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NMR STUDIES ON THE INTERACTIONS OF GLYMES WITH DIMETHYLTIN DICHLORIDE IN BENZENE

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The interactions between glymes (Gly) and dimethyltin dichloride (DMTC) have been studied by ^{1}H NMR spectroscopy. The coexistence of the 1:2 Gly/DMTC complexes with 1:1 complexes was found for the higher members of Gly. Benzene-induced shifts of proton signals of both DMTC and Gly suggest that the complexes possess the methyl groups attached to tin essentially in a trans arrangement.

With the rapid development of the crown ether chemistry, much attention has also been paid on the metal complexes of non-cyclic polyethers.$^{1)}$ However, it is rather limited to elucidate their behavior in solution because the metals employed in these studies are mostly inorganic alkali and alkaline earth metal ions. Dimethyltin dichloride (DMTC) is unique in having four substituents on the central metal and the interactions of polyethers with the organotin are expected to be sterically different from those with naked inorganic metal ions. The configuration of the complexes involving DMTC in solution has been extensively studied by ^{1}H NMR spectroscopy for a long time.$^{2)}$

As seen from Fig. 1,$^{3)}$ the value of δ_{CH_3-Sn} was changed markedly on adding DiG$^{4)}$ to the solution of DMTC in benzene, while little change was observed in dichloromethane. Apparently, the solvent effect caused by benzene disappeared upon coordination of DiG to tin. We have now investigated the interactions between Gly and DMTC in benzene by measuring the shifts of δ_{CH_3-Sn} values.

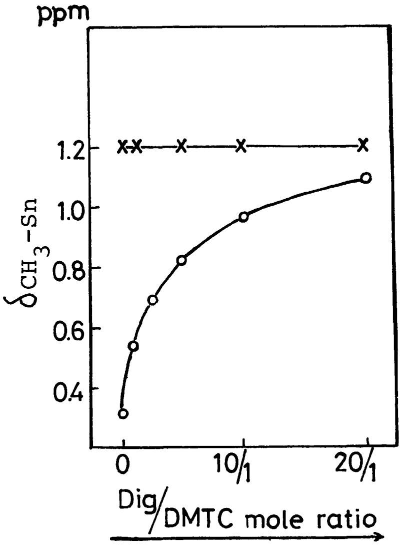


Fig. 1. δ_{CH_3-Sn} vs DiG/DMTC mole ratio at constant DMTC concentration (0.15 mol/L).

ο in benzene

× in dichloromethane

The stoichiometry of complexation was examined according to the Job's continuous variation method$^{5)}$ (Fig. 2). In the case of MoG, the interaction was so weak that no reliable curve could be drawn. On the other hand, DiG, TrG, and TetG were found to give the distinct 1:1 stoichiometry. The dependence of $\delta_{CH_3\text{-}Sn}$ and $J_{CH_3\text{-}^{119}Sn}$ on the added amount of these glymes is shown in Fig. 3. For equilibrium (1), stability constant, K, $\delta^{c}_{CH_3\text{-}Sn}$, and $J^{c}_{CH_3\text{-}^{119}Sn}$ were calculated by least square method using equations (2) and (3) and the results are given in Table 1. The values obtained for K reveal a large gap

$$(CH_3)_2SnCl_2 \quad + \quad Gly \quad \underset{}{\overset{K}{\rightleftharpoons}} \quad (CH_3)_2SnCl_2\cdot Gly \qquad (1)$$

$$\delta = \delta^{\circ} + \frac{\delta^{c} - \delta^{\circ}}{2}\left[(r + 1 + 1/A_0K) - \sqrt{(r + 1 + 1/A_0K)^2 - 4r}\right] \qquad (2)$$

$$J = J^{\circ} + \frac{J^{c} - J^{\circ}}{2}\left[(r + 1 + 1/A_0K) - \sqrt{(r + 1 + 1/A_0K)^2 - 4r}\right] \qquad (3)$$

δ, δ°, and δ^{c}; values of $\delta_{CH_3\text{-}Sn}$ for the observed, the uncomplexed, and the 1:1 complexed, respectively.

J, J°, and J^{c}; values of $J_{CH_3\text{-}^{119}Sn}$ for the observed, the uncomplexed, and the 1:1 complexed, respectively.

A_0; concentration of DMTC

r; Gly/DMTC mole ratio

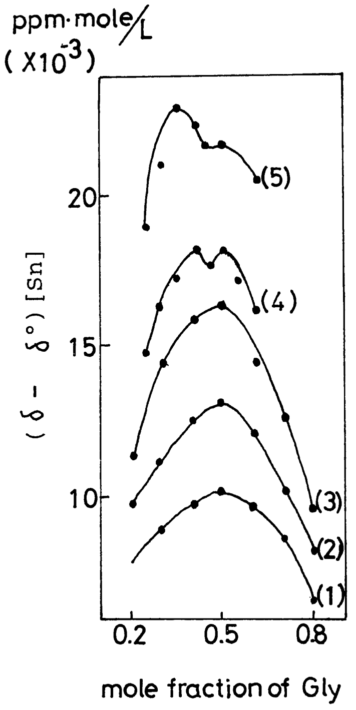


Fig. 2. Job's plot for Gly/DMTC in benzene at total concentration of 0.2 mol/L. (1) DiG (2) TrG (3) TetG (4) PeG (6) HexG

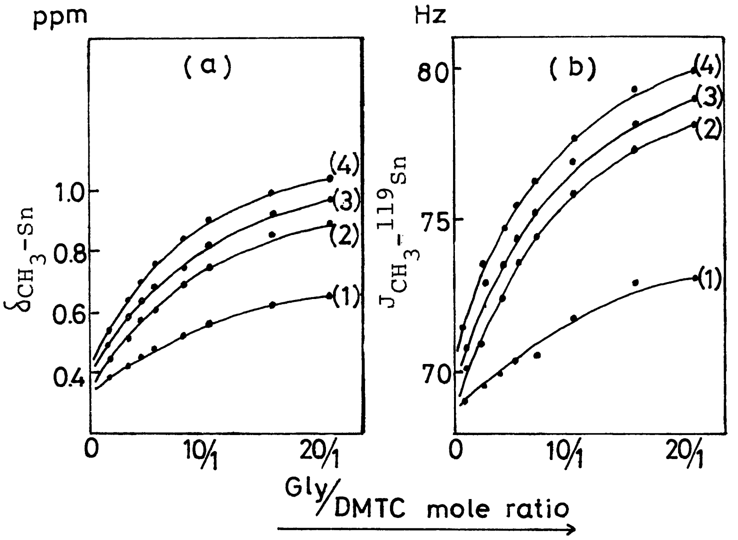


Fig. 3. $\delta_{CH_3\text{-}Sn}$ (a) and $J_{CH_3\text{-}^{119}Sn}$ (b) vs Gly/DMTC mole ratio in benzene at constant DMTC concentration of 0.05 mol/L.
(1) MoG (2) DiG (3) TrG (4) TetG

Table 1. Stability constant, K, $\delta^{c}_{CH_3-Sn}$ and $J^{c}_{CH_3-{}^{119}Sn}$ for Gly/DMTC in benzene at 35° C.

	K	$\delta^{c}_{CH_3-Sn}$	$J^{c}_{CH_3-{}^{119}Sn}$
MoG*	0.47	1.18 ppm	85.4 Hz
DiG	2.0	1.20	83.5
TrG	2.9	1.19	82.0
TetG	3.5	1.26	83.4

*MoG was assumed to give the 1:1 stoichiometry.

Table 2. Benzene-induced shifts for δ_{CH_3O} and δ_{CH_2} at 1/10 Gly/DMTC mole ratio.

	solvent	$\Delta\delta_{CH_3O}$* (ppm)	$\Delta\delta_{CH_2}$* (ppm)
DiG	CH_2Cl_2	+0.04	+0.04
	C_6H_6	-0.02	-0.10
TrG	C_6H_6	-0.06	-0.08, -0.11
TetG	C_6H_6	-0.01	-0.06, -0.06
PeG	C_6H_6	-0.03	-0.09, -0.07
HexG	C_6H_6	-0.05	-0.10, -0.08

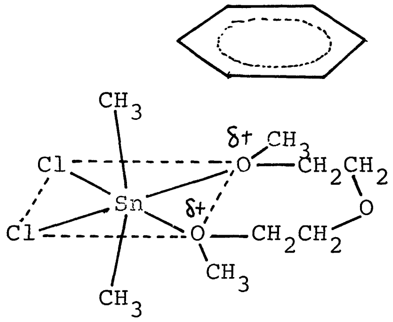
* $\Delta\delta$(ppm) = δ(with DMTC) - δ(without DMTC)

of the complexing ability between MoG and DiG. This trend is similar to the results described for some alkali metal salts in THF, in which the value for DiG is larger by 10^2 times than that for MoG.$^{7)}$ The values of $J^{c}_{CH_3-{}^{119}Sn}$ are comparable to those of trans octahedral dimethyltin derivatives with slightly bent C-Sn-C moieties such as dimethyltin diacetate$^{8)}$ and dikojate.$^{9)}$ Accordingly analogous configurations are suggested for the 1:1 complexes formed between Gly and DMTC.$^{10)}$ For the complexes of PeG and HexG, unexpected Job's plots were encountered. The appearance of two peaks demonstrates the formation of 1:2 and 1:1 complexes in equilibrium (4). Obviously

$$2(CH_3)_2SnCl_2 \underset{}{\overset{Gly}{\rightleftharpoons}} [(CH_3)_2SnCl_2]_2\cdot Gly \underset{}{\overset{Gly}{\rightleftharpoons}} 2(CH_3)_2SnCl_2\cdot Gly \qquad (4)$$

an intramolecular chelation of Gly leading to a six-coordinate configuration becomes sterically unfavored on increasing the chain length of Gly. To our knowledge, the 1:2 complex which presumably involves an intermoleculaly bridging glyme molecule has not yet been reported for inorganic metals, although MoG/$(CH_3)_3SnCl$ in dichloromethane has been speculated to have the 1:2 stoichiometry.$^{11)}$

Another notable feature of the present system consists in the chemical shift behavior of methyl and methylene protons of Gly (δ_{CH_3O} and δ_{CH_2}). Table 2 gives these values for the systems containing Gly and DMTC in a 1:10 mole ratio, in which more than 90 % of Gly are complexed. In dichloromethane the values of δ_{CH_3O} and δ_{CH_2} were shifted to lower fields upon coordination; this fact is quite normal and can be explained by a decrease in electron densities on the respective protons in the complexes. On the other hand, these values showed considerable high field shifts in benzene. This phenomenon may be due to a shielding effect of the benzene ring which interacts with the coordinating Gly of increased polarity[11] as depicted below. The analogous



benzene-induced shift has been proposed for dimethyltin N,N'-dimethyldithiocarbamate.[12] The mechanism of the low field shift of δ_{CH_3-Sn} upon coordination can be accounted for from these configurations in which the methyl protons attached to tin experience decreased shielding by the benzene ring.

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References and Notes

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3) The ^{1}H NMR spectra were obtained with a Hitachi R-24B spectrometer operating at 60 MHz at 35° C. The chemical shifts, δ(ppm), were measured relative to TMS as an internal standard and are accurate to ± 0.01 ppm.
4) Abbreviation for $CH_3O(CH_2CH_2O)_nCH_3$: MoG, DiG, TrG, TetG, PeG, and HexG for n = 1, 2, 3, 4, 5, and 6, respectively.
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