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The ^{1}H NMR Spectra of [$(CH_3)_2SbCl_2$(oxine)] in Several Solvents

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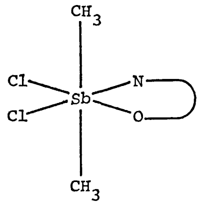
Synopsis. The ^{1}H NMR spectra of dichlorodimethyl(8-quinolinolato)antimony(V), [$(CH_3)_2SbCl_2$(oxine)], were measured in several solvents. Two methyl signals were observed in some aromatic and aliphatic solvents, although only one signal was detected in dichloromethane. The results were explained by the presence of two isomers in solution.

The structure of dichlorodimethyl(8-quinolinolato)antimony(V), [$(CH_3)_2SbCl_2$(oxine)], was studied by Meinema, Rivalora, and Noltes.[1)] They reported that the IR spectrum of this compound shows one Sb–C and two Sb–Cl stretching bands in the solid state, while the ^{1}H NMR spectra in chloroform-*d* and dichloromethane give only one methyl signal, and no broadening of this signal is observed even at −100 °C. From these facts and the UV spectral data, they concluded that the compound has a hexacoordinate structure with a distorted *trans*-dimethyl configuration(**1**).[1)]



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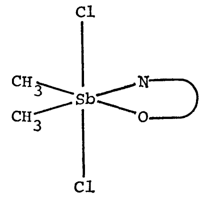

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As we have been interested in the solvent dependence of the ^{1}H NMR spectra of several organometallic compounds,[2,3)] we measured the ^{1}H NMR spectra of [$(CH_3)_2SbCl_2$(oxine)] in several solvents in order to elucidate the solute-solvent interaction and structure in solution.

The ^{1}H NMR data of the compound are shown in Table 1. The chemical shifts of the 2-, 3-, and 4-protons of the 8-quinolinolato ligand move to a higher field in benzene as compared with those in nonaromatic solvents. Especially, the upfield shift of the 2-proton in a benzene solution has been explained in terms of the coordination of the nitrogen atom of the 8-quinolinolato ligand to the antimony atom.[3)] This result is consistent with the UV spectral data of the compound.[1)]

One of the most remarkable results of the solvent dependence of the ^{1}H NMR spectra of the compound is that two methyl proton signals were observed in some solvents (see Table 1). These results are different from those obtained by Meinema *et al.* in chloroform-*d* and dichloromethane.[1)] The signal intensity at the higher field(I_h) is larger than that of the lower field(I_l) in nonpolar solvents. However, the opposite results were obtained in polar solvents. The signal contour and the intensity ratio(I_h/I_l) do not show any appreciable change upon a change in the temperature from the ambient temperature to −24 °C in carbon disulfide and to 58 °C in 1-chloronaphthalene. Figure 1 shows the methyl-proton chemical shifts and relative intensities of the higher-field methyl signal($I_h/(I_h+I_l)$) in mixed solvents of benzene and dichloromethane. The methyl-proton chemical sihfts move to a higher field as the relative volume of benzene ($V_b/(V_b+V_m)$) increases, but the intensity ratio is almost insensitive to the volume fraction of benzene in the 0.1—0.9 range. The relative intensity of the higher-field methyl signal, extrapolated to pure dichloro-

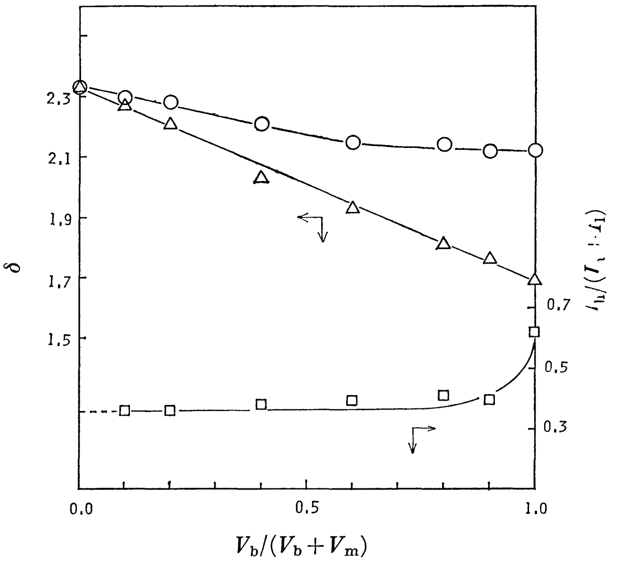

Fig. 1. Methyl proton chemical shifts and relative intensities of higher field methyl signal in mixed solvents of benzene and methylene chloride.

TABLE 1. ^{1}H NMR DATA OF [$(CH_3)_2SbCl_2$(oxine)] IN SEVERAL SOLVENTS

Solvent	$\delta(CH_3)_h$	$\delta(CH_3)_l$	I_h/I_l[a)]	δ(2-H)	δ(3-H)	δ(4-H)
CCl_4	2.23	2.29	0.55/0.45	9.28	7.59	8.47
CS_2	2.12	2.22	0.63/0.37	9.35	7.63	8.49
C_6D_6	1.70	2.11	0.62/0.38	8.82	6.31	7.32
$CDCl_3$[b)]	2.38			9.36		8.64
CH_2Cl_2	2.33		(0.35/0.65)[c)]	9.32	7.69	8.57
$C_{10}H_7Cl$(1-)	1.79	2.28	0.26/0.74			
CH_3NO_2	2.18	2.22	0.41/0.59			

a) Intensity ratio of high-field signal to low-field signal. b) Ref. 1. c) Extrapolated value.

methane, is found to be 0.35. This value is similar to that obtained in 1-chloronaphthalene. The observation of only one signal of the methyl protons of $[(CH_3)_2SbCl_2(\text{oxine})]$ in dichloromethane, therefore, may be an accidental coincidence of the two methyl-proton signals.

The observation of the two methyl signals in the ^{1}H NMR spectra with unequal signal intensities seems to suggest that the compound has two isometic structures, probably **1** and **2**, in solution. The presence of two isomers in solution has also been reported for some hexacoordinate (acethylacetonato)diaryldihaloantimony(V) compounds,$^{4,5)}$ although only one isomer with a *trans*-dimethyl configuration corresponding to **1** has been reported for (acetylacetonato)dihalodimethylantimony(V).$^{6,7)}$

Experimental

The compound, $[(CH_3)_2SbCl_2(\text{oxine})]$, was prepared and purified by the method reported in the litarature.$^{1)}$ The solvents used was purified by distillation. The ^{1}H NMR spectra were measured by using a JEOL JNM PS-100 spectrometer. The chemical shift was measured relative to the internal TMS.

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