHCl_2$	1838 vs	1753 vs			803 s			
$AlHBr_2$	1848 vs	1761 s			803 s			
$AlHClBr$	1851 s	1765 s			812 s			
$AlHI_2$		1792 sh 1746 s				792 w		

[a] All bands are reported in cm^{-1} within an estimated error of ±2 cm^{-1}. vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. [b] Chemical analysis indicated $AlD_2I\cdot 3(THF)$.

inum atom[3,8,12,13] Four-coordinate aluminum has generally given a higher Al–H frequency than five- and six-coordinate aluminum. Increases in Al–H frequencies have been observed when electronegative elements are attached to the aluminum atom. The relative basicities and steric hindrance of coordinating ligands explain the frequency shifts associated with polymerization and hydrogen bridging in different solvents.

Vibrational frequencies for the hydrides are tabulated in Table V. The Al–H stretching frequencies appear in the 1700–1900-cm^{-1} region and the Al–D stretching frequencies in the 1200–1400-cm^{-1} region. Bending vibrations or deformations appear in the 850–700-cm^{-1} region for Al–H and 650–500 cm^{-1} for Al–D. Our data do not support hydrogen bridging in these THF complexes. Therefore, the splitting of the Al–H band in the 1700–1900-cm^{-1} region can be attributed to crystal splitting, site symmetry, or absence of band degeneracy because of low symmetry. When the monohydride THF complexes were dissolved in an excess of THF, a single band at lower frequency was normally observed. This can be attributed to the removal of site symmetry or simply to the increase of the coordination number to six.

The vibrational frequencies near 1840 cm^{-1} are lower than those reported for the four-coordinate $AlH_yX_{3-y}\cdot N(C_2H_5)_3$ complexes.[8] The reported frequencies could not be reproduced in this laboratory, although the observed frequency for $AlHCl_2\cdot N(C_2H_5)_3$ was higher than that of the corresponding THF complex. Al–H stretching frequencies were observed at 1866 and 1812 cm^{-1} for $AlHCl_2\cdot N(C_2H_5)_3$, and at 1835 and 1773 cm^{-1} for $AlH_2Cl\cdot N(C_2H_5)_3$. The reported values are 1897 cm^{-1} for $AlHCl_2\cdot N(C_2H_5)_3$ and 1852 cm^{-1} for $AlH_2Cl\cdot N(C_2H_5)_3$.

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[12] R. Ehrlich, A. R. Young, II, B. M. Lichstein, and D. D. Perry, *Inorg. Chem.*, **2**, 650 (1963).

[13] H. Roszinski, R. Dautel, and W. Zeil, *Z. Physik. Chem.* (Leipzig), **36** (12), 26 (1963).

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The Shift of Ligand Stretching Frequencies upon Coordination with Special Reference to $SnCl_3^-$ Complexes

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We wish to report some interesting observations concerning the tin-chlorine stretching frequencies in complexes of $SnCl_3^-$ and a generalization relating to the internal vibration frequencies of σ-bonded ligands. In solution the free $SnCl_3^-$ ion is pyramidal and displays two Sn–Cl stretches at 297 and 256 cm^{-1}, respectively.[2] Furthermore, Raman polarization data show that the 297-cm^{-1} band arises from the totally symmetric mode.[2] In the infrared we observe these same two bands at 289 (ms) and 252 (s) cm^{-1} for mulls of solid $[(C_6H_5)_4As][SnCl_3]$. By contrast, the stretching frequencies of methyltrichlorostannane occur approximately 100 cm^{-1} higher; *viz.*, 366 and 384 cm^{-1}.[3] Thus,

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[1] (a) Northwestern University, Alfred P. Sloan Fellow, 1967–1969; (b) Union Carbide Corp.

[2] L. A. Woodward and M. J. Taylor, *J. Chem. Soc.*, 407 (1962).

[3] P. Tainsula and J. L. Wood, *Spectrochim. Acta*, **20**, 1043 (1964).

TABLE I

TIN-CHLORINE STRETCHING FREQUENCIES

No.	Compd	ν_s		ν_a	ν_{av}	Ref
1.	$[(C_6H_5)_4As][SnCl_3]$	289 ms		252 s	264[a]	*b*
2.	$[(C_6H_5)_3P]_3CuSnCl_3$	315 ms		288 s	297	*c*
3.	$[(C_6H_5)_3P]_3AgSnCl_3$	313 ms		288 s	296	*c*
4.	$[(C_6H_5)_3P]_3AuSnCl_3$	309 ms		286 s	294	*c*
5.	$(C_8H_{10})IrSnCl_3$	317 s 317 s 300 m		300 m 300 m 290 ms 290 ms	306 302 293	*d*
6.	$(C_7H_8)_2RhSnCl_3$	307 s		284 ms	292	*b*
7.	$[(C_6H_5)_3P]_3RhSnCl_3$	327 ms		302 s	310	*b*
8.	$[(CH_3)_4N]_4[Rh_2Cl_2(SnCl_3)_4]$	339 m		323 s	328	*b, e*
9.	$[(C_2H_5)_4N]_3[Pt(SnCl_3)_5]$		*Ca.* 337		337	*f*
10.	$[(CH_3)_4N]_2[RuCl_2(SnCl_3)_2]$		329		329	*b*
11.	$IrHCl(SnCl_3)(CO)(P(C_6H_5)_3)$	339		320	326	*b*
12.	$[(CH_3)_4N]_4[Ir_2Cl_6(SnCl_3)_4]$		*Ca.* 340		340	*b*

[a] Frequencies are in cm^{-1}. The value of ν_{av} is weighted according to degeneracy of the observed bands; ν_s is symmetric and ν_a is asymmetric Sn–Cl stretch. [b] This work. [c] J. A. Dilts and M. P. Johnson, *Inorg. Chem.*, **5**, 2079 (1966). [d] L. M. Venanzi, private communication. [e] As explained in the text, Adams and Chandler[5] propose a different assignment. [f] See ref 5.

an increase in oxidation state from Sn(II) in the trichlorostannate ion to what is formally regarded as Sn(IV) in methyltrichlorostannane leads to significant stiffening of the tin–chlorine bond.[4] Therefore, metal $SnCl_3^-$ complexes might be expected to fall between these extremes and to show the highest SnCl stretching frequency with the metals of greatest electron pair affinity.

To test this idea we have collected far-infrared data from the literature and obtained new data on a representative group of complexes (Table I). In most cases the identity of the $SnCl_3$ stretch vibrations was clear from their relatively high intensities and the similarity in band contours from one compound to the next. However, several cases were less straightforward and deserve special comment.

Adams and Chandler have previously determined the far-infrared spectrum of $[(CH_3)_4N]_3[Rh_2(SnCl_3)_4Cl_2]$, and they assigned the $SnCl_3$ stretching frequencies to bands at 363 (w) and 336 (ms) cm^{-1}.[5] On the basis of band intensities and contours, we are of the opinion that the 363-cm^{-1} band is probably not a $SnCl_3^-$ fundamental and we suggest a more reasonable assignment in the table.

The spectrum of $(C_8H_{12})_2IrSnCl_3$, which was kindly supplied by Dr. L. M. Venanzi, shows three absorptions in the Sn–Cl stretch region. We are inclined to assign the band at 317 (s) cm^{-1} to the symmetric stretch and the bands at 300 (m) and 290 (ms) cm^{-1} to two asymmetric modes split by the influence of the site symmetry in the crystal. However, the situation is ambiguous without detailed study and this will be taken into account in the correlations discussed below.

Finally, the compounds $[(CH_3)_4N]_2[RuCl_2(SnCl_3)_2]$ and $[(CH_3)_4N]_4[Ir_2Cl_6(SnCl_3)_4]$ each have only one intense absorption in the Sn–Cl stretch region (329 and 340 cm^{-1}, respectively) and the former has a series of shoulders on the low-frequency side (*ca.* 318, 300, 282, and 257 cm^{-1}). While these are not the expected contours, the lack of other intense bands in this region indicates these bands are $SnCl_3^-$ stretching frequencies.

For the sake of comparison, an average $SnCl_3$ stretching frequency (weighed according to degeneracy) is presented in Table I for each of the compounds. It may be seen that the free $SnCl_3^-$ ion has the lowest stretching frequency. The next lowest frequencies are found for central metals in the +1 oxidation state, while the two complexes with +2 oxidation state central metals absorb even higher. The data are more clearly summarized in Figure 1 where the weighted average frequencies are plotted against electron affinity for the gaseous metal ions with charges corresponding to formal oxidation states in the complexes. It will be noted that there is a general correlation but that there

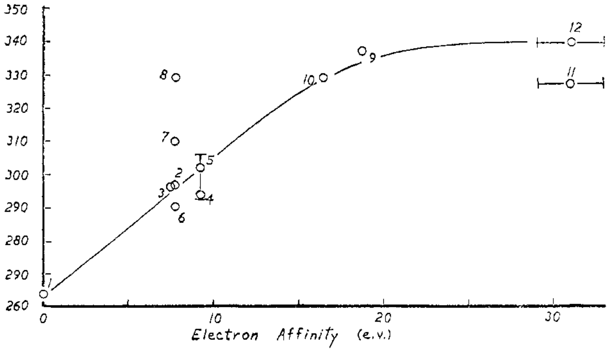

Figure 1.—Weighted average $SnCl_3$ stretch frequency *vs.* electron affinity of the gaseous metal ion with charge equal to the oxidation state of the metal in the complex. The numbers correspond to the compounds listed in Table I. The indicated uncertainty in frequency for point 5, $(C_8H_{12})_2IrSnCl_3$, corresponds to various possible assignments. The uncertainty in electron affinity for points 11 and 12 is due to the lack of data on the third ionization potential of iridium. Very little change in the correlation occurs when Mulliken electronegativities are used for the various oxidation states in place of electron affinities.

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(4) Normal coordinate vibrational analysis verifies this inference: K (Sn–Cl) = 0.98 mdyne A^{-1} for $SnCl_3^-$ and 2.33 mdynes A^{-1} for $SnCl_4$. These bond-stretch force constants were determined using a Urey–Bradley potential: D. F. Shriver, M. P. Johnson, and J. F. Jackovitz, unpublished data; and T. Shimanouchi, *Pure Appl. Chem.*, **7**, 131 (1963), respectively.

(5) D. M. Adams and P. J. Chandler, *Chem. Ind.* (London), 269 (1965).

are several striking disparities. It would be unwise to press the correlation much further because of the following factors. (1) The $SnCl_3$ group frequencies are undoubtedly influenced to some extent by coupling with the rest of the molecule and also they may be influenced by the crystalline environment. (2) It is a rather gross approximation to use formal oxidation states and gas-phase ionization potentials to infer the relative electron-pair affinity of the metal atom in the complex independent of the other ligands.

Several simple physical models may be used to explain the influence in $SnCl_3$ stretching frequencies with increased electron affinity of the metal acceptor. Basically these fall into two categories: (1) changes in hybridization of the tin orbitals involved in Sn–Cl bonding[6] and (2) decrease in the electron density on tin upon donor–acceptor bond formation.[7]

Consider first the change in hybridization to be expected upon coordination. The Cl–Sn–Cl bond angle in free $SnCl_3^-$ is about 90° and this implies that the Sn–Cl bonds involve nearly pure p orbitals from tin, so that the lone pair on tin will occupy an s orbital.[8] Since the p orbital energy is higher than s orbital energy, a more favorable donor orbital may be obtained by increasing the p character of the lone-pair orbital. Thus, upon coordination, the tin orbitals will rehybridize so that more s character will be involved in the Sn–Cl bond. The result will be a stronger bond between tin and the more electronegative chlorine. This rehybridization might occur in a continuous fashion and would thus account for the increase in Sn–Cl frequency with increasing electron-pair affinity of the metal acceptor.

On the other hand, an electrostatic model also leads to the observed trend, since an increase in the positive charge on tin upon coordination should increase the $Sn^{\delta+}$–$Cl^{\delta-}$ restoring force. This is expected to occur in a continuous fashion and would explain the observed trend.

Because of its simplicity, we are inclined to favor the electrostatic picture for qualitative predictions and correlations. However, the two models are not mutually exclusive. In approximate two-center molecular orbital language, the effect of coordination will be to increase the s content of the tin orbital involved in Sn–Cl bonding with a resulting increase in the electron-core interaction, while the shift in electron density from tin will decrease one-center and two-center electron repulsion which results in more negative diagonal matrix elements of the Hamiltonian. Thus, the diagonal matrix element primarily associated with tin will more nearly match the corresponding element for chlorine, and a stronger bond is expected, to which both electrostatic and hybridization effects contribute.

On the basis of the foregoing discussion the following generalization is presented. *For a ligand LX_n the L–X force constant will increase upon coordination of L to an electron acceptor if X is significantly more electronegative than L and it will decrease for the converse situation.* It is also to be expected that these effects will be most pronounced with the strongest acceptor. Two conditions must be added: coordination must not disrupt or alter π bonding within the ligand, and σ donation from L to the acceptor must predominate over any back π bonding from the acceptor.

An additional test of this generalization for the case in which X is more electronegative than L is afforded by a comparison of $GeCl_3^-$ which has a lower average stretching frequency, 286 cm^{-1}, than is found in the protonated form, $HGeCl_3$, where the weighted average Ge–Cl stretch falls at 428 cm^{-1}.[9] Similarly, the average PF stretching frequency increases by 110 cm^{-1} on going from PF_3 to H_3BPF_3,[10] and even in mixed nickel carbonyl–phosphorus trifluoride complexes a slight increase in the average PF stretching frequency occurs;[11] however, this case is complicated by extensive back π bonding.[12] Finally, we note that, in keeping with the generalization, the weighted average Sn–Br stretching frequency is increased from 191 to 264 and 257 cm^{-1} in $[(C_2H_5)_4N]_4[Rh_2Br_2(SnBr_3)_4]$ and $[(C_2H_5)_4N]_3[Pt(SnBr_3)_5]$, respectively.[2,5]

If the terminal groups in a ligand are less electronegative than the donor atom, a decrease in stretch frequency is expected upon coordination. One of the most frequently studied ligands in this class is NH_3. The results here are somewhat complicated by hydrogen bonding but the preponderance of evidence indicates the N–H frequency decreases as a result of a lowering of the N–H valence force constant.[13–15] Furthermore, a general positive correlation is noted between the decrease in N–H stretch frequency and the stability of the complex.[14] The relationship between acceptor strength and the N–H force constant is clearly brought out by the recent normal coordinate analysis of a series of metal amine complexes where it was found that complexes with the highest M–N bond stretching force constant have the lowest N–H bond stretch force constants.[13]

Several additional examples for the case in which X is less electronegative than L have been studied and show the expected decrease in L–X frequency. Thus, the decrease in C–O stretch frequencies upon coordina-

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(6) The influence of hybridization on force constants and frequencies has been invoked many times to explain spectral data; *e.g.*, D. F. Heath and J. W. Linnett, *Trans. Faraday Soc.*, **44**, 556 (1948); H. A. Bent, *J. Inorg. Nucl. Chem.*, **19**, 43 (1961); R. C. Taylor, *J. Chem. Phys.*, **26**, 1131 (1957).

(7) For discussions of the connection between electrostatic forces and vibrational frequencies see: J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4461 (1955); R. G. Pearson, *J. Chem. Phys.*, **30**, 1537 (1959); R. S. Berry, *ibid.*, **30**, 286, 1104 (1959); W. Klemperer, W. G. Norris, and A. Büchler, *ibid.*, 1534 (1960); J. R. Platt," Handbuch der Physik," Vol. XXXVII, Springer-Verlag, Berlin, 1961, p 173.

(8) R. E. Rundle and D. H. Olson, *Inorg. Chem.*, **3**, 596 (1964).

(9) S. L. N. G. Krishnamachari, *Indian J. Phys.*, **29**, 384 (1955).

(10) R. C. Taylor and T. C. Bissot, *J. Chem. Phys.*, **25**, 780 (1956).

(11) R. J. Clark and E. O. Brimm, *Inorg. Chem.*, **4**, 651 (1965).

(12) It should be noted that for a number of adducts the electron-acceptor strength of the acid is insufficient to cause a noticeable frequency change; *e.g.*, PI_3BBr_3 and PI_3BI_3: A. H. Cowley and S. T. Cohen, *ibid.*, **4**, 1200 (1965).

(13) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22**, 759 (1966).

(14) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 145.

(15) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4461 (1955).

tion of ethers has been noted by many investigators.[16–18] A general correlation also appears to exist between the acceptor strength of the acid and the decrease in frequency.[16] Also, the decrease in C–N stretching frequencies of trimethylamine when it coordinates to boron halides has been noted by Amster and Taylor.[19]

It should be pointed out that previous investigators have presented discussions similar to the present one for individual ligands (*e.g.*, ref 14); however, to our knowledge a simple generalization which applies to a wide variety of ligands has not been presented before. Also, most discussions of intraligand stretch frequencies, for ligands which contain both σ and π bonds, concentrate exclusively on changes in the π bonds which occur upon coordination. The present results indicate that cognizance of changes in σ bonds may be in order.

Experimental Section

Spectra were recorded for Nujol mulls of the compounds on Beckman IR-11 and IR-12 instruments. The complexes were prepared according to published methods[20–21] and C, H, N, and Cl analyses were as good as or better than the original reports.

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[16] N. Ya. Turova, K. N. Semenenko, and A. V. Novoselova, *Russ. J. Inorg. Chem.*, **8**, 452 (1963), and references therein.

[17] J. Lewis, J. R. Miller, R. L. Richards, and A. Thompson, *J. Chem. Soc.*, 5850 (1965).

[18] D. E. H. Jones and J. L. Wood, *ibid.*, 1448 (1966).

[19] R. L. Amster and R. C. Taylor, *Spectrochim. Acta*, **20**, 1487 (1964).

[20] R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, **5**, 20 (1966).

[21] J. F. Young, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 5176 (1964).

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The Nature of Aqueous Divalent Xenon[1]

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Aqueous solutions containing divalent xenon can be prepared by dissolving XeF_2 in water.[2] In the communication reporting this fact it was concluded that XeF_2 itself was the principal molecular entity present.[2] However, the presence of such species as XeF^+, Xe^{2+}, $XeF(OH)$, and XeO was not entirely excluded. Appreciable formation of such species should impart measurable conductance to XeF_2 solutions, while if rapid equilibria are involved, even very slight formation of these species should bring about fluorine exchange between XeF_2 and aqueous fluoride.

This note reports measurements of the conductance of aqueous XeF_2 solutions and of the fluorine exchange between XeF_2 and aqueous HF and F^-.

Experimental Section

Xenon difluoride was prepared by heating a 10:1 mole mixture of xenon and fluorine overnight at 300° in a Monel container. The excess xenon was pumped off, and then about 10% of the product was distilled away to remove any XeF_4 that might have been formed. The final product was distilled under vacuum into a Kel-F tube, and water was added to make a saturated solution at 0°. The solution was analyzed by addition of sulfuric acid and sodium iodide and titration with standardized thiosulfate.[2] It was found to be 0.153 ± 0.0015 *M* in divalent xenon. The tube containing the solution was capped with a Kel-F stopper and stored in Dry Ice.

Mallinckrodt "Low-Sulfur" carbon tetrachloride was used in the exchange experiments. Other chemicals were commercial products of reagent grade. Distilled water was redistilled from alkaline permanganate or through hot copper oxide before use.

The conductance of a saturated XeF_2 solution at 0° was measured with a probe-type cell using shiny platinum electrodes and a 60-cycle ac bridge. Solid XeF_2 in a Kel-F tube was washed with several portions of 0° water and then dissolved as quickly as possible to make an approximately saturated solution for measurement. The conductances of HF solutions at 0° were also measured in Kel-F tubes. The conductance cell was calibrated with 1.00×10^{-3} *M* HCl at 25°. The specific conductance of this solution was taken to be 4.21×10^{-4} $(\text{ohm cm})^{-1}$.[3]

Fluoride-containing solutions were analyzed by titration with thorium nitrate that had been standardized against sodium fluoride. The fluoride solution was first neutralized and then buffered with an equimolar mixture of chloroacetic acid and sodium chloroacetate. Sodium alizarin sulfonate was the indicator both for the neutralization and for the thorium titration.[4] If the fluoride solution contained XeF_2, it was first made alkaline to bring about rapid reduction of the XeF_2 by water, with formation of Xe, O_2, and F^-.[2] Titration with thorium then gave the total fluorine content of the solution.

Solutions containing radioactive fluorine-18 were counted in small tubes placed between two 3-in. sodium iodide scintillation crystals oriented face-to-face. The output of each crystal's photomultiplier tube was amplified and fed through a single-channel pulse height analyzer set to pass only pulses corresponding to the 510-kev annihilation radiation of F^{18}. The analyzer outputs went to a coincidence circuit that recorded only pulses coming simultaneously from the two analyzers. In this way the F^{18} annihilation radiation could be counted with high efficiency and very low background. Counting data were corrected for decay of the F^{18}.

To make HF^{18} for fluoride exchange measurements, a 3 *M* HF solution in a Kel-F tube was irradiated with neutrons and γ rays formed by electron bombardment of a tungsten target in Argonne National Laboratory's Linear Accelerator. This stock solution was used directly to make up reaction mixtures containing HF^{18} and XeF_2, and a portion of it was partially neutralized with KOH to make up reaction mixtures containing KF^{18}, HF^{18}, and XeF_2. The mixtures were made up in Kel-F tubes at 0°, and aliquots were counted and analyzed for total fluorine content. After standing for 2 hr at 0°, each mixture was transferred to a glass cylinder graduate and was shaken with about five times its

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2297 (1964).

[3] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p 537.

[4] R. J. Rowley and H. V. Churchill, *Ind. Eng. Chem., Anal. Ed.*, **9**, 551 (1937).