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Mössbauer Spectroscopy of Octahedral Tin Complexes

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The tetramethylammonium salts of a number of octahedral tin–halogen complexes have been prepared and characterized by infrared and Mössbauer spectroscopy. For the anions $SnCl_6^{2-}$, $SnBr_6^{2-}$, SnI_6^{2-}, $SnCl_4Br_2^{2-}$, $SnCl_2Br_4^{2-}$, $SnCl_2I_4^{2-}$, and $SnBr_2I_4^{2-}$, the isomer shift (from the centroid of the SnO_2 Mössbauer spectrum) is found to be a linear function of the sum of the Pauling electronegativities. The data for $SnBr_4I_2^-$ and $SnCl_4I_2^-$ can be understood in terms of the distortion from octahedral symmetry caused by the presence of two large ligands in the *cis* positions. The isomer shift–electronegativity systematics have been used to estimate a group electronegativity of 3.18 for the azide ligand (N_3). Infrared, electronegativity, and Mössbauer-effect temperature dependence data suggest that the azide group in the hexaazidostannate ion is a nonbridging ligand and that the solid is composed of $(CH_3)_4N^+$ cations and $Sn(N_3)_6^{2-}$ anions.

In the past several years ^{119}Sn Mössbauer spectroscopy has become an important tool in the study of chemical bonding and structure of both inorganic and metal–organic tin compounds. The usefulness of this technique has rested to a considerable extent on the development of correlations between the Mössbauer parameters and other quantitative parameters which are descriptive of the compounds used as absorbers. In this context, one of the earliest correlations which was found was that between the isomer shift (IS) and the electronegativity (χ) of the tetrahedral tetrahalogen compounds of tin, and a number of extensive discussions of this correlation have appeared in the literature.[2,3]

The extension of this IS–χ correlation to octahedral complexes has met with only limited success due to the lack of a sufficiently extensive group of structurally related complexes on which this type of systematics could be rigorously tested. In the present study are reported data for a number of octahedral complexes of the type $[(CH_3)_4N]_2SnA_mB_n$, in which A and B are Cl, Br, or I, m and n are even integers, and $m + n = 6$, and for $[(CH_3)_4N]_2Sn(N_3)_6$.

Experimental Section

(a) **Preparation of Octahedral Halogen Complexes.**—These compounds were prepared by a previously reported method[4] in which ethanol solutions of $SnCl_4$ or $SnBr_4$ were allowed to react with ethanol solutions of the corresponding tetramethylammonium halide, and the resulting precipitates were washed with ethanol or CCl_4. In the case of the iodide, SnI_4 was dissolved in chloroform and allowed to react with a hot, saturated methanol solution of $(CH_3)_4NI$. In all cases elemental analysis for C, H, and N gave satisfactory values and the physical properties of the compounds corresponded with those previously reported.

(b) **Preparation of $[(CH_3)_4N]_2Sn(N_3)_6$ and $[(C_2H_5)_4N]_2Sn(N_3)_6$.**—These complexes were prepared by the method of Forster and Horrocks[5] in which the appropriate tetraalkylammonium hexachlorostannate(IV) complex was mixed with NaN_3 in an agate mortar, the solid was suspended in acetone and agitated at room temperature for 24 hr, and the hexaazido complexes were then precipitated by the addition of ether. Further purification was effected by repeated dissolution of the solid in nitromethane and subsequent reprecipitation with ether, the initial portions being discarded in each cycle. Elemental analysis data were in good agreement with calculated values. The infrared spectra show a strong absorption for the nitrogen asymmetric stretch at 2074 cm^{-1} for the $(CH_3)_4N$ salt and at 2062 cm^{-1} for the $(C_2H_5)_4N^+$ salt for which the earlier reported value was 2080 cm^{-1}.

(c) **Mössbauer Spectra.**—Mössbauer parameters were obtained at liquid nitrogen temperature using a barium stannate ^{119}Sn source at room temperature by methods which have been described earlier.[6,7]

Although no particular effort was made to regulate sample thicknesses, these amounted to approximately 70 mg/cm^2. For a molecular weight of $\sim$700 and an assumed $f = 0.5$ this leads to a t of $\sim$3.4 and a line width for ^{119}Sn of $\sim$0.95 mm/sec in good agreement with the experimental results.

Each spectrum was accumulated to give at least 5×10^5 counts/channel so that the statistical counting error amounted to less than 0.14% to give a signal to noise ratio of at least 10:1. Velocity calibration of the spectrometer was effected by means of a Pd(^{57}Co) *vs.* 0.5-mil iron foil experiment as previously described.[8] All isomer sifts are reported with respect to the centroid of an SnO_2 spectrum at room temperature.

Results and Discussion

The Mössbauer spectra of all of the hexahalogen complexes here reported consist of well-defined single absorption maxima having a full width at half-maximum of 0.94–1.22 mm/sec. The isomer shifts are summarized in Table I and a representative spectrum is shown in Figure 1. In those cases where comparison with previously published values[9-12] is possible, the agreement is found to be satisfactory, although it is

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(2) (a) V. I. Gol'danskii, *At. Energy Rev.*, **4**, 3 (1963); (b) M. Cordey-Hayes, *J. Inorg. Nucl. Chem.*, **26**, 915 (1964).

(3) See also the extensive discussion by V. I. Gol'danskii and E. F. Makarov and by M. Cordey-Hayes in "Chemical Applications of Mössbauer Spectroscopy," V. I. Gol'danskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968.

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(5) D. Forster and W. D. Horrocks, Jr., *ibid.*, **5**, 1510 (1966). Although no explosive decompositions were experienced in the course of this work, it should be remembered that azide salts are potentially dangerous and adequate care should be exercised in their handling.

(6) H. Sano and R. H. Herber, *J. Inorg. Nucl. Chem.*, **30**, 409 (1968).

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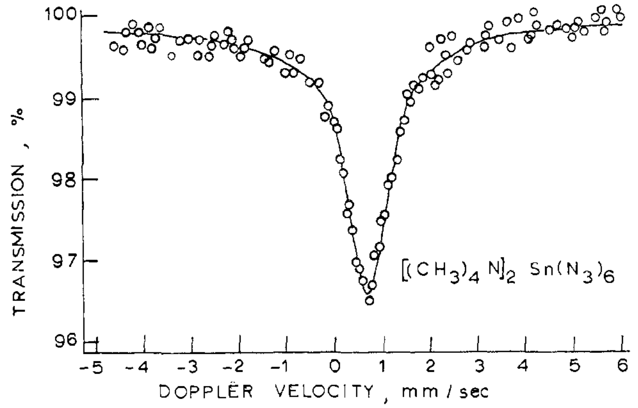

Figure 1.—Mössbauer spectrum of $[(CH_3)_4N]_2Sn(N_3)_6$ at 78°K. The source used was $BaSnO_3$ at 294°K. The full width at half-maximum is 1.0 mm/sec and is due, in part, to sample thickness broadening in the absorber.

clear from such a comparison that appreciable differences may exist between ammonium and tetraalkylammonium salts of the same anion where such information is presently available.

TABLE I

SUMMARY OF MÖSSBAUER PARAMETERS FOR TIN(IV) HALIDES

Absorber[a]	IS,[b] mm/sec from SnO_2	Line width, mm/sec	Ref
$SnCl_6^{2-}$	0.48	1.06	
K_2SnCl_6	0.5		16
$(CH_3NH_3)_2SnCl_6$	0.50		10, 11
$SnCl_4Br_2^{2-}$	0.66	1.10	
$SnCl_4I_2^{2-}$	0.53	1.00	
$(NH_4)_2SnCl_4I_2$	0.54		9
$SnBr_6^{2-}$	0.89	0.94	
K_2SnBr_6	0.9		16
$[(C_2H_5)_4N]_2SnBr_6$	0.86	1.12	10
$(NH_4)_2SnBr_6$	0.87		11
$SnCl_2Br_4^{2-}$	0.74	1.06	
$(NH_4)_2SnCl_2Br_4$	0.65		9
$SnBr_4I_2^{2-}$	0.89	1.22	
SnI_6^{2-}	1.43	1.16	
K_2SnI_6	1.6		16
$SnCl_2I_4^{2-}$	1.17	1.12	
$SnBr_2I_4^{2-}$	1.35	1.11	
K_2SnF_6	−0.50		9
Cs_2SnF_6	−0.44		9
Cs_2SnF_6	−0.4		12

[a] Those absorbers for which no cations are shown are the tetramethylammonium salts prepared in the present study measured at liquid nitrogen temperature. The data cited in ref 10 refer to isomer shifts obtained with a Pd(Sn) source at 80°K. The second-order Doppler shift correction for this source between 80 and 300°K may be as large as 0.06 mm/sec. [b] All isomer shifts obtained in this work are given relative to the center of a room-temperature spectrum of $BaSnO_3$. Such shifts are identical with those with respect to the centroid of the (broad) SnO_2 spectrum within the experimental error of ±0.035 mm/sec at 296°K.

From the data in Table I it is clear that the isomer shifts for the $(R_4N)_2SnX^6$ complexes decrease as the electronegativity of the halogen increases. The isomer shift is given by the relationship

$$\mathrm{IS} = \frac{4}{5}\pi Ze^2R^2\left(\frac{\Delta R}{R}\right)\left\{|\psi(0)|_a^2 - |\psi(0)|_s^2\right\}\frac{c}{E}$$

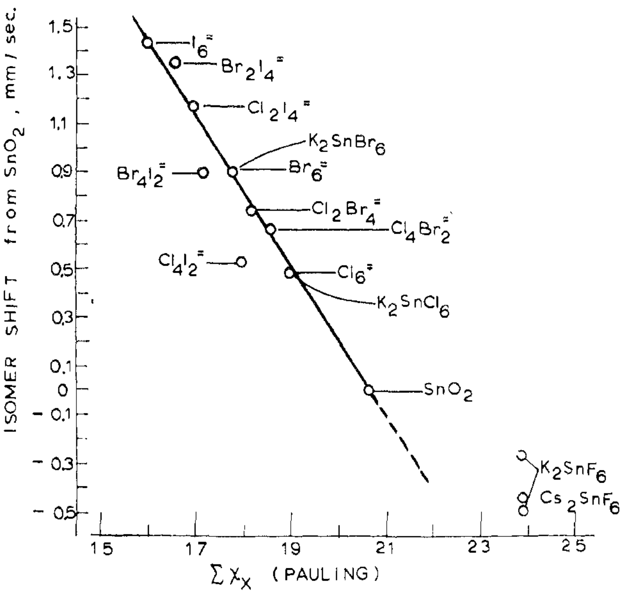

Figure 2.—Isomer shift–Pauling electronegativity correlation for octahedral tin complexes. The isomer shifts are those for the absorbers at 80°K with respect to the centroid of the SnO_2 resonance absorption at 294°K.

in which $\Delta R = R_e - R_g$ is the difference in the nuclear excited and ground-state radii, and $|\psi(0)|_a^2$ and $|\psi(0)|_s^2$ refer to the electron densities at the tin nucleus in the absorber and source, respectively. It is by now well established[13] that the quantity $\Delta R/R$ is positive, so that a comparison of isomer shifts for various absorbers which have been obtained using the same source permits a relative estimation of the electron density in the absorber nuclei from the variation in the IS parameter. As the electronegativity of the halogen increases, the ionicity of the tin–halogen bond increases, thus increasing the relative contribution from the (ionic) [Kr core]$4d^{10}5s^05p^0$ configuration and thus decreasing $|\psi(0)|_a^2$. This effect is in consonance with the earlier observations based on the data for the tetrahedral halogen complexes, SnX_4 (X = Cl, Br, I).

In the case of the hexahalogen complexes this relationship between the isomer shift and the ligand electronegativity becomes even more striking, as is demonstrated by the data summarized in Figure 2. The variation in IS in going from $SnCl_6^{2-}$ to SnI_6^{2-} is 50% greater than in going from $SnCl_4$ to SnI_4, a phenomenon which presumably reflects a combination of steric differences in four- and six-coordination and differences in the shielding parameters arising from sp^3 and sp^3d^2 hybridization. The linear relationship defined by the data points for $SnCl_6^{2-}$, $SnBr_6^{2-}$, and SnI_6^{2-} is seen to accommodate the experimental results for the mixed complexes $SnCl_4Br_2^{2-}$, $SnCl_2Br_4^{2-}$, $SnCl_2I_4^{2-}$, and $SnBr_2I_4^{2-}$ as well, but not those for $SnBr_4I_2^{2-}$ and $SnCl_4I_2^{2-}$. The results for the first four mixed complexes imply, of course, that within the limited isomer shift range covered by these measurements, each ligand

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[13] J. P. Bocquet, Y. Y. Chu, O. C. Kistner, M. L. Perlman, and G. T. Emery, *Phys. Rev. Letters*, **17**, 809 (1966).

makes a unique contribution to the total observed shift. Such additivity of "partial isomer shift" values has been previously reported for hydrated ferrous chlorides[14] as well as for a large number of diamagnetic organometallic iron compounds[15] but has so far not been observed in ^{119}Sn Mössbauer data.

The fact that the data points for the two diiodo mixed complexes do not fall on the straight line defined by the other complexes in Figure 2 can be readily understood in terms of the known structures of these materials. Clark, *et al.*,[4] have reported detailed infrared and Raman measurements on the tetraethylammonium complexes. From the coincidences in the absorptions which are observed it is possible to choose between C_{2v} (*cis*) and D_{4h} (*trans*) symmetry, and Clark, *et al.*,[4] concluded from their data that $SnCl_4Br_2^{2-}$, $SnCl_4I_2^{2-}$, $SnCl_2Br_4^{2-}$, and $SnCl_2I_4^{2-}$ all occur in the *cis* form in the solid. (It was not possible to draw any conclusions about $SnBr_4I_2^{2-}$ and $SnBr_2I_4^{2-}$ since these were found to decompose in the laser beam used for the Raman excitation.) In the *cis* configuration, the greatest distortion from perfect O_h symmetry occurs when the two *cis* ligands are larger than the other four, and the larger distortion will occur for the greater size difference between the two types of ligands. This is confirmed for the two mixed diiodo complexes, the difference between the observed and straight-line value being 0.20 mm/sec for $SnBr_4I_2^{2-}$ and 0.30 mm/sec for $SnCl_4I_2^{2-}$. This interpretation also gives the correct sign for the difference between the observed and "straight-line" value. Maximum overlap (and hence covalent bond character) will occur for O_h symmetry, while any distortion from this octahedral arrangement will reduce the s-electron density at the tin nucleus. As mentioned above, such a decrease in $|\psi(0)|_a^2$ leads to a decrease in IS in consonance with the experimentally observed facts.

It is interesting to note that the data for SnF_6^{2-} do not fall on the straight line defined by the other undistorted hexahalogen complexes.[11] Since the preparation of the tetramethyl- and tetraethylammonium salts starts with the tetrahedral tetrahalides, it has, so far, not been possible to prepare the analogous tetraalkylammonium hexafluorides, since SnF_4 is known to be an octahedral polymeric species. However, the isomer shift values for K_2SnF_6 and Cs_2SnF_6 have been reported to be -0.50 and -0.44 mm/sec, respectively.[16] It might be argued that the reason these data do not fall on a straight line with those for the tetraalkylammonium salts is due to the very much smaller size of the alkali metal cations. That this argument may not be valid, however is suggested by the fact that the data points[16] for K_2SnCl_6 and K_2SnBr_6 do, in fact, fall on the straight-line curve for the tetraethylammonium salts. It should also be noted in this context that the data point for SnO_2 can be accommodated by this linear relationship, as shown in Figure 2. Tin dioxide is well known to have the metal atom at the center of a slightly distorted octahedral structure. Why this structure—in which no cationic species need to be accommodated in the lattice—follows the IS–electronegativity correlation for the other octahedral complexes, while the hexafluoro complexes do not is not clear at present and may simply reflect a fortuitous cancellation of several factors. The isomer shifts observed for $[(CH_3)_4N]_2Sn(N_3)_6$ and $[(C_2H_5)_4]_2Sn(N_3)_6$ do not differ significantly outside the quoted experimental error and thus the difference in cationic size cannot be used to elucidate this point further.

The correlation summarized in Figure 2 makes it possible to evaluate group electronegativities for polyatomic pseudohalogen ligands which can be obtained in the form of tetraalkylammonium–tin complexes. The observed isomer shift for $[(CH_3)_4N]_2Sn(N_3)_6$ at 80°K is 0.48 mm/sec with respect to SnO_2 leading to a value of $\Sigma\chi_X = 19.08$, from which the (Pauling) electronegativity for N_3 is 3.18, compared to the tabulated value of 3.04 for nitrogen. It is also possible to obtain a group electronegativity for the azide group by considering the Mössbauer data for $(CH_3)_3SnX$, where X = halogen or N_3. The value so obtained is $\chi_{N_3} = 2.95$ and the isomer shift which is observed is smaller by $\sim$0.05 mm/sec than that which is predicted from the electronegativity value based on the data for the octahedral complexes. This difference may reflect the change in hybridization of the tin atom and its effect on the ligand electronegativity. In this context it is interesting to note that the N_3 asymmetric stretching frequency is observed[17] at 2091 cm^{-1} in NaN_3, 2071 cm^{-1} in $[(CH_3)_4N]_2Sn(N_3)_6$, and 2054 cm^{-1} in $(CH_3)_3SnN_3$, suggesting that the azide group is acting as a covalent, bridging ligand in the trialkyltin compound.

The nonbridging nature of the N_3 group in the octahedral complex is also suggested by the large temperature dependence of the resonance-effect magnitude over a relatively small temperature range.[18–20] Measurements at 84, 107, 118, and 156°K on $[(C_2H_5)_4N]_2Sn(N_3)_6$ have shown that the change[21] in $\epsilon = (N_{v_m} - N_{v_\infty})/N_{v_\infty}$ is larger than a factor of 12 over this temperature range. Such large values of $-(\mathrm{d}\ \ln f/\mathrm{d}T)$ have been associated[18] with nonpolymeric structures for the neat solid absorbers. While the present data do not rule out the existence of "soft" (*i.e.*, low-frequency, far-infrared or Raman-active) vibrational modes which could account for the observed temperature dependence of the recoil-free fraction even if the N_3 group exists as

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[20] V. I. Gol'danskii, *et al.*, *Dokl. Akad. Nauk SSSR*, **156**, 400 (1964).

[21] Here ϵ is the resonance-effect magnitude, and N_{v_m} and N_{v_∞} are the total number of counts at the resonance maximum and at "infinite" velocity, respectively.

a bridging ligand, the infrared, isomer-shift, and temperature-dependence data are all consistent with the presence of essentially independent $Sn(N_3)_6^{2-}$ moieties.

From the present results it is clear that Mössbauer isomer shift systematics for a given structure type (*i.e.*, O_h, C_{3v}, D_{4h}, etc.) can be used to give useful estimates of group electronegativities for polyatomic ligands and that, moreover, such data are sensitive enough to reflect subtle changes in bonding and structure of these species.

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Electron Capture Reactions of Group IVb Dicyclopentadienylmetal Dichlorides in the Gas Phase

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Resonance electron capture and dissociative electron capture reactions have been observed for the principal negative ions produced from $M(C_5H_5)_2Cl_2$ (M = Ti, Zr, Hf) in the mass spectrometer. Parent negative ions are formed in each metal compound at low electron energies by direct capture of thermal electrons. Fragment negative ions are detected in dissociative resonance capture reactions.

Introduction

Interest in mass spectrometry of organometallic compounds[1,2] has prompted a study of the negatively charged species produced *via* electron capture processes in the mass spectrometer. Since little is known about the negative ion mass spectra of organometallic compounds, a study of the formation of negative ions by electron bombardment may lead to a better understanding of electron capture reactions and dissociative capture reactions. In addition such studies may suggest the usefulness of negative ion mass spectrometry as an aid in elucidating molecular structures. In this paper an investigation of the electron capture and dissociative electron capture reactions for group IVb dicyclopentadienylmetal dichlorides is reported.

Experimental Section

The compounds used in this study $Ti(C_5H_5)_2Cl_2$, $Zr(C_5H_5)_2Cl_2$, $Hf(C_5H_5)_2Cl_2$, $C_6H_5NO_2$, and SF_6 were purchased from commercial sources and were used without additional purification. The zirconium compound contained about a 1% impurity of $Hf(C_5H_5)_2Cl_2$ and the hafnium compound contained about a 5% impurity of $Zr(C_5H_5)_2Cl_2$.

The investigation was carried out using an Hitachi Perkin-Elmer RMU-7E double-focusing mass spectrometer. The samples were introduced into the ionization chamber using the direct inlet probe. The solid inlet heater was maintained at 100° and the ionization chamber temperature was held at 150° for the electron capture studies.

Thermal stability of the compounds in the ion source was examined by measuring the intensity of the most abundant positive ions as a function of chamber temperature (100–300°) while the solid inlet temperature was kept at 100°. The values of the fractional intensity for the $M(C_5H_5)_2Cl_2^+$, $M(C_5H_5)_2Cl^+$, and $M(C_5H_5)Cl_2^+$ ions (M = Ti, Zr, and Hf) were determined as a function of chamber temperature. No thermal dependence of the intensity of the positive ions was noted as indicated in Figure 1 for $Zr(C_5H_5)_2Cl_2$. Similar temperature behavior was noted for positive ions from $Ti(C_5H_5)_2Cl_2$ and $Hf(C_5H_5)_2Cl_2$.

The pressure in the analyzer tube was maintained at less than 3.0×10^{-6} Torr in all experiments. It is assumed that the pressure in the ionization chamber differed by less than an order of magnitude from the analyzer tube pressure. In the determination of the dependence of the ion current in the electron capture reaction on pressure the solid inlet temperature was increased to provide a higher pressure in the ionization chamber and the electron capture curve for the ion in question was determined. The maximum in the ion capture curve was taken as the intensity of a particular ion for the measured analyzer tube pressure.

Mass calibration at 0.08 and 50 eV was accomplished by introducing perfluorokerosene (PFK) into the mass spectrometer simultaneously with the compounds studied. The identity of the negative ionic species was established by comparing the spectra of PFK[3] with the compound of interest. Identification of the parent negative ions was confirmed at 0.08 eV also by a comparison of calculated and observed isotopic abundances. The comparison is presented in Table I.

The electron energy was provided by a pair of 10.3-V mercury batteries and was varied using a 25-turn Helipot precision potentiometer. Since low-energy processes were of interest in this study, a positive bias was applied in the electron-accelerating circuit to obtain a suitable electron energy. Because the electron beam possesses a thermal energy distribution, the positive bias effectively allows only electrons with energy greater than the bias to enter the ionization chamber. In this way essentially

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