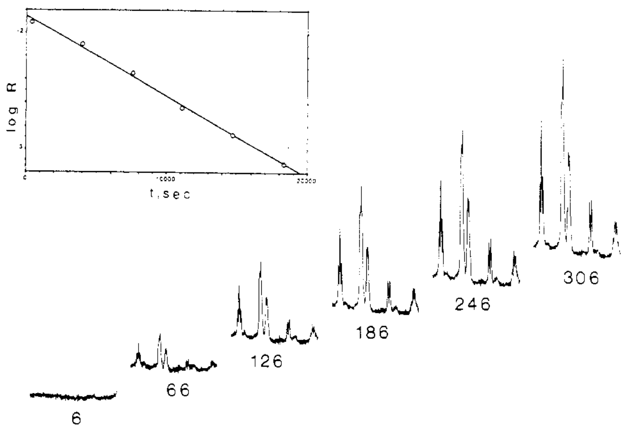

Figure 2. Time-dependent ^{1}H NMR spectra showing the appearance of the trans-I isomer of Ni(cyclam)$^{2+}$ at pD 7.81. The figure below each spectrum indicates the time (in minutes) after dissolution. The inset shows the first-order behavior of the rate of equilibration.

approximately 1.9 Å for low-spin Ni(II) and 2.1 Å for high-spin Ni(II).[21]

The smaller cavity size of the trans-I ligand may well be the reason that the trans-I complex, unlike the trans-III complex, is not in fast planar-octahedral exchange on the NMR time scale. The equilibrium constant for eq 5 must be small enough that

$$\text{trans-I (octahedral)} \rightleftharpoons \text{trans-I (planar)} + 2H_2O \qquad (5)$$

exchange, although rapid, is not sufficiently extensive to broaden the resonances into the characteristic pattern of a paramagnetic nickel(II) species.

The strain energies of the octahedral and planar trans-I isomers are essentially identical, yet no significant amount of octahedral complex is present in solution. It has been shown that, for saturated tetraaza macrocycles, the planar complex is favored by a large entropic contribution ($\sim$20 cal K^{-1} mol^{-1} for trans octahedral to planar[22]). Thus, for example although the octahedral trans-III complex is significantly less strained than the planar complex, the entropic contribution results in a preponderance of the low-spin species at room temperature (71% low spin, 29% high spin). The near-equality of strain energies of planar and octahedral trans-I isomers, coupled with the same entropic contribution, is consistent with the observation that the trans-I isomer must be nearly 100% planar at room temperature.

Kinetics of Trans-III to Trans-I Isomerization

It was observed that NMR spectra recorded immediately after sample dissolution did not contain significant amounts of the diamagnetic species but that these peaks appeared over a period of 1-2 h. Figure 2 illustrates the slow appearance of the diamagnetic isomer. We expected crystalline samples of the complex to be isomerically pure trans-III; consequently, it was not surprising to observe the growth of the trans-I peaks. The rate of approach to equilibrium is first order. Rate constants were determined at 18 °C over the pD range 7.6-9.1; in most experiments, no buffers were used in order to eliminate the possibility of catalytic effects but a few rates measured with phosphate buffer showed no significant differences. The reaction is base-catalyzed, with a second-order rate constant of 121 ± 21 M^{-1} s^{-1}. It has been pointed out by both Hay[23] and ourselves[24] that the rate constants for base catalysis of conformer interconversion of several nickel(II) complexes with linear or macrocyclic tetraaza ligands lie within a narrow range of values, from ca. 4.5 × 10^2 to 2.4 × 10^3 M^{-1} s^{-1}. The rate constant found in the present work is similar.

Summary

Spectroscopic evidence has been provided for the presence, in equilibrated aqueous solutions of Ni^{II}cyclam, of significant amounts of the trans-I conformer. The results and conclusions of previous solution studies of Ni^{II}cyclam, which assumed implicitly the presence of only a single isomer, must therefore be reexamined.

Registry No. Ni(cyclam)(ClO$_4$)$_2$, 41296-56-4.

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Intermolecular Association of Diorganotin Dihalides in the Solid State. Comparison of Solid-State and Solution NMR Structures of Me$_2$SnCl$_2$

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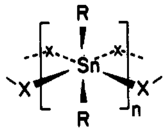
The X-ray structural investigation of diorganotin dihalides, R$_2$SnX$_2$ (where X = Cl, Br, I), has brought into focus the general question of what constitutes a real, or significant, bonding interaction. These molecules adopt highly distorted tetrahedral structures (range of angles: C-Sn-C = 123.5-135.9°; X-Sn-X = 93.0-104.0°) and are oriented in a planar array in the crystal lattice in a way suggestive of halogen bridging between adjacent tin atoms.[1-5] The overall stereochemistry at tin resembles that known for a number of distorted octahedral Me$_2$Sn(chelate)$_2$ complexes,[6] and most of the diorganotin dihalides have been assigned 6-coordinated configurations.



A weakness of this analysis is the relatively large intermolecular distances D(Sn-X) (e.g., D(Sn-Cl) = 3.44-3.78 Å for R = Me, Et, ClCH$_2$, cyclohexyl, and phenyl), which approach the sum of the van der Waals radii (3.85 Å for Sn and Cl[7]).

Recently, Zuckerman and co-workers[4] reported results for bis(biphenylyl-2)$_2$SnCl$_2$ that throw into doubt the assignment of higher coordination numbers to tin in diorganotin dihalides. This compound adopts the usual diorganotin dihalide crystal and molecular structure (Me-Sn-Me angle = 130.8 (3)°, Cl-Sn-Cl angle = 99.71 (9)°) yet has an intermolecular Sn-Cl distance of 6.189 (3) Å, which excludes the possibility of bonding. Tagliavini and his co-workers[5] also have recently presented arguments against 5-coordination of tin for the Cl and Br derivatives of (cyclohexyl)$_2$SnX$_2$.

We report here the results of a solid-state ^{13}C NMR study of the parent diorganotin dihalide Me$_2$SnCl$_2$. The results are used to compare the solution and solid-state structures of Me$_2$SnCl$_2$, and provide new insight into structural changes that occur in the crystal lattice. Additionally, a striking field strength dependence of the solid-state ^{13}C NMR line width is found for this compound.

Results and Discussion

Solid-state ^{13}C-NMR studies of a variety of X-ray-characterized 4-, 5-, and 6-coordinated di- and trimethyltin(IV) compounds have revealed a correlation of the magnitude of tin-carbon J coupling, $|^1J(^{119}\text{Sn}, ^{13}\text{C})|$, with the Me-Sn-Me angle.[8] A previous attempt[8b] to determine $|^1J(^{119}\text{Sn}, ^{13}\text{C})|$ for solid Me$_2$SnCl$_2$ failed because

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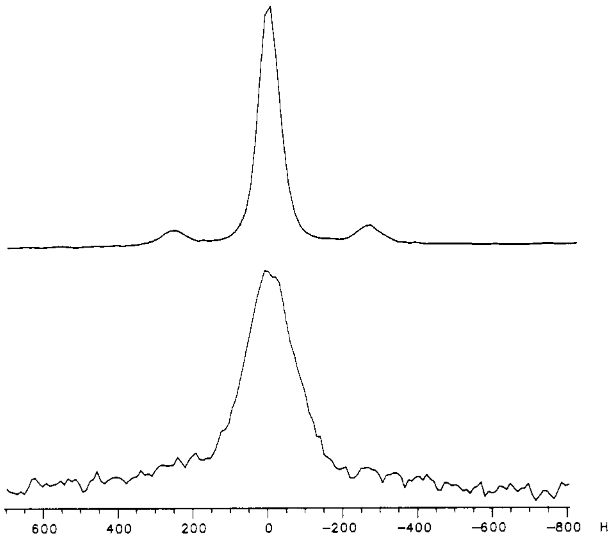

Figure 1. High-resolution solid-state ^{13}C NMR spectra of Me_2SnCl_2. At 7.0 T (top spectrum, 1964 scans) full width at half-height = 67 Hz; at 2.3 T (bottom spectrum, 16000 scans) full width at half-height = 139 Hz. Fused $^{119,117}Sn$ satellites (natural abundance = 8.6 and 7.6%, respectively) are visible at 7.0 T; $|^1J(^{119}Sn,^{13}C)|$ = 530 ± 20 Hz.

the presence of halogen atoms in the crystal lattice gives rise to strong dipolar broadening. The results of ^{13}C NMR analyses of solid Me_2SnCl_2 at field strengths of 2.3 and 7.0 T are shown in Figure 1. The full width at half-height of the central resonance decreases from about 210 Hz at 1.4 T[8b] to 139 Hz at 2.3 T and 67 Hz at 7.0 T. At the highest field strength, the fused $^{117,119}Sn$ satellites are well resolved from the central resonance and $|^1J(^{119}Sn,^{13}C)|$ is determined to be 530 ± 20 Hz (derived from the separation of the fused satellites × 1.023). These results provide a striking example of the field dependence of $^{35,37}Cl-^{13}C$ line broadening, an effect that has been demonstrated experimentally only recently.[9]

The observed linewidths may be described as a sum of two contributions, one inversely proportional and one proportional to the applied field

$$W(\text{Hz}) = (302\ \text{Hz}{\cdot}\text{T})/H_0 + (3.4\ \text{Hz}{\cdot}\text{T}^{-1})H_0$$

where W is the observed full width at half-height (Hz), and H_0 is the applied field (T). By its inverse field dependence, the first term must be due to unresolved dipolar broadening from $^{35,37}Cl$. The second term, 0.32 ppm, may arise from either an isotropic chemical shift dispersion or magnetic susceptibility anisotropy. Magic-angle spinning cannot remove any of these sources of broadening. The values above predict line widths of 221 (1.4 T), 139 (2.3 T), and 67 Hz (7.0 T). The large magnitude of the dipolar coupling to halogen indicates that high field may be expected to be generally advantageous in obtaining chemical shift MAS spectra of halide complexes of many spin-$^1/_2$ metal nuclei.

From the solid-state $|^1J(^{119}Sn,^{13}C)|$ value of 530 ± 20 Hz a Me–Sn–Me angle of 122° is calculated,[8a] in excellent agreement with the X-ray value (123.5 ± 4.5°). The agreement of these values builds confidence in the accuracy of the Me–Sn–Me angle estimated for Me_2SnCl_2 in solution in noncoordinating solvents (116.5° from $|^1J(^{119}Sn,^{13}C)|$ = 468.4 Hz in CCl_4, 469.4 Hz in benzene[10]) and makes possible the first comparison of solid-state and solution structures of a diorganotin dihalide. The difference between the solid-state and solution $|^1J(^{119}Sn,^{13}C)|$ values is well outside of experimental uncertainty and indicates a true, but small, change in the Me_2SnCl_2 molecular structure arising from solid-state effects. The solution NMR structure is substantially different from that derived from gas-phase electron diffraction data, which indicate an essentially undistorted tetrahedral geometry for Me_2SnCl_2.[11] Solvation effects are a plausible source for the striking difference between the gas-phase electron diffraction and solution NMR structures.

Comparison of the gas-phase and solid-state structures had suggested a large change in structure upon crystallization,[4] consistent with a profound change in coordination number at tin. While the small difference between the solid-state and solution structures of Me_2SnCl_2 (Me–Sn–Me angle change about 6°) could arise from a small, additional bonding interaction in the solid state, there is ample evidence that nonbonding crystal lattice effects also can give rise to Me–Sn–Me angle changes of comparable magnitude. For example, dimethyltin bis(*N*,*N*-diethyldithiocarbamate), $Me_2Sn(S_2CNEt_2)_2$, which consists of noninteracting monomeric units in the solid state, forms at least three distinct crystalline modifications with Me–Sn–Me angles varying between 135.6 (2) and 142.8 (3)°.[12] Further the difference in the gas-phase and solution structures of Me_2SnCl_2 mentioned above strongly emphasizes the low energy required to induce substantial bond angle changes in this compound.

The influence of steric factors on the conformation of diorganotin dihalides has been considered by Tagliavini and Zuckerman and their co-workers,[4,5] but these arguments are least secure when simple di-*n*-alkyltin dihalides are discussed. Perhaps the strongest previous argument[5] against bridging halogen interactions for solid di-*n*-alkyltin dihalides is that the Mössbauer quadrupole splitting value, which is sensitive to the coordination number of tin, is nearly the same for Me_2SnCl_2 (3.55 mm s^{-1})[1] as that for sterically encumbered $(cyclohexyl)_2SnCl_2$ (3.47 mm s^{-1}),[5] even though the latter can be no more than pentacoordinate at tin. The strongest evidence of polymeric association of diorganotin dihalides has always been the suggestive tin conformation and the packing of the molecules in the crystal lattice. In our opinion, however, the magnitude of the change in structure of Me_2SnCl_2 on crystallization is small enough to be accounted for without invoking a significant bridging halide interaction.

Experimental Section

Solid-state NMR analyses were performed on a sample of crystalline Me_2SnCl_2 obtained commercially. The solid-state ^{13}C NMR spectra were obtained on both a General Electric S-100 spectrometer (25.2 MHz) and a Bruker CXP-300 spectrometer (75.5 MHz). Dry nitrogen gas was used to drive MAS at rates of 2.5 (S-100) and 4.5 kHz (CXP-300). The Hartmann–Hahn matching condition for cross-polarization (CP) was calibrated by using adamantane, and both CP (5 ms) and decoupling (40 ms) were performed at the same proton-decoupling amplitude (50 kHz, S-100; 71 kHz, CXP-300). A 4-s recycle delay was used. Me_2SnCl_2 had a ^{13}C chemical shift of 17.1 ± 0.3 ppm relative to Me_4Si (using an external sample of adamantane as secondary reference).

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Registry No. Me_2SnCl_2, 753-73-1.

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