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# Trifluoromethyl Sulfates of Tin

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The synthesis of $Sn(SO_3CF_3)_2$, $Sn(SO_3CF_3)_4$, and a compound of the composition $Sn(SO_3CF_3)_3$ by the solvolysis of $SnCl_2$, $Sn(CO_2CH_3)_4$ and $Sn(C_2H_3)_4$ in trifluoromethanesulfonic acid is described. The compounds are characterized by their infrared and [119]Sn Mössbauer spectra. $Sn(SO_3CF_3)_3$ is found to contain both di- and tetravalent tin and should best be regarded as $Sn^{II}[Sn^{IV}(SO_3CF_3)_6]$.

## Introduction

In good analogy to the halides of tin, a number of monobasic oxy acids are found to form both Sn(II) and Sn(IV) derivatives with rather different structural and chemical features. For instance, tin(II) fluorosulfate, $Sn^{II}(SO_3F)_2$,[1-3] is best regarded as an ionic solid, even though the local symmetry of the fluorosulfate ion is reduced from $C_{3v}$ to $C_s$, presumably as a result of some anion–cation interaction. Conductance measurements in $HSO_3F$[3] indicate basic behavior; that is, $Sn^{II}$-$(SO_3F)_2$ acts as a $SO_3F^-$ ion donor.

On the other hand $Sn(SO_3F)_4$[4] is apparently polymeric with both bridging and monodentate $SO_3F$ groups, similar to $SnF_4$.[5] The existence of stable $[Sn(SO_3F)_6]^{2-}$ ions[6] implies that $Sn(SO_3F)_4$ may be regarded as a $SO_3F^-$ ion acceptor.

The present study is concerned with the synthesis and structural characterization of possible trifluoromethyl sulfates of tin. Only a limited number of organotin(IV) compounds containing the $SO_3CF_3$ group, such as $(CH_3)_2Sn(SO_3CF_3)_2$[7-9] and $(CH_3)_3SnSO_3CF_3$,[9-11] have previously been reported.

## Experimental Section

**1. Chemicals.** Commercially available chemicals of reagent or analytical grade were used without purification. Trifluoromethanesulfonic acid (Minnesota Mining and Manufacturing Co.) was distilled from concentrated $H_2SO_4$ prior to use. Tetravinyltin (Penninsular ChemResearch) was transferred by vacuum distillation into the reaction flask. Tin(IV) acetate was synthesized either by reaction of $SnI_4$ with $Tl^ICO_2CH_3$[12] or by interaction of tetravinyltin with acetic acid in a sealed tube at $\sim100$ °C.[13]

**2. Instrumentation.** A Perkin-Elmer 457 infrared grating spectrophotometer was employed in this study. Silver bromide windows were used. The samples were mulled with Nujol or hexachlorobutadiene. The Mössbauer spectrometer has been described elsewhere.[4] Moisture-sensitive materials were handled inside a Vacuum Atmosphere Corp. "Dri-Lab" Model No. He-43-2 filled with purified dry $N_2$. Filtration and other manipulations of moisture-sensitive materials outside the drybox were carried out in an apparatus described by Shriver.[14]

**3. Preparations. (a) $Sn(SO_3CF_3)_4$.** Tin(IV) (1.203 g, 3.39 mmol) and an excess of $HSO_3CF_3$ were combined in the drybox. During an exothermic reaction acetic acid was formed and subsequently removed in vacuo. A white, finely powdered precipitate formed which was best isolated by filtration and subsequent washing with only small amounts of $HSO_3CF_3$, since the solid was found to be somewhat soluble in the acid. Attempts to isolate the solid by evaporating the reaction mixture to dryness were unsuccessful. A second crystalline solid, tentatively identified as $CH_3CO_2H \cdot HSO_3CF_3$, was formed. Even though this by-product was low melting (mp +35 °C) and slightly volatile in vacuo, separation attempts by vacuum sublimation resulted in decomposition.

The white solid (mp 225–227 °C) was found to be very hygroscopic and analyzed as $Sn(SO_3CF_3)_4$.

**(b) $Sn(SO_3CF_3)_2$.** Tin(II) trifluoromethyl sulfate was formed when an excess of $HOS_3CF_3$ was reacted with 1.802 g or 9.5 mmol of anhydrous stannous chloride. Gaseous HCl was evolved in an exothermic reaction. To ensure complete reaction the mixture was heated first to +80 °C for 48 h and then for 1 h at 100 °C. After removal of all volatile products in vacuo a white, chloride-free hygroscopic solid was obtained. This residue did not melt below 300 °C and analyzed as $Sn(SO_3CF_3)_2$. The compound was sparingly soluble in $HSO_3CF_3$.

**Table I**

| Compd | | % Sn | % S | % F |
|---|---|---|---|---|
| $Sn(SO_3CF_3)_4$ | Calcd | 16.60 | 17.94 | 31.89 |
| | Found | 16.26 | 17.93 | 30.62 |
| $Sn(SO_3CF_3)_3$ | Calcd | 20.97 | 17.00 | 30.22 |
| | Found | 20.53 | 16.86 | 29.67 |
| $Sn(SO_3CF_3)_2$ | Calcd | 28.47 | 15.38 | 27.35 |
| | Found | 28.37 | 15.58 | 27.12 |

**(c) "$Sn(SO_3CF_3)_3$".** In a typical preparation 5.5 mmol of tetravinyltin was distilled in vacuo onto an approximately tenfold excess of trifluoromethanesulfonic acid. The mixture was allowed to warm from –78 °C to room temperature with the mixture protected from moisture by a $P_4O_{10}$ guard tube. A white solid was formed, while the acid solution turned brown. The acid solution was decanted and freshly distilled $HSO_3CF_3$ was again added. The white solid dissolved rapidly and the mixture was allowed to stand for 5 days at room temperature. During this period a white, crystalline precipitate formed slowly which was removed from the mixture by filtration and purified by repeated washing with $HSO_3CF_3$ until all brown color had disappeared.

The last traces of acid were removed by vacuum distillation. The resulting white, crystalline material did not melt below 300 °C and was virtually insoluble in $HSO_3CF_3$. Chemical analysis indicated the composition $Sn(SO_3CF_3)_3$.

Ligand redistribution with tin(IV) trifluoromethyl sulfate and tetramethyltin was accomplished at room temperature when approximately 2.2 mmol of $Sn(SO_3CF_3)_4$ was reacted with a four- to fivefold excess of $Sn(SH_3)_4$. The latter was removed in vacuo and the product identified by its IR and [119]Sn Mössbauer spectrum.[10]

**4. Analysis.** Microanalysis was carried out by A. Bernhardt Microanalytical Laboratories, Elbach, West Germany. The results together with the calculated values are given in Table I.

## Results and Discussion

**1. Synthesis.** The preparation of $Sn(SO_3CF_3)_2$ was accomplished conveniently by reacting anhydrous $SnCl_2$ with an excess of $HSO_3CF_3$ according to

$$SnCl_2 + 2HSO_3CF_3 \xrightarrow[48\ h]{+25\ to\ +100\ °C} Sn(SO_3CF_3)_2 + 2HCl$$
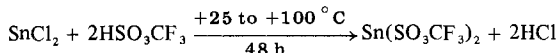
analogous to the synthesis of $Sn(SO_3F)_2$.[2,3]

Whereas $Sn(SO_3F)_4$[4] had been obtained by reacting $SnCl_4$ with peroxydisulfuryl difluoride,[4] $S_2O_6F_2$,[15] according to

$$SnCl_4 + 2S_2O_6F_2 \xrightarrow{+100\ °C} Sn(SO_3F)_4 + 2Cl_2$$
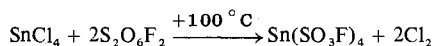
the corresponding peroxy compound $S_2O_6(CF_3)_2$ is only of limited thermal stability[16] which precludes its use in synthetic chemistry. Therefore, the solvolysis of suitable tetrasubstituted tin(IV) compounds in $HSO_3CF_3$ according to $SnX_4 + 4HSO_3CF_3 \rightarrow Sn(SO_3CF_3)_4 + 4HX$, with X = Cl, $CH_3$, or $O_2CCH_3$, was investigated as a possible synthetic route.

Complete reaction was accomplished when $Sn(O_2CCH_3)_4$ was used as reagent. This same route had been found successful in the recent synthesis of $Pb(SO_3CF_3)_4$ and $Pb(SO_3F)_4$.[17]

Isolation of $Sn(SO_3CF_3)_4$ by filtration and subsequent washing with small amounts of $HSO_3CF_3$ allowed facile separation from a by-product which is very soluble in the acid. This by-product was identical with a directly formed 1:1

complex between $HSO_3CF_3$ and $HO_2CCH_3$. Due to its limited thermal stability the complex was not characterized further.

In contrast to $Sn(SO_3F)_4$,[4] the trifluoromethyl sulfate is moderately soluble in its parent acid. Like the fluorosulfate, but unlike tin tetraacetate, $Sn(SO_3CF_3)_4$ will readily undergo ligand redistribution reactions as indicated by the reaction with tetramethyltin

$$Sn(SO_3CF_3)_4 + 3Sn(CH_3)_4 \xrightarrow{+25\,°C} 4(CH_3)_3SnSO_3CF_3$$
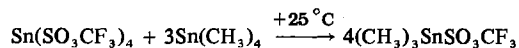
Since tin(IV) acetate is best prepared by the cleavage of all four tin–carbon bonds in tetravinyltin by acetic acid at elevated temperature,[13] it was only logical to study the reaction of $Sn(C_2H_3)_4$ with $HSO_3CF_3$ directly. Because tin–carbon bonds in vinyltin compounds are more readily cleaved by protonic acids[18] than in methyltin compounds, the reaction was carried out at −78 °C. A white solid was obtained and could be recrystallized from trifluoromethanesulfonic acid and purified by repeated washing with $HSO_3CF_3$ at room temperature. This solid analyzed as $Sn(SO_3CF_3)_3$ and proved to be virtually insoluble in $HSO_3CF_3$ in contrast to both $Sn(SO_3CF_3)_2$ and $Sn(SO_3CF_3)_4$. A qualitative test[28] suggested the presence of both divalent and tetravalent tin. Ligand redistribution with $Sn(CH_3)_4$ is accompanied by the occurrence of green to brown intermediates, but rather impure $(CH_3)_3SnSO_3CF_3$ could be identified in the gray mixture by its infrared spectrum.

Only two examples of well-defined compounds with tin in both the +2 and the +4 oxidation states seem to have been synthesized and characterized. Very recently the fluoride $Sn_3F_8$ was obtained by partial oxidation of $SnF_2$ in anhydrous HF.[19] The proposed approximate formula $(Sn^{II})_2Sn^{IV}F_6$ for the polymeric, fluorine-bridged material is based on x-ray diffraction and the [119]Sn Mössbauer spectrum. Shortly thereafter[20] an intermediate in the oxidation of tin(II) *o*-nitrobenzoate of the composition $Sn_2(O_2CC_6H_4NO_2-o)_4O \cdot$ THF was characterized by x-ray diffraction and found to contain both divalent and tetravalent tin.

In view of these two studies a formulation of $Sn(SO_3CF_3)_3$ as $Sn^{II}[Sn^{IV}(SO_3CF_3)_6]$ may be considered as a structural possibility. The mode of formation as partial reductive decomposition of a tin (IV) substrate appears to be a logical alternative to the partial oxidations mentioned above.

**2. Infrared Spectra.** As can be seen from Table II, the band positions found for $Sn(SO_3CF_3)_2$ fall into the region observed for the $SO_3CF_3^-$ ion[21] in $AgSO_3CF_3$. However, all bands are either rather broad, in particular between 1280 and 1050 cm$^{-1}$, or extensively split into two or three components. These splittings seem to affect E modes as well as $A_1$ modes, using the assignment proposed by Burger for ionic $SO_3CF_3^-$.[21] Both factor group splitting and the possible presence of two types of $SO_3CF_3^-$ groups are feasible explanations. Nonequivalence may be caused by different degrees of anion–cation interaction in $Sn(SO_3CF_3)_2$, which is not unexpected in the structural chemistry of divalent tin.[22] A similar interpretation has been reported for the vibrational spectrum of $Sn(SO_3F)_2$,[2] where the absence of the $CF_3$ vibrations produces a much simpler spectrum. Structural similarity is not surprising, considering also the identical [119]Sn Mössbauer spectra produced by $Sn(SO_3F)_2$ and $Sn(SO_3CF_3)_2$ (to be discussed later).

A relatively simple infrared spectrum is produced by the compound $Sn(SO_3CF_3)_3$, indicating the presence of only one type of trifluoromethanesulfonate group. The observed positions at ~1370, ~1210, and ~970 cm$^{-1}$ for $SO_3$ stretching modes and at 1240 and 1155 cm$^{-1}$ for $CF_3$ stretching modes agree well with a report for $(CH_3)_3GeOSO_2CF_3$[23] where the corresponding bands are found at 1365, 1205, 984, 1241, and 1164 cm$^{-1}$. Furthermore the $SO_3$ band positions compare well with similar bands at ~1400, ~1200, and ~990 cm$^{-1}$

Table II. Infrared Frequencies Observed for the $Sn(SO_3CF_3)_n$ Compounds

| AgSO₃CF₃ Freq, cm⁻¹ | Assignment | Freq,[a] cm⁻¹ | | |
|---|---|---|---|---|
| | | Sn(SO₃CF₃)₂ | Sn(SO₃CF₃)₃ | Sn(SO₃CF₃)₄ |
| 1270 | $\nu$[SO₃ (E)] | 1280 s, sh / 1260 s, b | 1375 s / 1350 ms, sh | 1390 m, sh / 1360 ms |
| 1237 | $\nu$[CF₃ (A₁)] | 1220 vs, b | 1240 ms / 1210 vs, b | 1240 ms, sh / 1210 vs, b |
| 1167 | $\nu$[CF₃ (E)] | 1170 s, sh / 1161 s | 1155 s | 1155 s |
| 1043 | $\nu$[SO₃(A₁)] | 1049 s / 1029 ms / 1020 s | 985 vs, b / 940 m, sh | 1040 mw / 980 s, b / 973 mw |
| 760 | $\nu$[S–C (A₁)] | 773 m | 780 m | 773 |
| 647 | $\delta$[SO₃(A₁)] | 643 s / 622 s | 640 m, sh / 630 s | 640 m, sh / 630 s |
| 582 / 579 | $\delta$[CF₃ (E)] | 583 s / 572 mw | 570 w, sh | 602 m, sh / 570 w, sh |
| 525 / 515 | $\delta$[SO₃ (E)] | 520 s / 510 vs / 500 ms | 520 ms | 525 w / 510 ms / 445 ms |
| 351 | $\delta$[CSO (E)] | 365 vw / 351 m / 345 s | 380 m, sh / 345 ms | 420 ms / 362 m |
| 320 | $\delta$[CF₃ (A₁)] | b | | 342 ms |
| 217 | $\delta$[CF₃ (E)] | b | | 320 w, sh |

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; b, broad. [b] Not observed.

for $K_2[Sn(SO_3F)_6]$.[6] For both tin compounds small splittings of the $SO_3$ stretching modes are found. These are better resolved in the Raman spectrum of $K_2[Sn(SO_3F)_6]$,[6] rather than in the infrared spectra, but unfortunately only very poorly resolved Raman spectra could be obtained for all three materials.

The observation of three $SO_3$ stretching modes indicates a reduction of the local symmetry of this group from $C_{2v}$ to $C_s$, most consistent with interpretation as a monodentate $OSO_2CF_3$ group and with the formulation suggested earlier as $Sn^{II}[Sn^{IV}(SO_3CF_3)_6]$.

Finally for $Sn(SO_3CF_3)_4$ a similar reduction in local symmetry of the $SO_3$ group is observed indicating some kind of coordination of oxygen to tin. However, the occurrence of bands in the 400–500-cm$^{-1}$ region is not consistent with previously mentioned observations for a monodentate $OSO_2CF_3$ or reports[10] of a bidentate bridging group. Again extensive splittings are observed in the $SO_3$ stretching region and the presence of two or more types of $SO_3CF_3$ groups cannot be ruled out.

A qualitative comparison of the observed infrared frequencies for all three compounds indicates that $Sn(SO_3CF_3)_3$ is a unique compound rather than a stochiometric mixture of both $Sn(SO_3CF_3)_2$ and $Sn(SO_3CF_3)_4$.

**3. Mössbauer Spectra.** [119]Sn Mössbauer data are given in Table III. The spectrum for $Sn(SO_3CF_3)_3$ is reproduced in Figure 1. The parameters for $Sn(SO_3CF_3)_2$ are very similar to those reported[1] for $Sn(SO_3F)_2$, and the two compounds presumably have similar structures. The isomer shifts ($\delta$) are greater than 4.0 mm s$^{-1}$, suggestive of highly ionic lattices. The small quadrupole splitting and the narrow line widths observed for $Sn(SO_3CF_3)_2$ imply the presence of only one environment for tin. In view of the extensive splitting of the infrared bands it seems likely that $Sn(SO_3CF_3)_2$ may have a structure analogous to that of $SnSO_4$[24] in which tin is surrounded by a distorted octahedron of oxygen atoms, with three short and three long Sn–O distances. Such a structure could account in part at least for the quadrupole splitting observed, although the major contribution to $\Delta E_Q$ is probably from fractional 5p character of the lone pair of electrons on the tin(II) ion.

Table III. $^{119}$Sn Mössbauer Data$^h$ of Tin(II) and Tin(IV) Sulfonates and Related Compounds at 77 K

| Compd | $\delta,^d$ | $\Delta,^e$ | $\Gamma,^f$ | Ref |
|---|---|---|---|---|
| Sn(SO$_3$CF$_3$)$_2$ | +4.15 | 0.84 | 0.98 | This work |
| Sn(SO$_3$F)$_2$ | +4.18 | 0.68 | 1.33 | 1 |
| Sn(SO$_3$CF$_3$)$_4$ | −0.21 | 0 | 1.11 | This work |
| Sn(SO$_3$F)$_4$ | −0.27 | 1.34 | 1.05, 1.32 | 4 |
| Sn(CO$_2$CH$_3$)$_4$ | +0.075 | | 1.45 | This work |
| Sn(NO$_3$)$_4$ | −0.04 | 0.40 | 0.84, 0.84 | $g$ |
| Sn(SO$_3$CF$_3$)$_3,^a$ | −0.24 | 0 | 1.08 | This work |
| Sn(SO$_3$CF$_3$)$_3,^b$ | +4.69 | 0 | 1.14 | This work |
| Sn(SbF$_6$)$_2$ | +4.44 | 0 | 1.21 | 1 |
| K$_2$[Sn(SO$_3$F)$_6$] | −0.26 | 0 | 1.14 | 6 |
| Cs$_2$[Sn(NO$_3$)$_6$] | +0.12 | 0 | 0.82 | $g$ |
| Sn(SO$_3$CF$_3$)$_3^{a,c}$ | −0.29 | 0 | 1.12 | This work |

$^a$ Tin(IV) environment. $^b$ Tin(II) environment. $^c$ Room temperature; only very small effect for the tin(II) environment. $^d$ Isomer shift relative to SnO$_2$ (error limit for δ and Δ: 0.03 mms mms$^{-1}$). $^e$ Quadrupole splitting. $^f$ Line width at half-peak height. $^g$ D. Potts, H. D. Sharma, A. J. Carty, and A. Walker *Inorg. Chem.*, 13, 1205 (1974). $^h$ Source: Ba$^{119m}$SnO$_3$ from New England Nuclear.
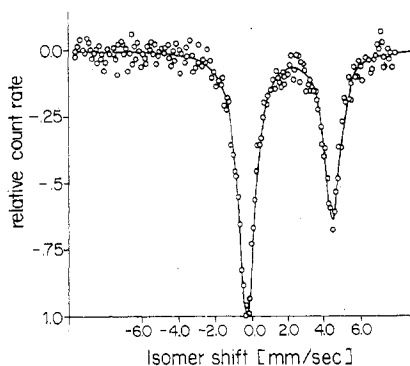


**Figure 1.** Mössbauer spectrum of Sn(SO$_3$CF$_3$)$_3$ at 80 K.

The Mössbauer data for Sn(SO$_3$F)$_4$ and Sn(SO$_3$CF$_3$)$_4$ show that the two Sn(IV) compounds have different structures. This is particularly interesting in view of the fact that for (CH$_3$)$_3$SnSO$_3$X and (CH$_3$)$_2$Sn(SO$_3$X)$_2$ almost identical spectra are observed when X = F or CF$_3$, indicating that corresponding fluorosulfate and trifluoromethyl sulfate derivatives produce a similar environment for tin.[8,10]

There are three possible environments for tin in compounds of the type SnL$_4$: (a) tetrahedral with four monodentate ligands, (b) octahedral with two monodentate and two bidentate ligands, and (c) eight-coordinate with four bidentate ligands. Bidentate SO$_3$CF$_3$ groups may act as bridging or chelating groups, leading to polymeric or monomeric structures. Of these, only the hexacoordinate type (b) will produce a substantial $\Delta E_Q$ (as observed, e.g., in Sn(SO$_3$F)$_4$ and SnF$_4$), due to differences in electron withdrawal by mono- and bidentate groups. An eight-coordinate dodecahedral structure of the Sn(NO$_3$)$_4$ type is expected to give only a small electric field gradient (see Table II) and should yield a Mössbauer spectrum composed of either a single line or a closely spaced and poorly resolved doublet. The absence of Mössbauer absorption at room temperature argues against a polymeric structure since this should lead to a small temperature dependence of the recoil-free fraction, although this negative evidence cannot be considered definitive. Since the infrared spectrum is not consistent with the presence of only monodentate SO$_3$CF$_3^-$ groups, the most likely structure for Sn(SO$_3$CF$_3$)$_4$ appears to be an octacoordinate one with chelating SO$_3$CF$_3$ groups.

The compound Sn(SO$_3$CF$_3$)$_3$ gave an unusual Mössbauer spectrum which immediately suggested the presence of both Sn(II) and Sn(IV). At liquid nitrogen temperature the spectrum consisted of two lines at −0.24 and +4.69 mm s$^{-1}$ (relative to SnO$_2$), with the high-velocity line having only about 60% the intensity of the low-velocity line. The possibility that this spectrum arises from a single tin species can be eliminated as follows. First, the isomer shift of 2.23 mm s$^{-1}$ required by this interpretation is unrealistic for a compound of this type. Second, the line at −0.24 mm s$^{-1}$ is precisely in the range expected for the isomer shift of a tin(IV) trifluoromethyl sulfate complex (see Table II). Third, when the sample was warmed to room temperature, it was found that the intensity of the high-velocity line had dropped nearly to zero, whereas there was still appreciable absorption for the low-velocity line. This behavior clearly implies two sites with different temperature dependences of the recoil-free fractions.

We can also rule out the possibility that Sn(SO$_3$CF$_3$)$_3$ is a stoichiometric mixture of Sn(SO$_3$CF$_3$)$_2$ and Sn(SO$_3$CF$_3$)$_4$, since in this case the spectrum would consist of three lines situated at ca. −0.2, +3.7, and +4.5 mm s$^{-1}$. The fact that no quadrupole splitting is observed for the Sn$^{IV}$ species is consistent with the formulation of the compound as Sn[Sn(SO$_3$CF$_3$)$_6$], since both K$_2$[Sn(SO$_3$F)$_6$][6] and Cs$_2$[Sn(NO$_3$)$_6$][25] also show unsplit resonances.

The isomer shift for the Sn$^{II}$ species in Sn(SO$_3$CF$_3$)$_3$ is of considerable interest, being the highest value yet reported and being significantly greater than that for Sn(SbF$_6$)$_2$. Several estimates for the isomer shift expected for a bare Sn$^{II}$ (5s$^2$) ion have appeared, ranging from 4.68[26] to 7.6 mm s$^{-1}$ [27] (relative to BaSnO$_3$). It is, of course, legitimate to question how closely the Sn$^{II}$ species in Sn(SO$_3$CF$_3$)$_3$ corresponds to a pure 5s$^2$ electronic configuration. For Sn(SO$_3$X)$_2$ (X = F, CF$_3$) the observed quadrupole splitting implies an imbalance of 5p-orbital charge densities at tin, and hence these compounds do not contain pure 5s$^2$ stannous ions. In Sn$^{II}$-[Sn$^{IV}$(SO$_3$CF$_3$)$_6$] on the other hand, δ for Sn$^{II}$ has increased by more than 0.5 mm s$^{-1}$ from its value in Sn(SO$_3$CF$_3$)$_2$, showing a very substantial increase in the s-electron density of the tin nucleus. Moreover, the absence of quadrupole splitting indicates either that there is essentially zero 5p-electron density on the tin ion or that any p-electron density which is present is equally distributed among the three p orbitals. For Sn(SbF$_6$)$_2$, which gave the highest $^{119}$Sn isomer shift previously recorded,[1] vibrational spectra indicate that the symmetry of the SbF$_6^{2-}$ ion is lower than octahedral, implying the presence of some cation–anion interaction, probably via fluorine bridging. However, the present infrared data suggest little if any cation–anion interaction in Sn[Sn(SO$_3$CF$_3$)$_6$].

Although these observations do not firmly establish the presence of a pure 5s$^2$ tin(II) ion, we feel that Sn$^{II}$[Sn$^{IV}$-(SO$_3$CF$_3$)$_6$] approximates fairly closely to this situation. We would therefore suggest that the estimate of 4.68 mm s$^{-1}$ for the isomer shift of an ideal 5s$^2$ Sn$^{II}$ ion obtained by Lees and Flinn,[26] although perhaps a bit low, is still probably more realistic than the much higher value (7.6 mm s$^{-1}$) derived by Donaldson and Senior.[27]

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# New Interpretation of Proton Magnetic Resonance Powder Spectra of the Sodium Silicates Na₂O·SiO₂·5H₂O and Na₂O·SiO₂·9H₂O

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Proton magnetic resonance powder spectra at 85 K of sodium silicates Na₂O·SiO₂·5H₂O and Na₂O·SiO₂·9H₂O have been reinterpreted using a model of three spin ¹/₂ nuclei located at the apexes of an isosceles triangle. The findings confirm that these solids are hydrogenomonosilicates with the formula Na₂(SiO₂(OH)₂)·(n − 1)H₂O (n = 5 and 9). However, the occurrence of distorted H₃O⁺ ions cannot be ruled out in the nonahydrate.

## Introduction

The dipolar interaction of nuclei with spin $^1/_2$ is the main effect observed from the magnetic resonance of these nuclei in solids. Interaction models must be used to interpret the experimental spectra with precision by calculating shape functions. The number of nuclei taken into account in these models and their relative geometric positions should represent, as closely as possible, the actual patterns formed by the resonating nuclei in the solids studied.

When studying monocrystals we noticed that these patterns have only a limited number of orientations in relation to the applied magnetic field. On the contrary, all orientations must be considered for powdered samples. Furthermore, to take into account interactions between patterns, a Gaussian broadening is superposed on the absorption of supposedly isolated patterns.

The proton magnetic resonance (¹H NMR) study of hydrates was initiated by Pake.[2] The two-spin model proposed by this author agrees with the fact that the distance $R$ between the two H atoms of a given water molecule is distinctly less than the shortest distances between two H atoms not belonging to the same water molecule (the effect observed is proportional to $\alpha = 3\mu/2R^3$, where $\mu$ is the proton magnetic moment).

Gutowsky et al.[3,4] have tried to interpret the ¹H NMR spectra of hydrated hydrogeno salts by taking the weighted sum of the contributions of two two-spin patterns; one pattern represents the H atoms of water molecules and the other pattern represents the "acidic" H atoms considered two by two (the values of $R$ in the two patterns are then very different). This method leads to good results if the two types of patterns are actually far enough from each other in the compounds being analyzed, but it cannot be generalized without caution. In practice, the interactions between H atoms belonging either to one or more water molecules of hydration or to one or more neighboring "acidic" H atoms are seldom weak enough to be neglected to the required level of approximation.

The model formed by three spin $^1/_2$ nuclei located at the apexes of an equilateral triangle has been proposed by Andrew and Bersohn[5] and reexamined by Richards and Smith.[6] This

**Table I.** Model Proposed to Interpret the ¹H NMR Spectra of Powder Solid Hydrates

| No. of H in pattern | Parameters involved | Ref |
|---|---|---|
| 2 | $\alpha = 3\mu/2R^3$; $R$ = HH distance in the pattern<br>$\beta = 3\mu/2X^3$; $X$ = lowest averaged distance between H of different patterns | 2 |
| 2 | Two distinct patterns: four parameters $\alpha_1$, $\alpha_2$, $\beta_1$, $\beta_2$; $+\omega$ weighting factor defining the proportion of H atoms in the two patterns | 3, 4 |
| 3 | Pattern: equilateral triangle $\alpha$, $\beta$ | 5, 6 |
| 3 | Isosceles triangle<br>$\alpha = 3\mu/2R_{23}^3$; $R_{23}$ = base of triangle<br>$\lambda = R_{12}/R_{23}$; $R_{12} = R_{13}$ = equal sides of triangle<br>$\beta$ | 9 |

model can be used, in particular, for the salts of the H₃O⁺ ion.[7,8] It can be applied to monocrystalline and powdered samples.

Andrew and Finch[9] have proposed a model with three spin $^1/_2$ nuclei located at the apexes of an isosceles triangle. This model has been used to interpret the ¹H NMR spectrum of H₂(AlP₃O₁₀)·2H₂O.[10] The two H atoms of a water molecule would define the base of the triangle, an "acidic" H atom being located at the opposite apex.

Pedersen and Håland[11] used a scalene triangle model to interpret the ¹H NMR spectra of monocrystalline dihydrated oxalic acid, but these authors did not generalize the use of their model to powder spectra.

The different models used and the parameters they involve are summarized in Table I.

## Purpose of the Study

In a preceding article,[12] we undertook the interpretation of the ¹H NMR spectra (at 85 K) of sodium silicates Na₂O·