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INFRARED, MÖSSBAUER* AND NMR STUDIES OF SOME STANNOUS CHLORIDE AND BROMIDE COMPLEXES OF THIOUREA AND TETRAMETHYLTHIOUREA

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ABSTRACT

Complexes having the formulas $Sn(TU)_2Cl_2$ and $Sn(TU)_2Br_2$ (TU= Thiourea); $Sn(TMTU)Cl_2$ and $Sn(TMTU)Br_2$ (TMTU = Tetramethylthiourea) have been prepared in methanol solutions or by the solid state reaction method. These pure, solid complexes and solutions of the complexes have been studied by Infrared, Mössbauer, and NMR Spectroscopy. A discussion of the relative merits of each technique in determining properties such as the symmetry and the bonding of these complexes is presented.

Infrared data have shown these ligands to be coordinated to the tin through the sulfur with sulfur acting as a bridging atom only in the TMTU complexes. The infrared data of the respective chloride and bromide complexes are not very different and do not point out in a clear cut fashion the relative tin to sulfur bond strengths.

Complexation of the sulfur donors to tin causes a rearrangement of the tin bonding orbitals and the resulting isomer shifts of the complexes are less than the parent tin (II) halides. An increase in the shielding of the tin outer s electrons from the nucleus by the electrons of the coordinated sulfur ligands can also account, in part, for the above mentioned observation. TMTU is observed to have a greater rearranging and shielding effect than TU and, therefore, forms a stronger tin to sulfur bond.

Quadrupole splittings ranging from 0.61 - 1.15 ± 0.05 mm/sec have been observed for all of the complexes. These values can be interpreted in terms of steric factors of both the ligands and the halogens. A correlation plot of the isomer shifts as a function of the quadrupole splittings, similar to that of Lees and Flinn has been made. The bromide complexes show an equatorial field gradient asymmetry. Unexpectedly the electric field gradient asymmetry for the chlorides lies on a third line between that of the axial and equatorial field distortions. The slopes of the three lines are in the ratio of 2: 3: 4. A relationship between the electronegativity of the elements bonded to the tin and the three lines of the δ, Δ plot has been noted.

Mössbauer data have been obtained for these complexes in organic solvents frozen to liquid nitrogen temperatures. Spectra of the glassed alcohol solutions of the TU complexes indicate that the solvent molecules are coordinated along with the sulfur ligands to the tin halides. Tin (IV) species have also been found to be present in several of these solutions resulting mainly from the air oxidation of the tin (II) halides. Methanol has the same effect on the isomer shift of both of the 2: 1, thiourea complexes of $SnCl_2$ and $SnBr_2$ after a compensation for the effects of the thiourea has been made. Data for these complexes in Dimethylsulfoxide (DMSO) are also discussed.

NMR data for these complexes in CH_3OH and DMSO solutions show a direct correlation with the Mössbauer data. A correlation between the IR, Mössbauer, and NMR data for the $Sn(TU)_2Br_2$ and $Sn(TU)_2Cl_2$ complexes can be achieved if it is assumed that $Sn(TU)_2Br_2$ is only 3 coordinate in the solid state and the ion $(Sn(TU)_2Br)^+$ is being observed.

INTRODUCTION

Complexes of tin (II) halides are formed by the donation of ligand electron pairs to the empty 5p and 5d orbitals of the central tin atoms. The free tin (II) ion has an electron configuration, (Kr core) $4d^{10}\ 5s^2\ 5p^o\ 5d^o$ and the hybridization of the tin electronic orbitals in these complexes should include the non-bonded electron pair. Four possible configurations are most likely to be observed for tin (II) dihalide complexes as illustrated in Table 1.

TABLE 1
Hybridization, Configuration and Coordination Number of Tin (II) X_2 Complexes

Number and Type of Hybrid Orbitals		Configuration of Orbitals	Coordination Number
4	sp^3	Tetrahedral	3
5	sp^3d	Bipyramidal	4
5	sp^2d^2	Tetragonal Pyramid	4
6	sp^3d^2	Octahedral	5

The acutal geometric shapes of these complexes will not be that of the configurations of the hybrid orbitals because one of the orbital positions of the complex is occupied by the non-bonded pair of electrons. For example, the pyramidal structure of the ion $SnCl_3^-$ can be explained in terms of sp^3 hybridization. One must also consider how the configurations of these complexes are incorporated into their solid lattices. It is well known that the ionic tin atom can easily fit into an octahedral environment and the closeness of the non-bonded nearest neighbors will tend to distort the molecular configurations.

Tin (II) compounds and complexes are known to be extremely labile with respect to hydrolysis and oxidation by air or various organic ligands. For example, compounds with the formula R_2Sn (R = alkyl or aryl groups) have been shown to posses tin-tin bonds (1). The non-bonded pair of electrons of tin (II) complexes can also enter into bond formation (2) resulting in oxidation of the tin. These observations can be explained by the ease with which the non-bonded $5s^2$ electron pair can become involved in bond formation in either ionic or covalent systems. As the covalent character of the bonds in tin (II) complexes increases, the s like character of the lone pair of electrons decreases as they are partially promoted to sp levels as noted for the hybrid orbitals in Table 1. One can also argue that as the strength of the crystal field about the tin in ionic tin (II) complexes increases, the relative energy of one of the 5p levels approaches that of the 5s level, allowing one of the s electrons to occupy a p orbital. Therefore, in ionic or covalent tin (II) complexes the non-bonded pair of $5s^2$ electrons loses its s character causing the tin to behave more like ionic or covalent tin (IV).

This investigation has been undertaken to obtain more information about the bonding and structure of complexes of tin (II) chlorides and bromides with the ligands (sulfur donors) thiourea (TU) and tetramethylthiourea (TMTU). These complexes have also been studied in solution because of the difficulty encountered in isolating a neat solid from the pure CH_3OH solution preparations. Neat solid complexes were isolated from a solvent mixture of petroleum ether and CH_3OH. TU and TMTU allow the observation of the effects of different sized ligands on the properties of tin (II) halide complexes while holding the donating atom constant.

Infrared studies have been carried out to verify that the TU and TMTU coordinate to the tin (II) halides, to determine which donor atom, the nitrogen or sulfur, of the TU and TMTU is coordinated to the tin, and to obtain relative bond strengths of TU and TMTU between the respective tin (II) chloride and bromide complexes. NMR data for these complexes in solution were obtained to ascertain if the TU and TMTU are coordinated to the tin halides and to determine relative donor strength wherever possible. Both of these methods, IR and NMR, provide direct information about how the tin (II) halides affect the TU and TMTU on complex formation, but only indirect information about tin is provided.

The major part of this study has been concerned with using the Mössbauer technique to obtain direct information about the tin atom's electron environment, i.e. oxidation state and symmetry, and how it is altered by various anions and neutral ligands. The relative donor strengths of the TU and TMTU to the tin (II) halides can easily be estimated from the isomer shift data which also directly measure the 5 s electron density at the tin nucleus in these complexes. Unfortunately, the Mössbauer method cannot be used to measure directly the relative ionic or covalent character of the bonds (3). A correlation of the isomer shift and quadrupole splitting data (4,5) should provide information about the behavior of the non-bonded pair of electrons in the tin atom in these complexes.

EXPERIMENTAL

TMTU and TU were obtained from Eastman Organic Chemicals. Anhydrous $SnCl_2$, reagent grade, was purchased from Matheson, Coleman and Bell. The anhydrous $SnBr_2$ was prepared by refluxing J.T. Baker's, analytical reagent grade, mossy tin with constant boiling HBr purchased from Fisher Scientific Company until all of the solid had dissolved. The excess water and acid were removed by distillation. The yellow solid was dried overnight at 110° C in a vacuum drying pistol. Certified reagent grade DMSO and CH_3OH were purchased from Fisher Scientific Company and dried over molecular sieves before use. The petroleum ether was obtained from Matheson, Coleman and Bell.

Complexes were prepared by mixing methanol solutions of the ligands and the tin (II) halides in the desired stoichiometric ratios and causing precipitation of the solid complexes by the addition of petroleum ether, or by mixing only the pure solids in the desired stoichiometric ratios in a Wig-L-Bug for five minutes. The solid state method works best when one of the components, ligand or metal halide, has a low melting point. The heat generated by the friction in the Wig-L-Bug is sufficient to cause the TMTU and/or the TU to melt, which allows the ligands to coordinate rapidly to the $SnCl_2$ and $SnBr_2$. The specific advantage of using the solid state reaction technique is that the problems of 1) oxidation of the tin by the dissolved oxygen or 2) contaminants in the solvent and the problem of solvent removal are eliminated. Infrared and Mössbauer data have shown that both methods of preparation can be used to prepare these complexes. The solid complexes were dried under vacuum for a minimum of 5 hours at 80° C. Elemental analysis for the percentages of carbon and hydrogen were found to be:

TABLE II

C AND H ANALYSIS

Formula	Carbon		Hydrogen	
	% Calculated	% Found	% Calculated	% Found
$Sn(CH_4N_2S)Cl_2$	4.52	4.79[a]	1.52	1.50[a]
$Sn(CH_4N_2S)_2Cl_2$	7.03	7.12[b]	2.36	2.33[b]
$Sn(CH_4N_2S)_2Br_2$	5.58	5.60	1.87	1.88
$Sn(C_5H_{12}N_2S)Br_2$	14.62	14.16	2.94	2.94

$Sn(TMTU)Cl_2$ was prepared only by the solid state reaction technique.

[a] average of 2 values

[b] average of 3 values

Mössbauer spectra were obtained with a constant acceleration velocity drive system similar to that developed at the National Bureau of Standards (6). Velocity calibration of the spectrometer was accomplished with a 10 mCi iron - 57 source of Co^{57} diffused into chromium and absorbers of iron foil and sodium nitroprusside. The detector for the 23.8 keV Sn^{119m} gamma was a Reuter Stokes RSG - 61 $Xe-CH_4$ detector. A 2.0 mCi, $BaSnO_3$, Sn^{119m} source at room temperature with a Pd filter was used. All of the tin isomer shifts are reported with respect to the centroid of the $BaSnO_3$ spectrum. All of the absorbers, solids and frozen solutions, were studied at liquid nitrogen temperature. Samples were mounted to a copper cold finger that was silver-soldered to the bottom of a copper liner. The entire liner and cold finger were insulated with rigid polyurethane foam. An absorber diameter of one inch was used. The solid powders, of approximately 5 mg of tin per cm^2, were supported between two pieces of lightweight aluminum foil with a small amount of silicone stopcock grease. Two polyethylene windows, separated by a 3/32" high, 1 1/4" diameter rubber gasket made up the cell for the frozen solutions.

This assembly was fastened to the cold finger and a face plate of 1/32" thick copper with a 1" diameter hole was placed above the cell and bolted to the cold finger. A syringe with a needle was used to transfer approximately 2 ml of the solutions into this cell. All solutions were allowed to cool for a minimum of 20 minutes before commencing to record data. Approximately 10^5 counts per channel were obtained for each spectrum. The isomer shifts and quadrupole splittings were determined chiefly from graphical plots of the data and in some cases from computer fitting the data to Lorentzian curves with an IBM 1130 computer.

Infrared spectra of the solid complexes in KBr disks were obtained at room temperature with a Perkin-Elmer Model 421 Infrared Spectrophotometer.

NMR spectra for the solutions of the tin complexes were obtained with a Varian A-60 spectrometer at room temperature. TMS (tetramethylsilane) was used as a reference standard for the measurements as an internal standard with CH_3OH and an external standard with DMSO.

The concentrations for all the solutions used were usually 1 molar except for the cases where the solubility of the complexes was limited in the solvents.

RESULTS AND DISCUSSION

Infrared Data

Coordination of TU, $(H_2N)_2\ C = S$, and TMTU, $\{(CH_3)_2N\}_2\ C = S$ to tin (II) halides has been demonstrated by comparing shifts of the vibrational frequencies of the free ligands to the complexed ligands. The observed shifts in the infrared region from 4000 cm^{-1} to about 500 cm^{-1} have been used to determine whether the nitrogen or sulfur of the ligands has been coordinated to the tin. TU and TMTU are generally considered to be sulfur donors but one cannot rule out the possibility that the amine nitrogen in these ligands can enter into dative bond formation with various acceptor atoms. Urea, $(NH_2)_2\ C{=}O$ which is normally considered to be an oxygen donor to Cr, Fe, Zn, and Cu has been observed to coordinate through nitrogen to Pt and Pd (7). The relative magnitudes of the observed ligand frequency shifts have been used to indicate the relative bond strengths of TU to $SnCl_2$ and $SnBr_2$ and of TMTU to $SnCl_2$ and $SnBr_2$. The IR technique was not used to establish the relative donor strength of TU and TMTU with $SnCl_2$, or with $SnBr_2$ because this requires the observation of the S $\longrightarrow$ Sn bond vibrations, which should occur at lower frequencies, outside of the spectral range studied. The Mössbauer data observed on these complexes have provided information about the relative S-Sn bond strengths.

Thiourea complexes of $SnCl_2$ were isolated from solution in the ratio of 1: 1 and 2: 1 but only a 2: 1 TU complex of $SnBr_2$ could be isolated. Yamaguchi et. al. (8) have shown that the chief indication of sulfur-to-metal complexation bond strengths is the observed shifts in the antisymmetric N—C—N stretching vibrations which occur at 1470 cm^{-1} for free TU. Coordination of the amine nitrogen would

result in an increase in the intensity and a decrease in the frequency of the $-NH_2$ stretching frequencies. The infrared spectra of these complexes show very little change in the $-NH_2$ vibrations but the N-C-N vibrations are shifted to higher frequency and are observed at 1483 cm^{-1} for $Sn(TU)_2Cl_2$ and at 1496 cm^{-1} for $Sn(TU)_1Cl_2$ as seen in Figure 1. The larger value observed for the 1: 1 complex indicates a more polar $^{+}N=C(-N)-S^{-}$ character, which indicates a stronger S→Sn bond in $Sn(TU)_1Cl_2$ than in $Sn(TU)_2Cl_2$. This conclusion is verified by the frequency shifts observed for the C=S stretching vibration which occurs at 730 cm^{-1} in the free ligand, at 700 cm^{-1} in the $Sn(TU)_1Cl_2$, and at 710 cm^{-1} for $Sn(TU)_2Cl_2$. The band observed around1100 cm^{-1} for TU is thought to be due to contributions from the C=S stretching and the N-C-N stretching vibrations; it decreases in intensity upon complex formation. As seen in Figure 1, the 1: 1 chloride complex has a much weaker band at 1100 cm^{-1} than does the 2: 1 chloride complex; this suggests a stronger S-Sn bond for $Sn(TU)_1Cl_2$ than $Sn(TU)_2Cl_2$. This observation is not unreasonable if one considers that the tin atom in $SnCl_2$ can accommodate only so much electron donation upon complex formation. When one ligand coordinates to the tin, a larger portion of the ligand's electron density is donated than would be the case if two ligands were required to donate the same amount of electron density to the tin. In the latter case a weaker lignad-to-tin bond would result because each individual ligand would not contribute as much electron density.

Figure 2 illustrates the IR spectra for $Sn(TU)_2Br_2$ and $Sn(TU)_2Cl_2$. There are small differences observed between the NH_2 stretching and bending vibrations of the two complexes which may be due to the different manner in which the chloride and bromide atoms affect the crystal lattice. The N-C-N and C=S stretching frequencies observed

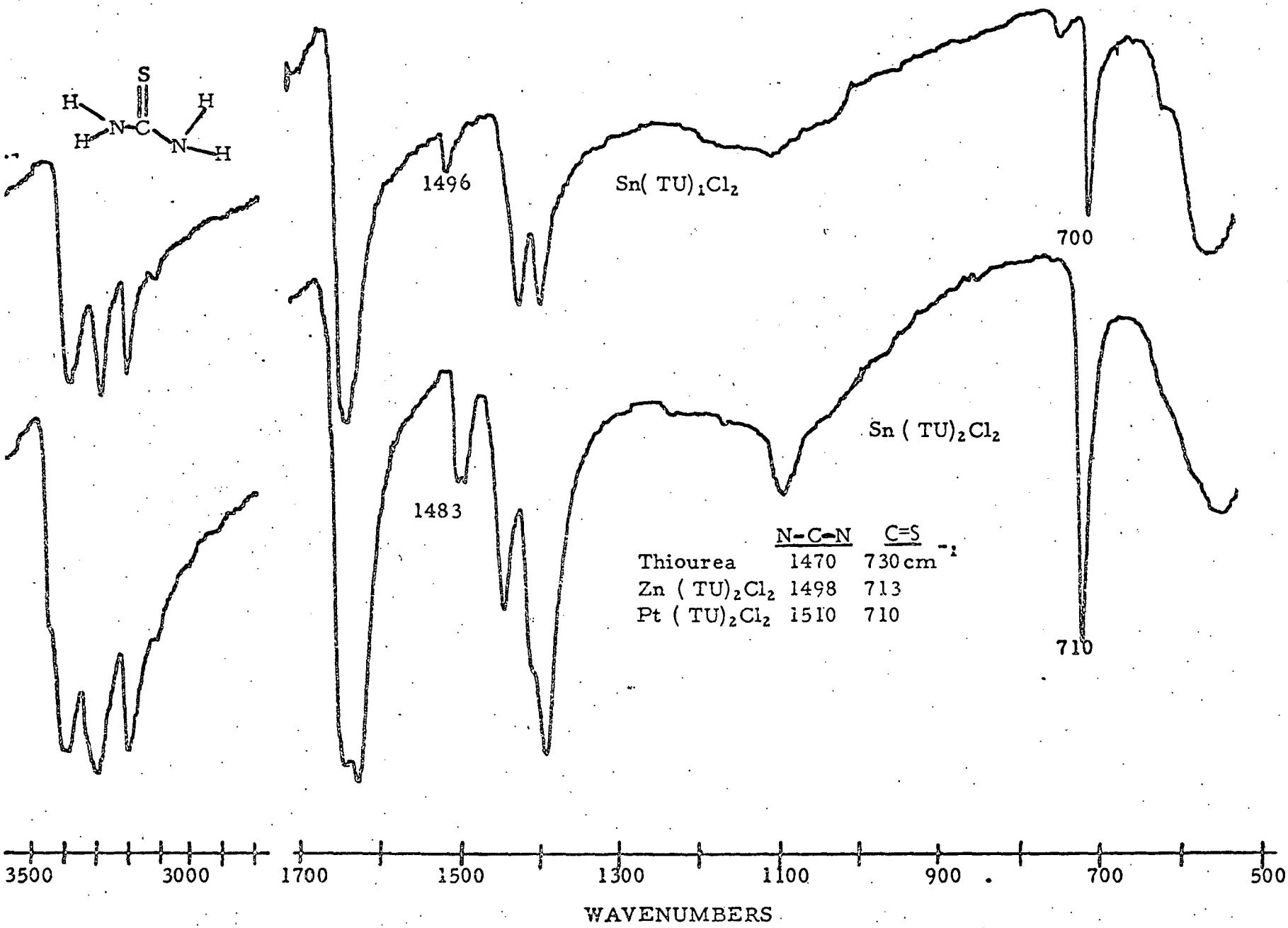


Figure 1. Infrared absorption spectra of $Sn(TU)_1Cl_2$ and $Sn(TU)_2Cl_2$ obtained in KBr discs.

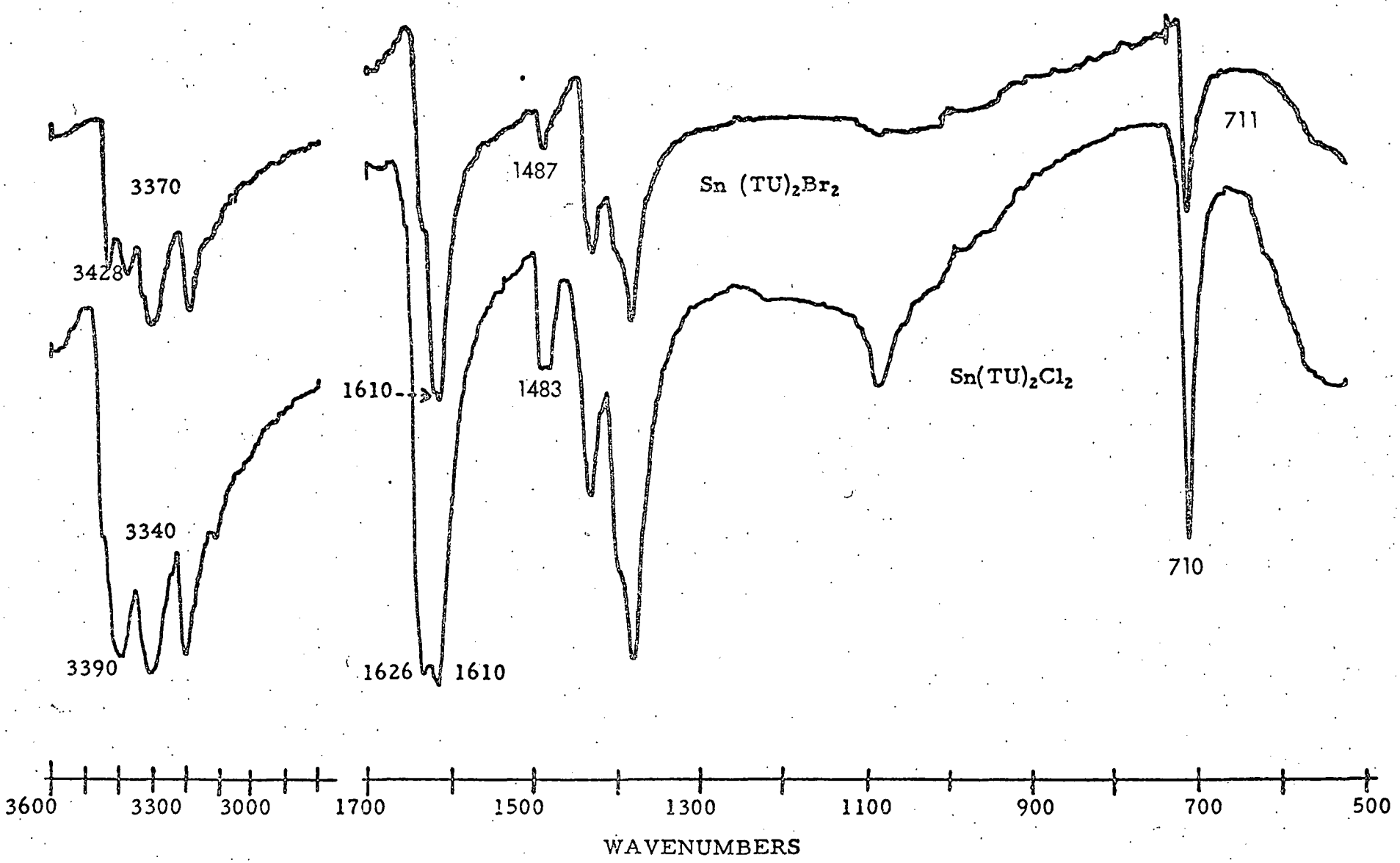
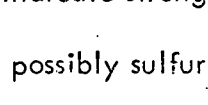


Figure 2. Infrared absorption spectra of $Sn(TU)_2Cl_2$ and $Sn(TU)_2Br_2$ in KBr discs.

for the $Sn(TU)_2Br_2$ indicate that its S - Sn bonds are as strong, if not stronger than those of the $Sn(TU)_2Cl_2$. This strength is also noted by the similarity between the bands at 1100 cm^{-1} for the two complexes $Sn(TU)_1Cl_2$ and $Sn(TU)_2Br_2$. One normally expects stronger metal-ligand bonds in the chlorides than the bromides if the structures are identical. Because of the aforementioned facts it has been concluded that there are structural differences between $Sn(TU)_2Cl_2$ and $Sn(TU)_2Br_2$. There is, however, no evidence for sulfur acting as a bridging agent. Basso et. al. (9) have noted that when the sulfur of TU does bridge between two metal atoms the N-C-N stretching vibration shifts about 55 cm^{-1} to higher frequency.

TMTU is structurally similar to TU with the protons of TU replaced by $-CH_3$ groups; x-ray diffraction studies have revealed that steric factors force both of the dimethyl groups out of the N-C(N)=S plane resulting in a decrease in the $^{+}N=C-S^{-}$ character in the molecule. Shifts in the antisymmetric N-C-N frequency at 1504 cm^{-1} and shifts in the bands around 1090 and 880 cm^{-1} which are attributed to both N-C-N and C=S stretching show that TMTU coordinates to $SnCl_2$ and $SnBr_2$ through the sulfur atom. As seen in Figure 3 the N-C-N antisymmetric vibration shifts to 1568 cm^{-1} for $Sn(TMTU)Cl_2$ and to 1560 cm^{-1} for $Sn(TMTU)Br_2$, suggesting a stronger S-Sn bond for the chloride complex. In various 2: 1 transition metal complexes the N-C-N vibrations occur around 1550 cm^{-1} and at 1553 cm^{-1} in $Pb(TMTU)Br_2$ and at 1660 cm^{-1} in $Pt(TMTU)Cl_2$ (10). The large shifts of the N-C-N vibrations indicate strong sulfur-metal bonds in the $Sn(TMTU)Cl_2$ and $Sn(TMTU)Br_2$ complexes, or possibly sulfur to metal bridging  as is observed for the $Ni(TU)_2X_2$ ($X = NO_3$, ClO_4) or as in the 1: 1 complex of TU with lead.

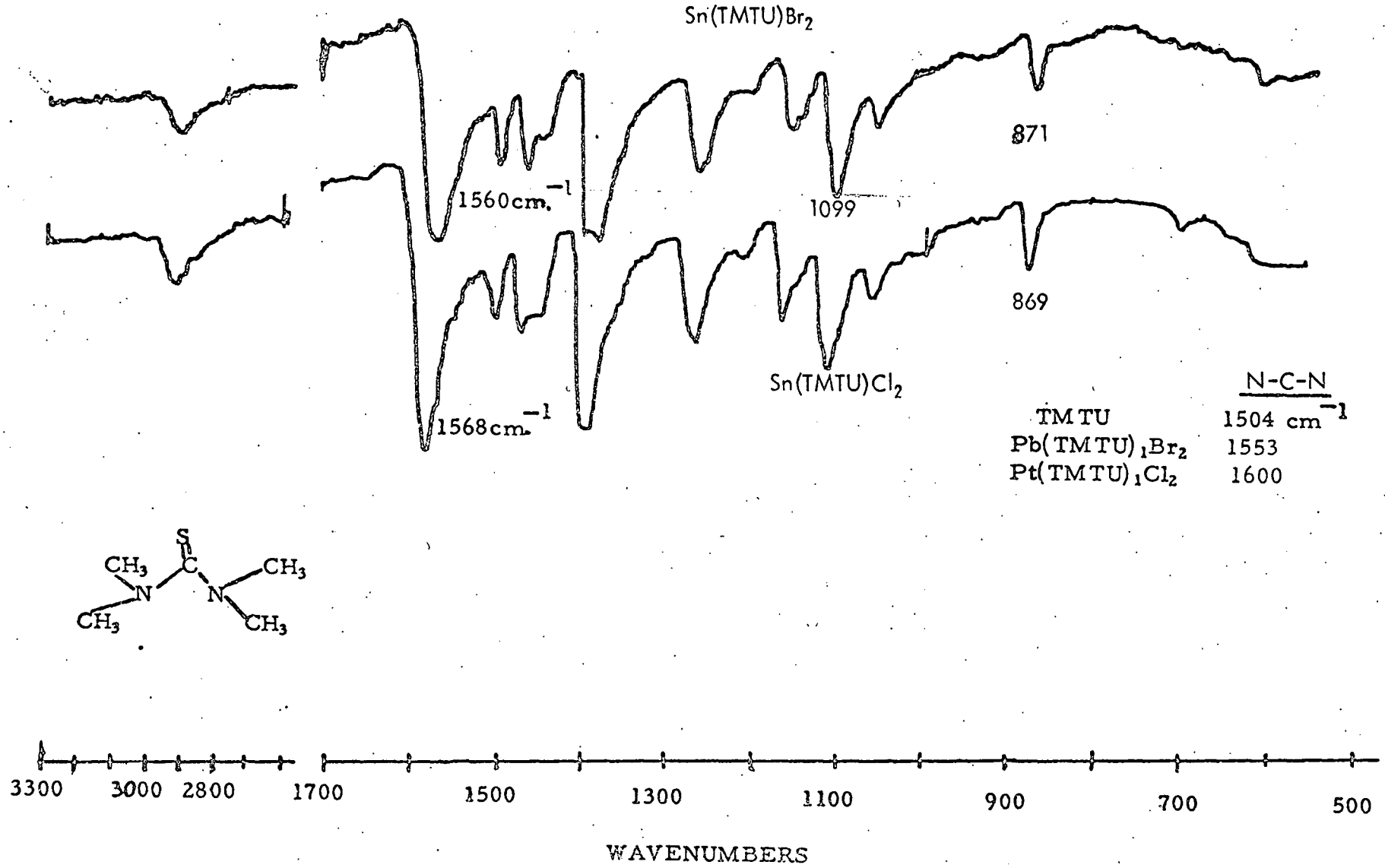


Figure 3. Infrared absorption spectra of $Sn(TMTU)Cl_2$ and $Sn(TMTU)Br_2$ in KBr discs.

MÖSSBAUER DATA

Extensive Mössbauer studies have been carried out on tin (IV) halogen complexes but very little has been reported in the literature on tin (II) complexes (11). Two reasons for this are that Sn (IV) halogen complexes are more easily isolated as stable complexes and the Mössbauer data are more readily interpreted because of the greater covalency of the Sn (IV) ligand and halogen bonds. Isomer shift data for tin are a direct measure of the s electron density at the tin nucleus and, because of the positive value of the nuclear radius change $\left(\frac{\Delta R}{R}\right)$ for Sn^{119m}, all tin (IV) compounds will have a negative isomer shift with respect to α-tin and all tin (II) compounds will have positive isomer shifts. The isomer shifts for tin (IV) halides increase more positive in the order, $I^- > Br^- > Cl^- > F^-$, thus correlating to the electronegativity of the halides. In TMTU complexes of $SnCl_4$ and $SnBr_4$ (12), the isomer shift for the bromide complex is more positive than that for the chloride complex. These observations are consistent with electronegativity data because of the high degree of covalent character of the Sn-X bond. Tin (II) halides, however, are observed (13) to have isomer shifts increasing more positive in the order of $Cl^- > Br^- > I^- > F^-$ (except for the position of the F^- the order is the same observed for the spectrochemical series) which can be accounted for in terms of ionic bonding. SnF_2 is out of place in the series because of the relatively stronger Sn-F bonds and its structural differences from the other three halides. As the ionic character of the Sn-X bond in the SnX_2 ($X = Cl^-, Br^-, I^-$) compounds increases there should be a decrease in the shielding of the tin $5s^2$ electrons from the nucleus by the electrons of the tin-halogen bond, resulting in an increase in isomer shift. The tin (II) ion in an ionic crystal lattice will also experience a crystal field

which can lower the relative energy difference between the 5 s and 5 p levels, allowing one of the 5 s electrons to more easily occupy a 5 p level. This effect cannot be very significant for SnX_2 compounds because it would cause the isomer shift to go in the opposite direction than that observed. A nephelauxetic effect, where the anion donates some of its electron density to the tin, can also explain the observed isomer shifts for the "ionic" SnX_2 compounds. Of the three ions Cl^-, Br^-, and I^-, the I^- would be expected to be the best electron donor, shielding the $5s^2$ electron from the nucleus, because of its low electronegativity and large electron cloud. The donor strength of these ions would decrease in the order of $I^- > Br^- > Cl^-$ which is the same as that observed for the nephelauxetic series. For a pure covalent situation one would expect ligand electron density to be donated to the 5 p levels which would shield the $5s^2$ pair from the nucleus, or a hybridization to take place which also decreases the $5s^2$ electron density at the tin nucleus. In forming a direct attachment of a group to the tin as through a covalent bond, an electronegativity effect would be expected to result which also causes electron density to be withdrawn from the tin nucleus. These two effects in a covalent Sn (II) system compliment one another and as they increase, a decreasing of the isomer shift would be predicted which is not the case for SnX_2 halides.

Data in Table III point out that the isomer shifts of the TU and TMTU complexes are less than the parent tin (II) halides, with the shifts for the chloride complexes less than those for the bromide complexes. A typical spectrum for one of the solid complexes, $Sn(TU)_2Br_2$, is shown is Figure 4. These shifts can be explained in terms of the donation of ligand electron density which shields the $5s^2$ electron pair from the nucleus and in terms of the halogen electronegativity if one assumes that the Sn-Cl and Sn-Br bonds have increased their covalent character.

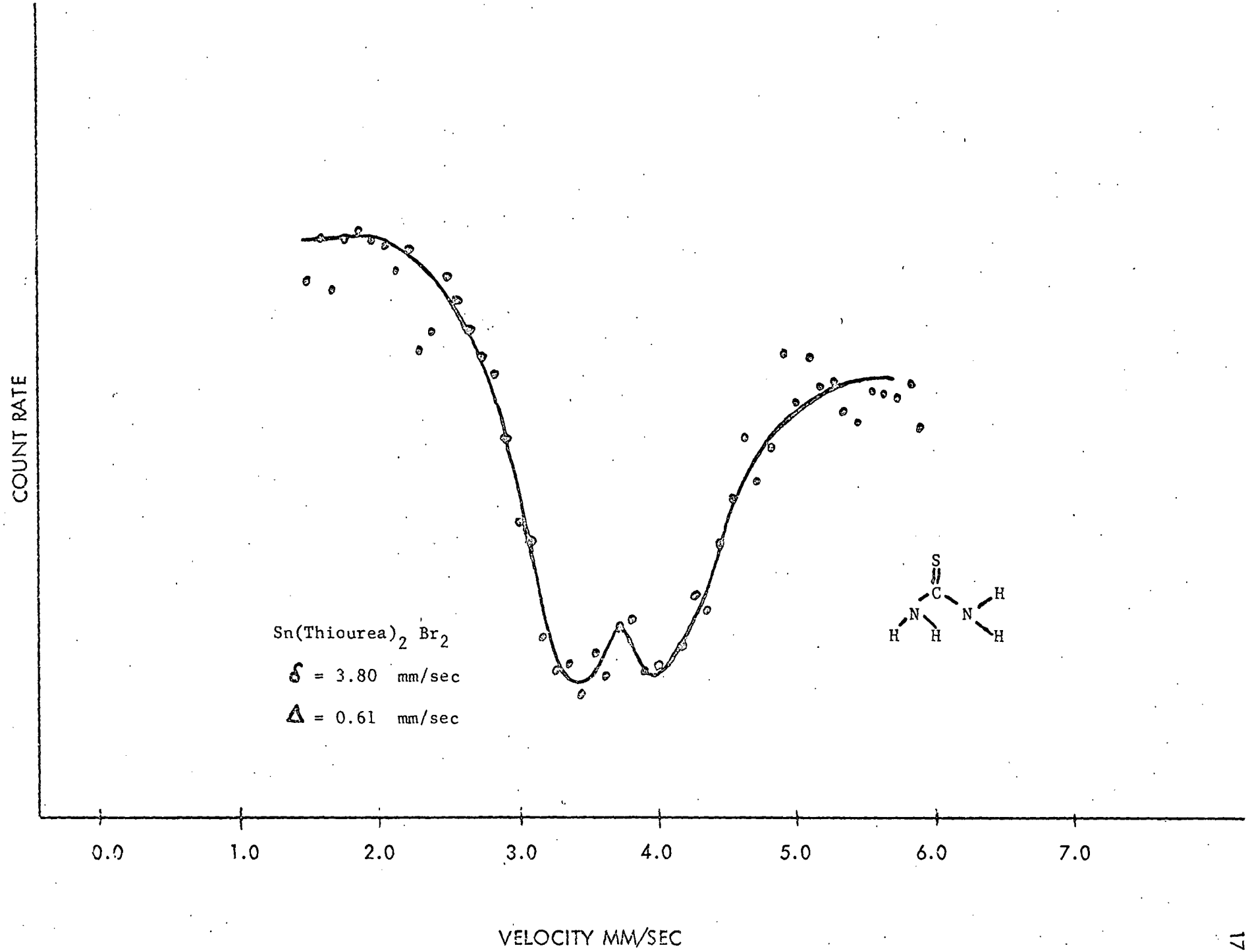
Differences in the coordinating power of the ligands TU and TMTU to the same tin (II) halide have been directly observed with the Mössbauer technique, where the

TABLE III

SUMMARY OF MÖSSBAUER PARAMETER
FOR
TIN (II) COMPLEXES

Absorber at 80° K	IS, mm/sec from $BaSNO_3$*	Quadrupole Splittings mm/sec
$SnCl_2$	4.09 ± 0.05	≤ 0.50
$Sn(TU)Cl_2$	3.73	0.93
$Sn(TU)_2Cl_2$	3.66	0.86
$Sn(TMTU)Cl_2$	3.48	1.15
$SnBr_2$	4.04	≤ 0.50
$Sn(TU)_2Br_2$	3.80	0.61
$Sn(TMTU)Br_2$	3.68	0.68

*All isomer shifts obtained are given relative to the center of the room temperature, $BaSnO_3$, source. These isomer shifts are identical with those with respect to the centroid of the wide-line spectrum of SnO_2.



Mössbauer spectrum of $Sn(TU)_2Br_2$ at liquid nitrogen temperature vs a $BaSnO_3$ source.

I.R. data obtained on the free ligands would only suggest this. The isomer shift data show that the TMTU forms a stronger S-Sn bond than does TU. This is seen from the larger decrease in isomer shifts from that of the parent halides for the TMTU complexes than the TU complexes. I.R. data have shown that the sulfur atom in TMTU has more charge density available for bond formation than the sulfur atom of TU. An inductive effect of the CH_3 groups attached to the nitrogen in TMTU can account for this observation.

Infrared data have indicated that the S-Sn bond in the $Sn(TU)_2Cl_2$ complex is stronger than in the corresponding 2: 1 complex. A small difference in isomer shifts between the 1: 1 and 2: 1 complexes has been observed. If the TU were to have the same coordinating power in both complexes, a much larger difference between the isomer shifts of the 2: 1 and 1: 1 complexes would be expected. It has been assumed that both the 2: 1 and 1: 1 complexes have two chloride ions in their first coordination spheres. The observed results can be explained as noted in the I.R. section if the S-Sn bond strength in $Sn(TU)_2Cl_2$ is less than in $Sn(TU)Cl_2$. Another argument for this conclusion can be made on the basis of partial isomer shifts (14). A partial isomer shift for Cl^- of -0.37 can be obtained by taking the difference between Lees and Flinn's (4) value of the isomer shift for the free tin (II) ion of 4.83 mm/sec (vs $BaSnO_3$) from the isomer shift for $SnCl_2$ and dividing by the number of chloride ions. The difference between the isomer shifts for $SnCl_2$ and $Sn(TU)Cl_2$ yields a partial isomer shift of -0.36 for TU. Using these values to calculate an isomer shift for the ion $\left[Sn(TU)_2Cl\right]^+$ by the equation $\delta_{Sn(II)ion} + \delta Cl^- + 2(\delta_{TU}) = 4.83 + (-0.37) + 2(-0.36) = 3.74$ mm/sec which is the value of the shift for the 1: 1 complex. Three arguments are introduced which can make the value approach 3.66 mm/sec, observed for the $Sn(TU)_2Cl_2$.

The first, which is most plausible, is that the ion $[Sn(TU)_2Cl]^+$ is not being observed. Instead, the neutral compound $Sn(TU)_2Cl_2$ with both chlorines attached to the tin is the actual species observed and where the partial isomer shifts (donating power) of both the TU and Cl has decreased. The second argument would be that the S-Sn bonds in the $[Sn(TU)_2Cl]^+$ ion are now stronger than in the 1:1 complex, donating more electrons to the tin. This would be in direct contradiction to that observed by the infrared studies. The third argument is that the chlorine-tin bond would be more covalent in the ion complex and the chlorine would donate more electron density to shield the tin $5s^2$ pair or it would withdraw electron density of the tin through a greater electronegativity effect. The last two arguments cast justifiable doubt on the validity of using the method of partial isomer shifts for various groups to determine coordination numbers because the bonding power of a specific group can vary so drastically from compound to compound. These arguments do interject the possibility that there could be inequivalency in both of the Sn-S or both of the Sn-Cl bond strengths in the $Sn(TU)_2Cl_2$ complex. It is interesting that partial isomer shifts can be used to conclude that the S-Sn bond is weaker in $Sn(TU)_2Cl_2$ than in $Sn(TU)Cl_2$.

The vibrational frequency shifts for TU from the infrared data have indicated that the S-Sn bonds for the $Sn(TU)_2Cl_2$ and $Sn(TU)_2Br_2$ are about equal in strength. From the Mössbauer data it at first appears that the S-Sn bond is weaker in $Sn(TU)_2Br_2$, in contradiction to the infrared data. If the principle of partial isomer shifts is used to evaluate the isomer shift for the ion $[Sn(TU)\ Br]^+$ as in the preceding paragraph, surprisingly a value of 3.81 mm/sec is calculated which is in agreement with that observed for the solid $Sn(TU)_2Br_2$. This will be further discussed in the next section in relation to the NMR data, but as noted, the arguments about relative bond strength must be made with caution until coordination numbers have been established with certainty.

Quadrupole splittings of these complexes result when the 3/2 excited state of Sn^{119} is split into two sub-levels by the interaction of its nuclear quadrupole moment with an asymmetric electric field gradient. The major contribution to the asymmetry of the electric field gradient at the tin (II) nucleus is due to the imbalance of the electron density in the 5 p bonding levels of the tin. Most tin (II) compounds have been observed to have quadrupole splittings ranging from approximately 0.50 mm/sec to about 2.4 mm/sec, whereas larger splittings, as high as 4.80 mm/sec, (15) have been observed for tin (IV) compounds. Tin (II) compounds are expected to have distortions of their bonded configurations because of the influence of their non-bonded pair of electrons. Increases in the coordination number of Tin (II) through dative bond formation will cause the nonbonded pair of electrons to become more localized and gain in p electron character resulting in larger quadrupole splittings. However, no definite relationship has been found to exist between the quadrupole splitting data and the coordination numbers of tin (II) complexes. As the strength of the crystal field increases, as in the case of electrostatic bonding, an increase in the quadrupole splitting would also be expected because it becomes more easy for one or both of the nonbonded 5 s electrons of the tin to occupy the 5 p sublevels. It has been shown (4) that the quadrupole splitting observed for a distortion in the $p_x - p_y$ plane will be half of that observed for a distortion of equal magnitude along the p_z axis. This observation makes it very difficult to relate the magnitude of the quadrupole splitting to the structure which causes the distortion.

The Sn^{119} quadrupole splittings for $SnCl_2$ and $SnBr_2$ increase on complex formation with TU and TMTU, with the chlorides exhibiting a larger quadrupole splitting than the bromides. The bromide complexes show lower quadrupole splittings because of their lower electronegativity and greater ability to overlap their electron cloud with the orbitals

of the tin. Larger quadrupole splittings are predicted and observed for the TMTU complexes because the TMTU is a larger ligand than TU. TMTU has also been shown to be a better electron donor to tin than TU which as mentioned in the preceding paragraph would result in an increase in the p character of the nonbonded pair of electrons on the tin atom. Infrared data has suggested that the sulfur in TMTU acts as a bridging group between tin atoms. This would result in a polymeric lattice which might have higher field gradient asymmetry than the monomeric lattices of the TU complexes. The three coordinate $Sn(TU)Cl_2$ complex has been observed to have a slightly larger quadrupole splitting than $Sn(TU)_2Cl_2$. The increase in coordination number may actually result in an increase in the field gradient in the $P_x - P_y$ plane of the complex but with a corresponding decrease in the P_z field gradient, resulting in a net decrease in the value of the quadrupole splitting.

Lees and Flinn (4) have shown that there is a correlation between the isomer shifts and quadrupole splittings observed for normal tin (II) compounds. Two linear relationships were obtained from a plot of the isomer shift data as a function of the quadrupole splitting data, and the slopes of the lines differed by a factor of two. The line with the larger slope represents data for compounds where the tin atoms are said to have field asymmetries along the P_z axis (axial asymmetry), the line with the more negative slope represents data for compounds which are said to have field asymmetry in the $P_x - P_y$ planes (equatorial asymmetry). Therefore, correlation of only the observed quadrupole splitting to the structure is difficult.

Data for the TMTU and TU complexes were plotted on a δ versus Δ plot (See Figure 5) in an attempt to determine something about the structural nature of the complexes. The data for the bromide complexes fall on line C in Figure 5 which has a slope of -0.80. Evidently, the solid state structures of these two complexes are similar to $SnBr_2$, SnS and

SnO (black form) resulting in a field asymmetry which lies in the $P_x - P_y$ plane of the tin atom. To a first approximation one may say that the symmetry of $Sn(TU)_2Br_2$ and $Sn(TMTU)Br_2$ is pyramidal or tetragonal pyramid. The data for the chloride complexes do not fall on either line of the Lees-Flinn plot but form a linear relationship with a slope half-way between that obtained for the pure P_z and pure $P_x - P_y$ asymmetries. The structure of the chlorides must be similar to distorted tetrahedrons or trigonal bipyramids with intermediate axial field asymmetries. The slopes of the three lines observed in figure 5 are in the ratio of 2: 3: 4. It is interesting to observe that the linear relationships appear to be fairly well correlated to the electronegativity of the elements attached to the tin. Herber and Cheng (16) have shown that the isomer shifts for octrahedral tin (IV) halogen complex anions are a linear function of the sum of the electronegativities of the bound halogens. They have pointed out that the linear relationship is not followed by complexes that have distorted octahedral symmetries. Only an approximate correlation of this type with tin (II) complexes is observed because the structures of the complexes can vary to a great degree. It appears that the most electronegative elements or the larger sum total of the electronegativities of all the bound groups in the tin (II) compounds dictate which of the lines they will fall on.

The most electronegative elements bonded to the compounds which fall on line A are oxygen and fluorine, on line B chlorine and on line C bromine. The sulfur atoms of TU and TMTU have a lower electronegativity than either Br or Cl and the complexes they have formed with $SnCl_2$ and $SnBr_2$ do not appear to have changed their electric field gradient asymmetries from that of the parent halides. It is observed that when oxygen coordinates to $SnCl_2$ in alcohol glasses (17) that the electric field gradient asymmetry of the tin changes to an electric field gradient along the p_z axis. A correlation of this

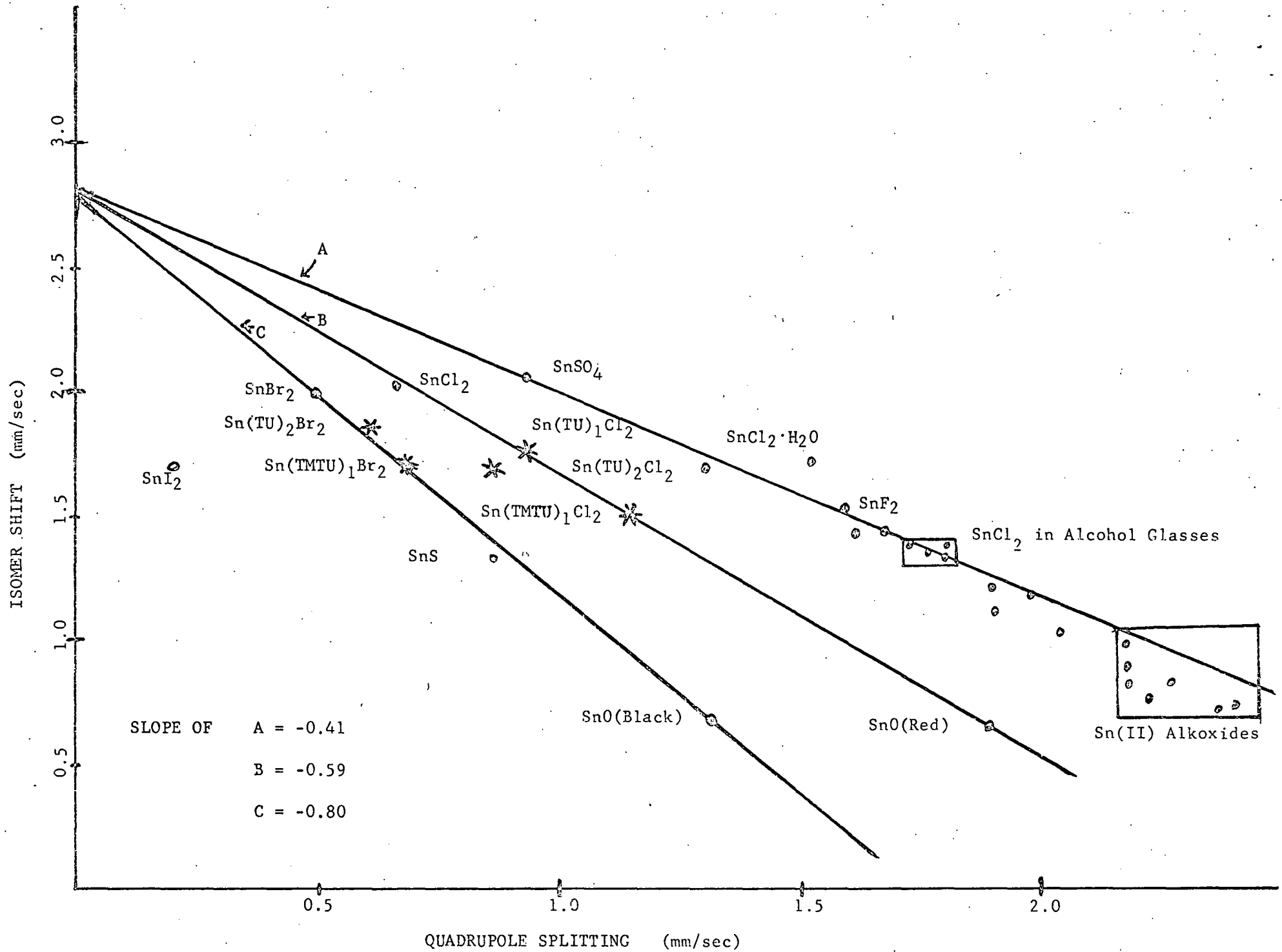


Figure 5. Isomer Shifts (Mg_2Sn is δ = 0 mm/sec (4)) as a Function of Quadrupole Splitting

type does not yield direct information about the coordination number of the tin but it does reveal valuable information about the orientation of the electric field gradient about the tin nucleus.

Solution

Mössbauer and NMR Spectra

Mössbauer spectra of these complexes in frozen solution have been studied because of their enhanced solubility in CH_3OH and because of the difficulty encountered in evaporating all of the solvent, CH_3OH, while trying to isolate the pure solids. These complexes oxidize readily in solution, as noted by the appearance of a small tin (IV) Mössbauer absorption peak in Figure 6. Some of the factors that must be considered when interpreting the NMR and Mössbauer data for these complexes in solution are now discussed. When a solute, such as those studied, is dissolved in solvents like CH_3OH and DMSO, several questions can be immediately asked. Does the solute dissociate? And, if so, to what species or ions? How fast does the solvent exchange between the coordinated and uncoordinated forms occur? Does rapid cooling of these solutions to liquid nitrogen temperature trap the solute and solvent in the configuration in which they existed at room temperature or does a two phase system result i.e., frozen solution and crystallized solute?

The Mössbauer technique has provided information about the general nature of the species which are present when the complexes are dissolved and studied in frozen solutions. NMR data for these solutions have also been obtained at room temperature in order to determine if the Mössbauer data for the frozen solutions resulted from the same tin complexes which are present in the solutions at room temperature. The two solvents chosen for this study were CH_3OH and DMSO, the former because it was used to prepare the complexes, the latter because it lacks acidic protons which cause the NMR absorptions of TU to be shifted by proton exchanges between the solvent and solute.

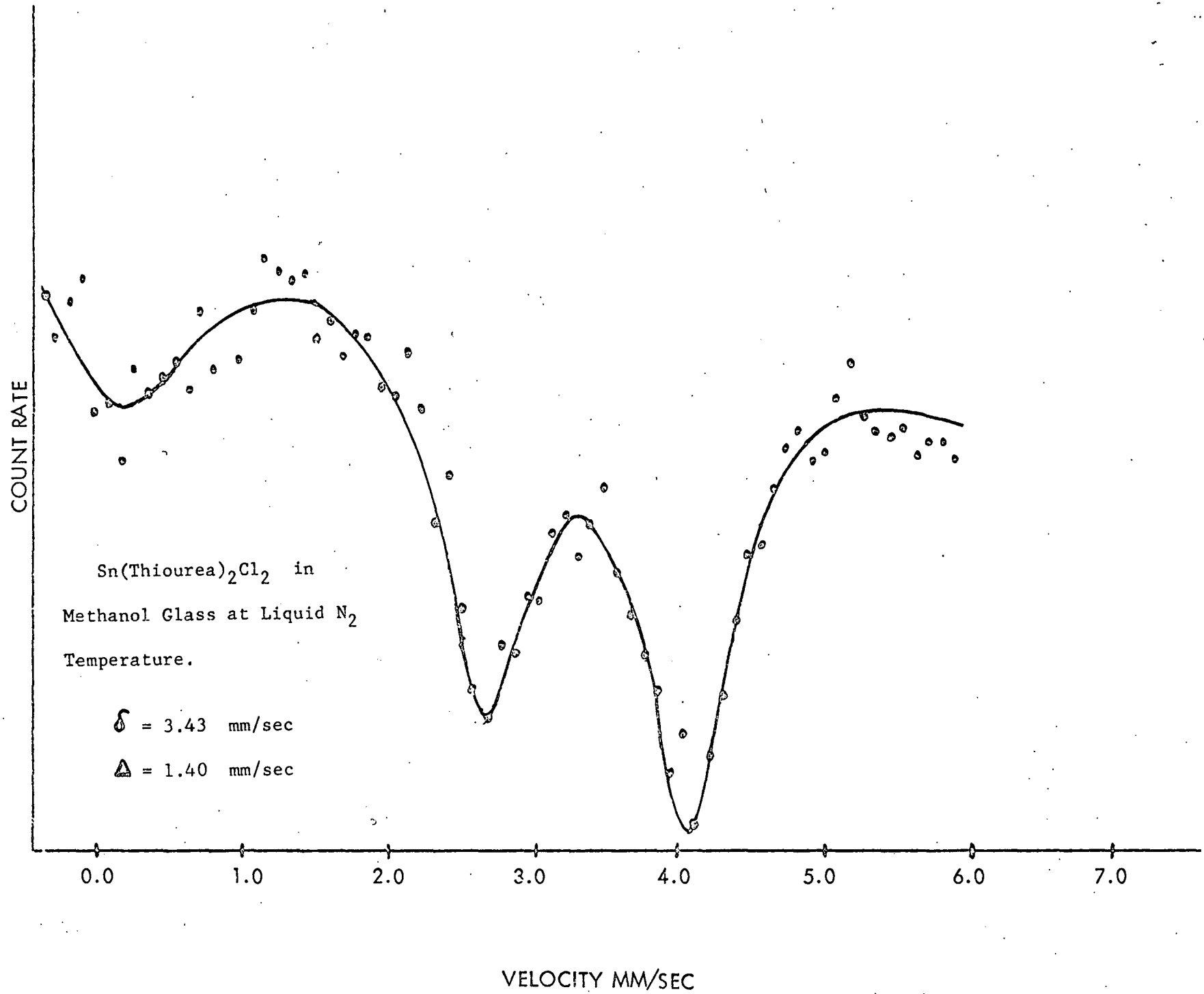


Figure 6. Mossbauer Spectrum of $Sn(TU)_2Cl_2$ in CH_3OH glass at liquid nitrogen temperature vs a $BaSn_3$ source

Mössbauer data for these complexes in frozen solution are reported in Table IV. The data for $SnCl_2$ and $SnBr_2$ show that the solvents, CH_3OH and DMSO, are coordinated to the halides and that the oxygen of CH_3OH is a stronger donor than the oxygen of DMSO. Both solvents appear to be better donors than either TU or TMTU. Mössbauer data reported on the solid, bis-DMSO and bis-TMTU, complexes of $SnCl_4$ and $SnBr_4$ have also shown that the DMSO is a better donor than TMTU with these two tin (IV) halides (12). Larger quadrupole splittings are observed for the tin (II) halides in CH_3OH than in DMSO solvent and both of the CH_3OH and DMSO, $SnCl_2$ and $SnBr_2$ complexes have axially asymmetric field gradients. Conductivity data for $SnBr_2$ and $SnCl_2$ in both CH_3OH and DMSO have been reported by Welna (18) and are given below in Table V. The data have been reported as the ratio of the equivalent conductivity of $(C_2H_5)_4NBr$ to that of the tin (II) halide.

Table V

EQUIVALENT CONDUCTIVITY RATIOS OF
$\Lambda(C_2H_5)_4NBr$ to $\Lambda SnCl_2$ and $\Lambda SnBr_2$ in DMSO and CH_3OH

	DMSO	CH_3OH
$\Lambda(C_2H_5)_4NBr$ / $\Lambda SnBr_2$	4.8	13.7
$\Lambda(C_2H_5)_4NBr$ / $\Lambda SnCl_2$	14.7	17.5

These data show a larger difference between the dissociation of $SnBr_2$ and $SnCl_2$ in DMSO than in CH_3OH, with the $SnBr_2$ being more highly dissociated. The two halides in CH_3OH show similar dissociations which are considered to be small. These data suggest that the Mössbauer spectrum of $SnBr_2$ in DMSO may be for a solvated ion such as $\left[SnBr(DMSO)_x\right]^+$ or $\left[Sn(DMSO)_x\right]^{+2}$ instead of the undissociated solvent complex, $SnBr_2(DMSO)_x$.

TABLE IV

SOLVENT EFFECTS ON THE ISOMER SHIFTS (I.S.)
AND
QUADRUPOLE SPLITTINGS (Δ) IN FROZEN SOLUTION
AT
LIQUID NITROGEN TEMPERATURE

	Solid		In CH_3OH		In DMSO	
	I.S. *	Δ	I.S.	Δ	I.S.	Δ
$SnCl_2$	4.09	≤ 0.5	3.36	1.76	3.38	1.37
$SnBr_2$	4.04	≤ 0.5	3.45	1.53	3.51	1.10
$Sn(TU)_2Cl_2$	3.66	0.86	3.43	1.40	3.47	1.13
$Sn(TU)_2Br_2$	3.80	0.61	3.58	1.09	3.48	0.95
$Sn(TMTU)Cl_2$	3.48	1.15	3.38	1.13	3.47	1.40
$Sn(TMTU)Br_2$	3.68	0.68	---- **	----	3.56	1.08

*All isomer shifts are reported in mm/sec ± 0.05 mm sec relative to the center of the room temperature, $BaSnO_3$, source.

**No resonance spectrum for a tin (II) complex was observed.

The Mössbauer data for the complexes in the frozen solutions are shifted between those observed for the pure solid complexes and the uncomplexed halides in frozen solution except for the data observed on the TMTU complexes in DMSO. This data suggest that the DMSO and not the TMTU is coordinated to the $SnCl_2$ and $SnBr_2$. The NMR data for the TMTU complexes at room temperature in DMSO as reported in Table VI, show that the difference between the CH_3 proton shifts of DMSO and the CH_3 protons shifts of TMTU decrease by the same amount when either $SnCl_2$ or $SnBr_2$ are added to the DMSO solutions of TMTU. It should be noted that the CH_3 proton resonance of TMTU in all three solutions remains the same with respect to the external standard TMS (tetramethylsilane) and that it is the CH_3 protons resonances of the solvent DMSO which are shifted down field. A possible explanation for the similar CH_3 -shifts of DMSO for the $SnCl_2$ and $SnBr_2$ solutions is that the signal for the complexed DMSO is not shifted very far from the free solvent absorption which has a much larger absorption intensity, causing a sum peak to be observed that does not distinguish between the two tin halides. Low temperature NMR data should permit the resonances for the complexed and uncomplexed DMSO to be resolved, this should give an indication of the difference in O--$SnCl_2$ and O-$SnBr_2$ bond strengths. It is interesting to note that both the room temperature NMR and frozen solution Mössbauer data show that TMTU is not complexed to any appreciable degree to $SnCl_2$ or $SnBr_2$ in DMSO.

The NMR data for $Sn(TMTU)Cl_2$ and $Sn(TMTU)Br_2$ in CH_3OH confirm that TMTU is complexed to the tin halides. NMR CH_3 shifts for TMTU indicate that the S--Sn bond strength will be greater for the chloride than for the bromide complex, in agreement with the infrared and Mössbauer data obtained on the solid complexes. The CH_3OH solution Mössbauer spectrum of $Sn(TMTU)Cl_2$ is in agreement with the NMR data but the isomer

TABLE VI

NMR CHEMICAL SHIFTS

	SOLVENTS	
	CH_3OH	DMSO[a,c]
NH_2 Shifts vs Methyl Shifts in		
Thiourea (TU)	----	270.0 cps
$SnCl_2$ + 1 TU	----	273.2
$SnCl_2$ + 2 TU	----	274.4
$SnBr_2$ + 1 TU	----	276.8
$SnBr_2$ + 2 TU	----	278.0
CH_3 Shifts in Methyl Shifts in		
TMTU	17.6 cps[b,c]	26.8 cps[a,d]
$SnBr_2$ + 1 TMTU	15.8	24.0
$SnCl_2$ + 1 TMTU	10.8	24.0

[a]The proton shifts for the NH_2 groups of TU and for the CH_3 groups of TMTU occur down field with respect to the proton shifts for the CH_3 groups of the solvent DMSO.

[b]The proton shifts for the CH_3 groups of TMTU occur up field with respect to the proton shifts for the CH_3 groups of the solvent CH_3OH.

[c]The shifts for the protons of the ligands upon coordination to the tin all are observed to move down field.

[d]Upon the addition of the $SnCl_2$ and $SnBr_2$ the CH_3 protons of the solvent DMSO shifts down field toward the uncomplexed ligand.

shift and quadrupole splittings suggest that only very weak bonding of CH_3OH to the complex in the frozen solution is present. A tin (II) Mössbauer spectrum of the $Sn(TMTU)Br_2$ in CH_3OH could not be observed for comparison.

The NMR data for the TU complexes as reported in Table VI show that the S-Sn bond is stronger in the $SnBr_2$ complexes than in those of $SnCl_2$. The proton shifts for both the chlorides and bromides in DMSO were observed to be dependent on the ratio of the concentrations of the ligand to the tin halide. This suggests that the NMR data is not being obtained on any one specific complex in solution but that an equilibrium mixture of complexes such as $Sn(DMSO)_yX_2$, $Sn(TU)(DMSO)_yX_2$, $Sn(TU)_2(DMSO)_yX_2$ along with possibly some uncomplexed ligand exists. It was noted earlier from conductivity data that $SnBr_2$ in DMSO is more highly dissociated than $SnCl_2$. This implies that ionic complexes of the bromide could be present in these solutions. The dissociation of $SnBr_2$ in DMSO can be used to account for the fact that the NH_2 proton shifts are greater for the bromide than the chloride complexes. The S-Sn bond strength to the solvated Sn^{+2} ions is expected to be greater than the neutral, solvated $SnBr_2$. This would be consistent with the Mossbauer and I.R. data obtained on the solid complexes. The Mossbauer data for $Sn(TU)_2Cl_2$ and $Sn(TU)_2Br_2$ in frozen solutions indicate that the TU and DMSO are definitely bound to $SnCl_2$. The evidence for TU being coordinated to $SnBr_2$ is not as convincing unless it is assumed that one of the bromides is dissociated from the complex $Sn(TU)_2Br_2$ by the DMSO. The quadrupole splitting for $Sn(TU)_2Br_2$ in DMSO is also smaller than would be expected if only DMSO were bound to $SnBr_2$.

The Mössbauer spectra for the thiourea complexes were also observed in CH_3OH solution and they indicated that the CH_3OH was also bound to the $Sn(TU)_2Cl_2$ and $Sn(TU)_2Br_2$ in the frozen solutions. The CH_3OH appears to affect the isomer shifts of both

complexes to the same degree although the quadrupole splitting for the $Sn(TU)_2Cl_2$ is affected to a larger degree than the $Sn(TU)_2Br_2$. This latter observation rules out the possibility that the CH_3OH causes only a lattice effect instead of a direct coordination effect. As mentioned earlier the NMR data of the TU complexes in CH_3OH were not obtained because the exchange of the solvent protons with the NH_2 protons of TU would have complicated the interpretation of the NMR data.

The Mössbauer data for the complexes in frozen solutions have been included in Figure 7, a plot of isomer shift versus quadrupole splitting. The oxygen donors in these solvents have different electronegativities. It is seen from the graph that CH_3OH increases the electric field gradient asymmetry of these compounds more than DMSO which indicates a greater axial distortion for the CH_3OH complexes in frozen solution. The scatter in the data now shows that a three line relationship between the isomer shifts and quadrupole splittings for tin (II) compounds does not exist. The data in Figure 7 seem to place limits on the values of the isomer shifts and quadrupole splittings which are possible for tin (II) compounds. All tin (II) compounds are expected to have isomer shifts and quadrupole splittings that fall within the limits of the two extremes of the electric field asymmetries. It has been observed that generally donors which may be classified as soft acids will give rise to $P_x - P_y$ distortions and as the hardness of the donors increase the distortions will increase to yield P_z asymmetry.

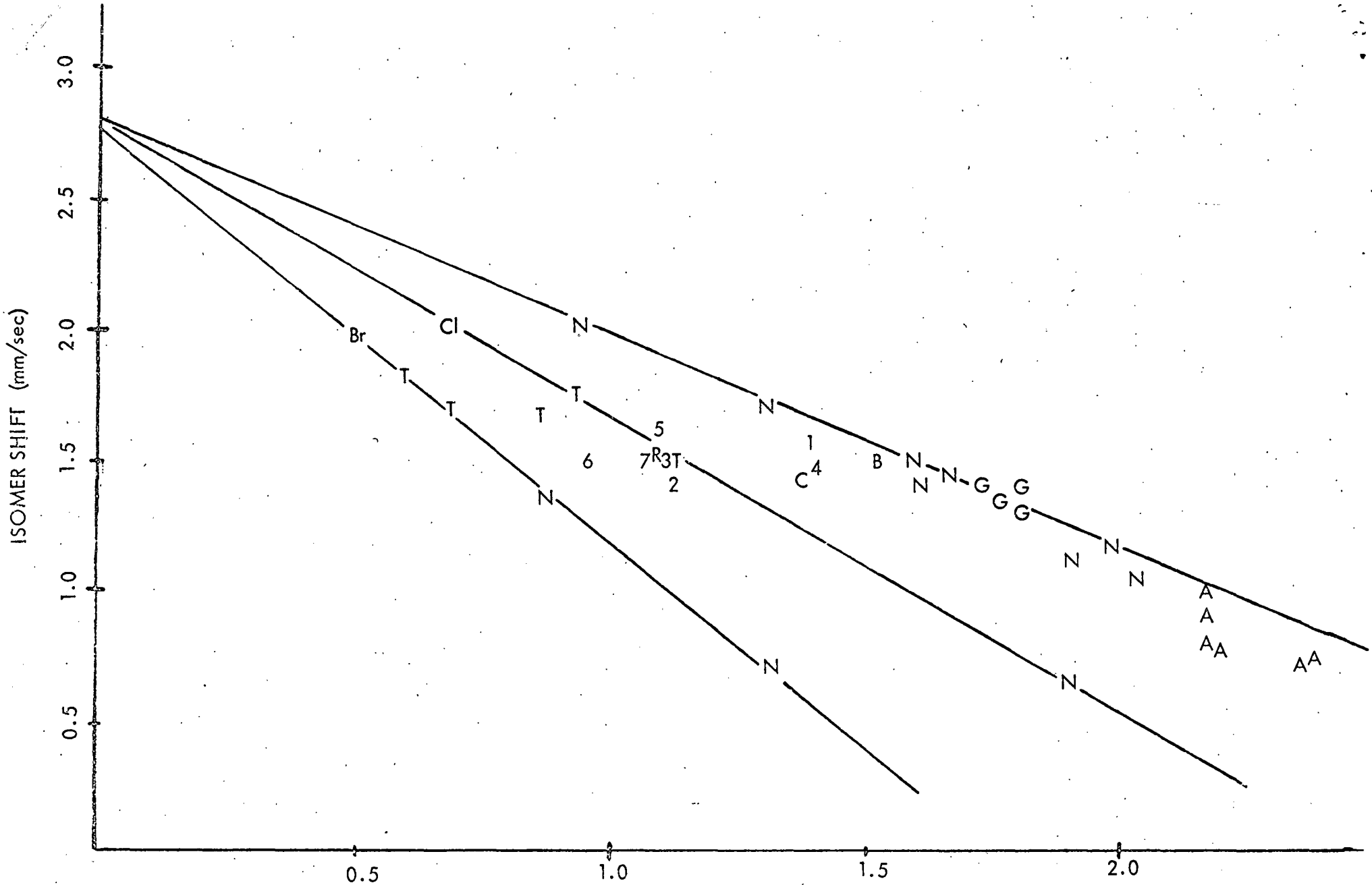


Figure 7:
Isomer shift (Mg_2Sn is δ = 0 mm/sec (4)) as a function of Quadruople splitting for the following tin (II) compounds, A = Tin (II) alkoxides and G = $SnCl_2$ in alcohol glasses (17); N = normal Tin (II) compounds, Cl = $SnCl_2$, and Br = $SnBr_2$ (4); Frozen solutions are B = $SnBr_2$ in CH_3OH, R = $SnBr_2$ in DMSO, C = $SnCl_2$ in DMSO, 1 = $Sn(TU)_2Cl_2$ in CH_3OH, 2 = $Sn(TMTU)Cl_2$ in CH_3OH, 3 = $Sn(TU)_2Br_2$ in DMSO, 4 = $Sn(TMTU)Cl_2$ in DMSO, 5 = $Sn(TU)_2Br_2$ in CH_3OH, 6 = $Sn(TU)_2Br_2$ in DMSO, 7 = $Sn(TMTU)Br_2$ in DMSO and T = the solid TU and TMTU, $SnCl_2$ and $SnBr_2$ complexes.

CONCLUSION

In summary, all three spectroscopic methods, Infrared, Mössbauer, and NMR have been found to be useful in studying the TU and TMTU complexes of $SnCl_2$ and $SnBr_2$. Infrared data from the solid complexes have been shown to be of value in determining if complexation of the ligands to the tin has taken place. Solution infrared data are difficult to obtain because the solvents used in this investigation have absorption bands similar to those of the ligands. NMR spectra of the complexes in solution have aided in the interpretation of the frozen solution Mössbauer data. It was noted that temperature studies of the NMR spectra will be of value in differentiating the solvation of the various tin (II) halides. The Mössbauer technique has proven to be a powerful tool with which to observe the central metal tin atom in these complexes. Correlations from the data of all three techniques provided more information about the complexes than the independent results of each technique.

The correlation of isomer shifts and quadrupole splittings for tin (II) compounds has shown to be of more value than the separate parameters in determining electric field gradient asymmetries. It is interesting that the isomer shift and quadrupole splitting values for tin (II) compounds appear to fall within specific boundaries. The tin (IV) species observed in some of the frozen solution Mössbauer spectra were not identified because of the scope of this investigation but they are definitely not SnO_2. The bromide complexes were observed to be more easily oxidized, which is in agreement with the conclusion about the S-Sn bond strengths of the complexes from the Mössbauer data. It is of particular interest that all three spectroscopic techniques suggest that $Sn(TU)_2Br_2$ is three coordinate and the other complexes have coordination numbers that are consistent with their stoichiometric formulas. TMTU has been observed to act as a bridging unit in the two complexes $Sn(TMTU)Cl_2$ and $Sn(TMTU)Br_2$.

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REFERENCES

1. V. T. Goldanskii, "The Mössbauer Effect and Its Applications in Chemistry," Consultants Bureau, New York, 1964.

2. M. T. Jones, Inorg. Chem., 6, 1249 (1967).

3. J. J. Zuckerman, J. Inorg. Nucl. Chem., 29, 2191 (1967).

4. J. K. Lees and P. A. Flinn, J. Chem. Phys., 48, 882 (1968).

5. J. D. Donaldson and B. J. Senior, J. Inorg. Nucl. Chem., 31, 881 (1969).

6. F. C. Ruegg, J. J. Spijkerman, and J. R. DeVoe, Rev. Sci. Instr., 36, 356 (1965).

7. R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, J. Amer. Chem. Soc., 79, 1575 (1957).

8. A. Yamaguchi, R. B. Penland, S. Mizueshima, T. J. Lane, C. Curran, and J.V. Quagliano J. Amer. Chem. Soc., 80, 527 (1958).

9. S. Basso, J.A. Costamagna and R. Levitus, J. Inorg. Nucl. Chem., 31, 1797 (1969).

10. M.-Schafer and C. Curran, Abstracts 148th ACS Meeting, Chicago, Illinois, September, pp. 27-0 (1964).

11. Editors: V. I. Goldanskii and R. H. Herber, "Chemical Applications of Mössbauer Spectroscopy," Ch. 5 and 6, Academic Press, New York and London (1968).

12. J. Philip, M. A. Mullins, and C. Curran, Inorg. Chem., 7, 1895 (1968).

13. J. D. Donaldson and B. J. Senior, J. Chem. Soc. (A.), 2358 (1969).

14. R. H. Herber, R. B. King, and G. K. Wertherin, Inorg. Chem., 3, 101 (1964).

15. A. Yu. Aleksandrov, N. N. Delyagin, K.P. Mitrofanov, L. S. Polak, and V.S. Shpinel, Soviet Phys. JETP, 16, 879 (1963).

16. R. H. Herber and H. S. Cheng, Inorg. Chem., 8, 2145 (1969).

17. D. C. Featherston and J. F. Lefelhocz, Abstracts 157th ACS Meeting, Minneapolis, Minnesota, April (1969).

18. W. Welna, Ph.D. Thesis, University of Notre Dame, June 1967.