resonance frequencies of the two nuclei are approximately equal.[14]

The line widths of the ^{31}P NMR peaks of $[Co(i\text{-}PrOPOCH_2CH_2O)_6]^{3+}$, $[Co(dl\text{-}n\text{-}PrOPOCHCH_3CHCH_3O)_6]^{3+}$, and $[Co\{(n\text{-}PrO)_{ax}POCH(CH_3)_{eq}CH_2CH_2O\}_6]^{3+}$ are narrow compared to those of complexes with less sterically demanding exocylic alkoxy groups of the ligand (see Table II and Figure 3). The narrower line widths in complexes with sterically demanding exocyclic groups are consistent with reduced ^{59}Co–^{31}P spin–spin coupling constants. Evidence for this are the similar ^{59}Co T_1 values for the four cobalt(III) complexes of the five-membered ring monocyclic phosphites (see Table I and eq 3). Recently we obtained UV and ^{59}Co NMR evidence for significant ligand–ligand repulsion in $[Co(i\text{-}PrOPOCH_2CH_2O)_6]^{3+}$, $[Co(dl\text{-}n\text{-}PrOPOCHCH_3CHCH_3O)_6]^{3+}$, and $[Co\{(n\text{-}PrO)_{ax}POCH(CH_3)_{eq}CH_2CH_2O\}_6]^{3+}$.[5] The ligand–ligand repulsions in these complexes may be sufficiently strong to lengthen the cobalt–phosphorus bonds and thereby reduce the ^{59}Co–^{31}P spin–spin coupling constants. The relatively small $^1J(^{59}Co–^{31}P)$ of $[Co\{P(OMe)_3\}_6]^{3+}$ (414 Hz)[28] compared with that of $[Co(PF_3)_4]^-$ (1225 Hz)[29] has been attributed to bond weakening arising from ligand repulsive interactions in addition to the smaller s character of the bonding electrons in the six-coordinate complex.[28,30] It is interesting in this respect to note that ^{195}Pt–^{31}P spin–spin coupling constants decrease substantially with increasing platinum–phosphorus distance in Pt(II) complexes of phosphorus ligands.[31]

In comparison to the broad signals observed in the ^{31}P NMR spectra of the $[CoL_6]^{3+}$ complexes studied here, the line widths of $[CoL_5]^+$ signals are relatively narrow as illustrated in Figure 2. The low-temperature line widths of the latter complexes are, in fact, comparable to ^{31}P NMR resonances where phosphorus is not coupled to a quadrupolar nucleus.[32] These narrower lines in the ^{31}P NMR spectra of the cobalt(I) complexes probably stem from the much faster relaxation times of ^{59}Co expected for the trigonal-bipyramidal symmetry of these complexes. The ^{59}Co in these five-coordinate complexes can be thought of as being "self-decoupled" from ^{31}P.[33]

Acknowledgment. The authors thank Dr. Dee Huang and Dr. Dave Scott for assistance in obtaining the T_1 measurements, Mark Mason for experimental assistance, and Dr. B. C. Gerstein for helpful discussions. J. G. V. thanks the National Science Foundation for support of this research through a grant.

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(28) Yamasaki, A.; Aoyama, T.; Fujiwara, S.; Nakamura, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 643.
(29) Lucken, E. A. C.; Noack, K.; Williams, D. F. *J. Chem. Soc. A* **1967**, 148.
(30) The larger coupling constant in the PF_3 complex is probably also due, in part, to the higher electronegativity of the substitutents on phosphorus: Socol, S. M.; Verkade J. G. *Inorg. Chem.* **1984**, *23*, 88.
(31) Mather, G. G.; Pidcock, A.; Rapsey, G. J. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2095.
(32) (a) Jesson, J. P.; Meakin, P. *J. Am. Chem. Soc.* **1974**, *96*, 5760. (b) Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 5751.
(33) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, 1983; p 138.

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^{1}H NMR Evidence for the *R,S,R,S* Isomer of the (1,4,8,11-Tetraazacyclotetradecane)nickel(II) Ion

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The *R,R,S,S* or trans-III[1,2] isomer and the *R,S,R,S* or trans-I isomer of nickel(II) tetramethylcyclam (tetramethylcyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) were prepared by Barefield and co-workers[3] some years ago. Recently Lincoln[4] reported the observation of the *R,S,R,R* or trans-II isomer by NMR in nitromethane.

For a labile metal ion such as Ni(II), N-substitution of methyl groups on the cyclam macrocycle appears to make isomerization reactions more sluggish and aids in the isolation of less stable isomers such as the trans-I. For Ni(II) complexes of the unsubstituted macrocycle, only the trans-III isomer has been observed in aqueous solution although very recently we reported the isolation of the kinetically unstable trans-V isomer, which can be prepared via the "folded" cis-V isomer, *cis*-$[Ni(cyclam)(H_2O)_2]^{2+}$.[5,6]

We now report the observation, by proton NMR spectroscopy, of a further conformational isomer of $Ni(cyclam)^{2+}$, to which we assign the trans-I geometry. In aqueous solution this isomer is in equilibrium with the trans-III isomer and constitutes approximately 15% of the total complex at 25 °C.

Experimental Section

Synthesis. $Ni(cyclam)(ClO_4)_2$ and cyclam were prepared according to Barefield et al.[7] The chloro complex was prepared by mixing ethanol solutions of $NiCl_2·6H_2O$ and ligand. Both the perchlorate and chloro complexes were recrystallized from aqueous solution.

NMR Measurements. Proton NMR spectra were recorded on a Varian XL300 spectrometer using a 5 mm broad-band probe. A typical sample consisted of 15–20 mg of the complex dissolved in 0.5 mL of D_2O (Aldrich). The pD was adjusted with DCl or NaOD. When pD values between 7 and 8 were desired, the complex was dissolved in 3 mM phosphate buffer solution. In general, 64 transients were accumulated for each spectrum, with a total acquisition time of approximately 1 min. The final pD was measured with a glass electrode by using the relationship pD = pH + 0.4.[8]

Kinetic measurements were made by acquiring successive spectra over a period of hours. The chloro complex was used for these studies because of its ease of dissolution. The perchlorate complex gave identical results. Data were acquired at the ambient spectrometer temperature (18 ± 1 °C). The spectra were integrated by computer and R, the ratio of the diamagnetic integral to total complex integral, was plotted vs. time. In nearly all cases, the isomerization was sufficiently rapid to permit determination of the final R value; R was independent of pD over the range 7.4–9.0 (nine measurements). Plots of ln $(R_\infty - R_t)$ vs. t were linear, and the first-order rate constant was obtained by linear regression.

Temperature dependence of the equilibrium was investigated for a sample of approximately 20 mg of the perchlorate complex in 0.5 mL of D_2O adjusted to pH 9.0. The NMR temperature probe was calibrated by using standard techniques.[9] The temperature of the sample was varied; after an equilibration period of $^1/_2$ h a spectrum was recorded. R', the ratio of diamagnetic integral to paramagnetic integral, was determined. Plots of ln R' vs. $1/T$ were linear, and $\Delta H°$ and $\Delta S°$ were determined by linear regression.

Molecular mechanics calculations were performed by using a locally modified version of MODEL, a program utilizing Allinger's MM2 force field.[10] The parameters for Ni–N bonding, C–N–Ni and H–N–Ni bending were taken from the literature.[11] No attempt was made to account for charge–dipole or solvent interactions.

For the trans-octahedral complexes, dummy atoms were added to the axial coordination sites.[12] It was found that minimization with and without the dummy atoms gave essentially identical results and the

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(1) Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102.
(2) The five possible planar conformers of complexes of cyclam are trans-I (++++), trans-II (+−++), trans-III (+−−+), trans-IV (++−−), and trans-V (+−+−), where + indicates that the hydrogen of the NH group is above the plane of the macrocycle and − indicates that it is below.
(3) (a) Wagner, F.; Mocella, M. T.; D'Aniello, M. J.; Wang, A. H. J.; Barefield, E. K. *J. Am. Chem. Soc.* **1974**, *96*, 2625. (b) Barefield, E. K.; Wagner, F. *Inorg. Chem.* **1973**, *12*, 2435.
(4) Lincoln, S. F.; Pisaniello, D. L.; Coates, J. H.; Hadi, D. A. *Inorg. Chim. Acta* **1984**, *81*, 9.
(5) Billo, E. J. *Inorg. Chem.* **1981**, *20*, 4019.
(6) Barefield, E. K.; Bianchi, A.; Billo, E. J.; Connolly, P. J.; Paoletti, P.; Summers, J. S.; Van Derveer, D. G. *Inorg. Chem.* **1986**, *25*, 4197.
(7) Barefield, E. K.; Wagner, F.; Herlinger, A. W.; Dahl, A. R. *Inorg. Synth.* **1976**, *16*, 220.
(8) Glasoe, P. K.; Long, F. A. *J. Phys. Chem.* **1960**, *64*, 188.
(9) VanGeet, A. L. *Anal. Chem.* **1970**, *42*, 679.
(10) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.
(11) McDougall, G. J.; Hancock, R. D.; Boeyens, J. C. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1438.
(12) Hambley, T. W. *J. Chem. Soc., Chem. Commun.* **1984**, 1228.

0020-1669/87/1326-3224$01.50/0 © 1987 American Chemical Society

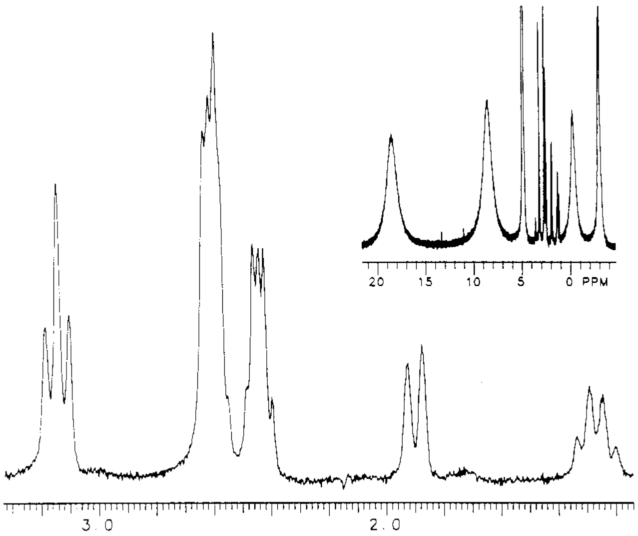

Figure 1. 300-MHz ^1H NMR spectrum of Ni^{II}cyclam in the 1–3 ppm range. The inset shows the complete paramagnetic spectrum; the peak at 5 ppm is due to HDO.

calculations were subsequently carried out without the dummy atoms.

Results and Discussion

The proton NMR spectrum of $Ni(cyclam)^{2+}$ in D_2O reveals four broad resonances at 19, 8.8, −0.5, and −3.2 ppm, characteristic of a paramagnetic species. This spectrum is consistent with rapid equilibrium between the paramagnetic diaqua species and the diamagnetic square-planar species; the high spin–low spin interconversion has been examined by Hunt and co-workers[13] using temperature-jump relaxation studies and shown to be fast. The range of chemical shifts in D_2O is smaller than that seen in DMSO[14] or that for the fully paramagnetic species in chloroform[15] (from −6.2 to +170 ppm in the former; from −14.2 to +319.8 ppm in the latter), which is also consistent with a rapidly equilibrating mixture of low- and high-spin species. The high spin–low spin equilibrium in aqueous solutions of $Ni(cyclam)^{2+}$ was first pointed out by Fabbrizzi,[16] who estimated from spectrophotometric measurements that at 25 °C and 0.1 M $NaClO_4$, the complex exists as 29% high-spin *trans*-diaqua complex and 71% diamagnetic planar complex.

We observe that, in addition to the paramagnetic absorptions, the region between 1 and 3 ppm contains some weak but well-defined resonances, suggesting a fully diamagnetic species not in rapid equilibrium with the diaqua species. In order to ensure that these resonances were not due to an impurity, samples of both the perchlorate and chloro complexes were recrystallized from aqueous solution. After repeated recrystallization both samples still showed the diamagnetic peaks. The peaks were not due to free cyclam.

In order to minimize dynamic range problems arising from the strong HDO peak at 4.75 ppm, the perchlorate complex was recrystallized several times from D_2O and the NMR spectrum obtained by using 99.96 atom % D_2O. After the sample was allowed to equilibrate for several hours, a spectrum was recorded (Figure 1). Integration measurements indicated that the magnetic species was approximately 15% of the total complex present. The lines are somewhate broadened, probably because of spin–lattice relaxation caused by the paramagnetic species, and as a result much of the detailed coupling information is lost.

Table I. Relative Strain Energies for Planar and Octahedral Conformers of Ni^{II}cyclam Complexes[a]

	planar	octahedral		planar	octahedral
trans-I	0.32	2.35	trans-IV	7.74	8.21
trans-II	1.30	2.91	trans-V	2.36	4.20
trans-III	0.00	0.00			

[a] Energies in kcal mol^{-1}.

The resonances in Figure 1 comprise a ten-proton spectrum, and thus require a conformational isomer with 2-fold symmetry; decoupling and 2-D experiments showed that the complex has six nonequivalent protons. The protons at 1.3 and 1.93 ppm have chemical shifts similar to those we have previously observed and assigned[17] to β protons of six-membered rings in the chair conformation of saturated polyaza ligands.

Of the five possible planar conformational isomers of $Ni(cyclam)^{2+}$, there are three isomers which have the correct symmetry to give rise to six nonequivalent protons: trans-I, trans-III, and trans-IV. The trans-III isomer has been shown to be in rapid diamagnetic–paramagnetic equilibrium by ^{17}O NMR studies, and this rapid exchange produces the broad paramagnetic spectrum that is observed for the 70% planar–30% octahedral equilibrium mixture. In contrast, the species we observe comprises 15% of the total complex and is not in rapid exchange. The trans-IV isomer has both six-membered rings in the boat form and both five-membered rings in the eclipsed form and, therefore, is expected to be highly strained and should not be present in detectable concentration. As well, it must be eliminated since we have identified the six-membered rings as being in the chair form. This leads us to the conclusion that the observed isomer is the trans-I isomer, where both six-membered rings are in the chair form and both five-membered rings in the eclipsed form.

The temperature dependence of the paramagnetic–diamagnetic equilibrium yielded $\Delta H°$ and $\Delta S°$ values for eq 1, and by using

$$\text{trans-III (octahedral + planar)} \rightleftharpoons \text{trans-I (planar)} \quad (1)$$

the known values[16] $\Delta H° = 5.4$ kcal mol^{-1} and $\Delta S° = 20$ cal K^{-1} mol^{-1} for eq 2, it was possible to obtain the resolved thermodynamic quantities shown in (3) and (4).

$$\text{trans-Ni(cyclam)(H}_2\text{O)}_2^{2+} \rightleftharpoons \text{Ni(cyclam)}^{2+} + 2\text{H}_2\text{O} \quad (2)$$

$$\text{trans-III (octahedral)} \rightleftharpoons \text{trans-III (planar)} + 2\text{H}_2\text{O} \quad (3)$$

$$\Delta H° = 5.2 \text{ kcal mol}^{-1},\ \Delta S° = 18.8 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$\text{trans-III (planar)} \rightleftharpoons \text{trans-I (planar)} \quad (4)$$

$$\Delta H° = 1.2 \pm 0.3 \text{ kcal mol}^{-1},\ \Delta S° = 1.0 \pm 0.3 \text{ cal K}^{-1} \text{ mol}^{-1}$$

Recognition of the presence of the trans-I species in equilibrated solutions of the trans-III species results in a decrease of about 5% in the thermodynamic quantities for the trans-III species.

Molecular Mechanics Calculations

The final minimized strain energies of the square-planar and trans-octahedral species of the Ni^{II}cyclam conformers are shown in Table I. The calculated strain energy of the octahedral trans-III species is 2.35 kcal mol^{-1} less than that of the octahedral trans-I, a smaller energy difference than previously estimated.[18] In contrast, the planar trans-I and trans-III species have comparable strain energies. Examination of the contributions to the total strain energies indicates that although the ligand is more strained in the trans-I conformer than in the trans-III conformer, it is also more flexible. This allows the trans-I isomer to adopt the shorter Ni–N bond length of the low-spin species with little change in total strain energy. In contrast, the trans-III isomer shows a significant increase in Ni–N bond strain energy in going from high spin to low spin. In agreement with the calculations of Hancock and co-workers,[19] we find a best-fit metal–nitrogen bond distance of 2.01 Å for the trans-I isomer. This may be contrasted with a metal–nitrogen distance of 2.07 Å for the trans-III geometry.[20] Ideal metal–nitrogen bond distances are

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(13) Coates, J. H.; Hadi, D. A.; Lincoln, S. F.; Dodgen, H. W.; Hunt, J. P. *Inorg. Chem.* **1981**, *20*, 707.

(14) This laboratory.

(15) Dei, A. *Inorg. Chem.* **1979**, *18*, 891.

(16) Anichini, A.; Fabbrizzi, L.; Paoletti, P.; Clay, R. M. *Inorg. Chim. Acta* **1977**, *24*, 21.

(17) Billo, E. J.; Connolly, P. J.; Sardella, D. J., submitted for publication.

(18) Whimp, P. O.; Bailey, M. F.; Curtis, N. F. *J. Chem. Soc. A* **1970**, 1956.

(19) Thom, V. J.; Fox, C. C.; Boeyens, J. C. A.; Hancock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 5947.

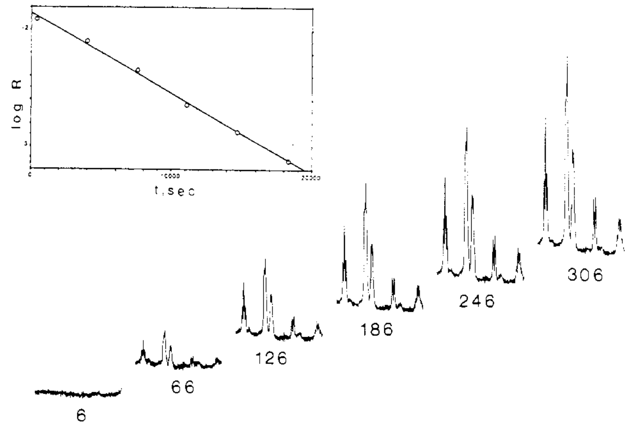

Figure 2. Time-dependent ^{1}H NMR spectra showing the appearance of the trans-I isomer of Ni(cyclam)$^{2+}$ at pD 7.81. The figure below each spectrum indicates the time (in minutes) after dissolution. The inset shows the first-order behavior of the rate of equilibration.

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 (~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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[20] Martin, L. Y.; DeHayes, L. J.; Zompa, L. J.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 4047.

[21] Fabbrizzi, L. *J. Chem. Soc., Dalton Trans.* **1979**, 1857.

[22] Sabatini, L.; Fabbrizzi, L. *Inorg. Chem.* **1979**, *18*, 438. Hinz, F. P; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2941. Vitiello, J. D.; Billo, E. J. *Inorg. Chem.* **1980**, *19*, 3477.

[23] Hay, R. W.; Akbar Ali, M. *Inorg. Chim. Acta* **1985**, *103*, 23.

[24] Martin, A. M.; Grant, K. J.; Billo, E. J. *Inorg. Chem.* **1986**, *25*, 4904.

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Intermolecular Association of Diorganotin Dihalides in the Solid State. Comparison of Solid-State and Solution NMR Structures of Me_2SnCl_2

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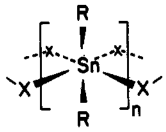
The X-ray structural investigation of diorganotin dihalides, R_2SnX_2 (where X = Cl, Br, I), has brought into focus the general question of what constitutes a real, or significant, bonding interaction. These molecules adopt highly distorted tetrahedral structures (range of angles: C–Sn–C = 123.5–135.9°; 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 $Me_2Sn(chelate)_2$ 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_2SnCl_2. The results are used to compare the solution and solid-state structures of Me_2SnCl_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, $|^{1}J(^{119}Sn, ^{13}C)|$, with the Me–Sn–Me angle.[8] A previous attempt[8b] to determine $|^{1}J(^{119}Sn, ^{13}C)|$ for solid Me_2SnCl_2 failed because

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