2590 © 1985 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, *58*, *2590—2594 (1985)* [Vol. 58, No. 9

A Temperature Dependence Study of ^{35}Cl NQR Frequencies in Dimethylammonium Hexachlorostannate(IV), Hexachlorotellurate(IV), and Hexachloroplatinate(IV)

Keizo Horiuchi, Hiroyuki Ishida, and Daiyu Nakamura*
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

(Received February 14, 1985)

The temperature dependence of ^{35}Cl NQR frequencies was observed for $[(CH_3)_2NH_2]_2SnCl_6$, $[(CH_3)_2NH_2]_2TeCl_6$, and $[(CH_3)_2NH_2]_2PtCl_6$. Two ^{35}Cl NQR frequencies were recorded for the tin complex between 77 and *ca.* 260 K, the intensity ratio of which was 2:1 for the high- to the low-frequency line. An unusual temperature variation of both frequencies attributable to the motion of the cation was observed, and the existence of a phase transition was suggested. For the tellurium complex, the NQR frequencies were observed below *ca.* 240 K. At higher temperatures, two signals having the same intensity ratio as that of the tin complex were detected as expected from the isomorphous relation between both complexes proved at room temperature. A phase transition was newly located for this complex at 98 K in addition to another one at 171 K previously reported. The intermediate phase yielded three broad signals having equal intensity, whereas four broad lines could be detected in the low-temperature phase where more than four lines may be expected by referring to the temperature-dependence curves of the NQR lines.

Recently, we studied the differential thermal analysis (DTA) of dimethylammonium (hereafter abbreviated as diMA) hexachlorotellurate(IV) and found a phase transition at 169 K.[1] Knop *et al.*[2] reported the occurrence of a phase transition in $(diMA)_2SnCl_6$ at 100 K from the study of IR absorptions. Dillon *et al.*[3] revealed a phase transition at 253 K in $(diMA)_2SnBr_6$ isomorphous with $(diMA)_2SnCl_6$ from the temperature dependence study of ^{79}Br NQR frequencies. For these hexachloro complexes, we also studied the ^{1}H NMR spin-lattice relaxation time, T_1, and the second moment of ^{1}H NMR absorptions at various temperatures in a fairly wide range of temperature.[1] This reveals the occurrence of the usual C_3 reorientation of the methyl groups of the cation and the 180 ° flip motion of the whole cation about its twofold pseudo-symmetry axis. However, no anomaly indicating the existence of phase transition was observed from these NMR measurements of both complexes.

Since NQR frequencies are very sensitive to a change in the structure of ionic crystals involving resonant nuclei, the NQR spectroscopy is a powerful means for the detection of phase transition and also for the precise location of the transition temperature, T_{tr}. The present investigation of the temperature dependence of ^{35}Cl NQR frequencies in $(diMA)_2SnCl_6$, $(diMA)_2TeCl_6$, and $(diMA)_2PtCl_6$ has been undertaken in order to confirm the existence of phase transitions for the former two complexes and to clarify the participation of the cationic motions in the temperature dependence of the ^{35}Cl NQR frequencies of these complexes.

Experimental

A modified Dean-type superregenerative spectrometer[4] was employed for the observation of chlorine NQR frequencies. The rf coil of the spectrometer including the sample sealed in a glass ampoule was placed in a Dewar vessel filled with petroleum ether. The sample temperature wanted was obtained by adding Dry-Ice or liquid nitrogen to petroleum ether. A chromel-alumel thermocouple was used for the determination of temperature. The sample temperature determined was estimated to be accurate within ±1 K. A homemade apparatus was employed for the experiments of DTA.[5] Copper-constantan thermocouples were used for the detection of heat anomalies and also for the determination of the sample temperature which was measured to be accurate within ±1 K.

The samples, $(diMA)_2SnCl_6$ and $(diMA)_2TeCl_6$, prepared for the previous NMR experiments were used for the present investigation. The platinum complex was synthesized in a method similar to that used in the preparation of $(diMA)_2SnCl_6$[1] from hexachloroplatinic acid and dimethylammonium chloride. Found: Cl, 42.55; N, 5.61; C, 9.63; H, 3.25%. Calcd for $[(CH_3)_2NH_2]_2PtCl_6$: Cl, 42.55; N, 5.60; C, 9.61; H, 3.23%.

Results

$[(CH_3)_2NH_2]_2SnCl_6$. The temperature variation of ^{35}Cl NQR frequencies observed for this complex is shown in Fig. 1. The resonance frequencies determined at various temperatures are given in Table 1 along with those of the other complexes.

At 196 K (Dry-Ice temperature), two ^{35}Cl NQR frequencies which were confirmed by observing the corresponding ^{37}Cl NQR signals were recorded. The high-frequency ($S/N \approx 100$) line was about twice as strong as that of the low-frequency one. With increasing temperature, the resonance frequency of the two lines decreased smoothly and the intensity of both lines became weak above *ca.* 250 K until they disappeared in the noise level at *ca.* 270 K, although the weak low-frequency line faded out at a slightly lower temperature. The DTA experiments carried

Table 1. ^{35}Cl NQR frequencies observed at various temperatures in $[(CH_3)_2NH_2]_2SnCl_6$, $[(CH_3)_2NH_2]_2TeCl_6$, and $[(CH_3)_2NH_2]_2PtCl_6$*

T/K	ν/MHz		
	$[SnCl_6]^{2-}$	$[TeCl_6]^{2-}$	$[PtCl_6]^{2-}$
77	16.762±0.005	16.44 ±0.02	26.86 ±0.01
	16.060±0.005	16.22 ±0.02	26.629±0.005
		16.13 ±0.02	
		15.90 ±0.02	
102	16.669±0.005	16.22 ±0.02 (100K)	26.829±0.008 (100K)
	16.110±0.005	16.04 ±0.02 (100K)	26.607±0.005 (100K)
		15.92 ±0.02 (100K)	
150	16.600±0.003	16.11 ±0.02	26.754±0.005
	16.120±0.003	16.01 ±0.02	26.537±0.005
		15.89 ±0.02	
170	16.576±0.003	16.02 ±0.01 (171K)	26.725±0.005
	16.109±0.003	15.88 ±0.01 (171K)	26.507±0.005
196	16.547±0.003	15.996±0.005	26.685±0.005
	16.089±0.003	15.865±0.005	26.467±0.005
220	16.524±0.003	15.969±0.005 (229K)	26.650±0.005
	16.065±0.003	15.834±0.008 (229K)	26.423±0.005
258	16.486±0.005		26.566±0.005 (273K)
	16.027±0.008		26.33 ±0.01 (273K)

* Two lines observed for this complex may be assigned to different crystalline modifications.

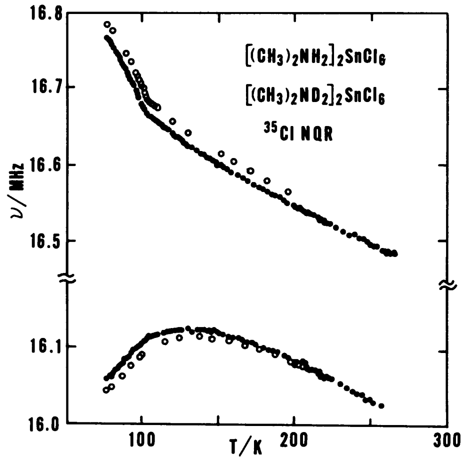

Fig. 1. Temperature dependences of ^{35}Cl NQR frequencies in dimethylammonium hexachlorostannate(IV). Dots and Circls indicate the resonance frequencies of $[(CH_3)_2NH_2]_2SnCl_6$ and $[(CH_3)_2ND_2]_2SnCl_6$, respectively.

out previously showed no heat anomaly up to 420 K.[1)]

From the X-ray analysis of this complex,[2,6)] it is known that the all complex anions in the crystal are crystallographically equivalent and there exist two nonequivalent chlorine atoms in the anion, *i.e.* two axially elongated chlorine atoms and four equatorial ones. Accordingly, the high- and low-frequency lines, respectively, can be unequivocally assigned to the equatorial and axial chlorine atoms of the hexachlorostannate(IV) anion by referring to the intensity ratio of the observed signals. It is quite reasonable that the axial chlorine atoms having a Sn–Cl bond longer than that of the equatorial ones yield a lower NQR frequency at a given temperature, because chlorine atoms having a longer metal-ligand bond is expected to be more ionic and to give a lower-frequency NQR line.

When the temperature decreased from 196 K, both lines of $(diMA)_2SnCl_6$ decreased their intensity gradually although the intensity ratio remained unchanged. The high-frequency line increased its frequency almost linearly with decreasing temperature down to 102 K, where the temperature coefficient, $d\nu/dT$, was changed discontinuously. Below this temperature, the absolute value of $d\nu/dT$ became larger as can be seen in Fig. 1. On the other hand, the low-frequency line exhibits quite unusual temperature variation. When the temperature increased from 77 K, the resonance frequency of the line increased almost linearly and fairly steeply up to *ca.* 100 K, indicating that the line has an unusual positive temperature coefficient. Above *ca.* 100 K, the temperature gradient of the line became discontinuously gentle and the ν *vs.* T curve yielded a broad maximum around 140 K. With increasing the temperature furthermore, the frequency of the line decreased monotonously.

Knop *et al.*[2)] studied the temperature variation of the IR spectra of $(diMA)_2SnCl_6$ and concluded the occurrence of a phase transition near 100 K by observing the splitting of the N–H stretching band of the NHD^+ group into a doublet below 100 K. They attributed the splitting of the IR band to the appearance of nonequivalent NH hydrogen atoms in the $(diMA)_2SnCl_6$ crystal. The present NQR investigation revealed a discontinuous change at 102 K in the gradient of both ν *vs.* T curves observed. This strongly suggests the existence of a higher-order phase transition in this crystal although no heat anomaly could be detected near 100 K on the DTA measurements repeatedly and carefully carried out.

To obtain further information about the phase transition suggested above, we prepared a partially deuterated analog, $[(CH_3)_2ND_2]_2SnCl_6$, and observed the temperature dependence of ^{35}Cl NQR frequencies. The results are also shown in Fig. 1. The temperature dependence curves obtained are very similar to those of the undeuterated analog. The curve of the high-frequency line shifts by *ca.* 20 kHz to the high-frequency side by *N*-deuteration whereas the curve of the low-frequency line moves to the low-frequency side by *N*-deuteration although the separation of the two curves increases gradually with decreasing temperature.

$[(CH_3)_2NH_2]_2TeCl_6$. The temperature dependence of ^{35}Cl NQR frequencies observed for this complex is exhibited in Fig. 2.

At 196 K, two fairly sharp ^{35}Cl NQR frequencies were observed having the intensity ratio approximately equal to 2:1 for the high- to the low-frequency line ($S/N \approx 8$). With increasing temperature, the resonance frequency of both lines lowered almost linearly and the high- and low-frequency lines disappeared in the noise level at *ca.* 240 and 230 K, respectively. The disagreement of the fade-out temperatures is thought as arising from the unequal intensity of both lines. With increasing temperature, each line gradually weakened from the temperature which was lower than each fade-out temperature by *ca.* 10 K. These results are very similar to those of $(diMA)_2SnCl_6$. This is a reasonable consequence because $(diMA)_2TeCl_6$ is isomorphous with $(diMA)_2SnCl_6$ as confirmed already by X-ray powder patterns taken at room temperature.[1] No heat anomaly, of course, was detected above 196 K for $(diMA)_2TeCl_6$ in the DTA experiments performed previously.

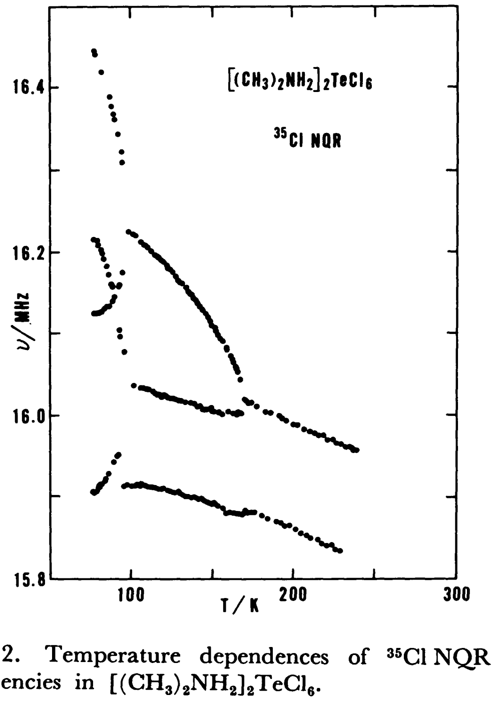

Fig. 2. Temperature dependences of ^{35}Cl NQR frequencies in $[(CH_3)_2NH_2]_2TeCl_6$.

When the temperature decreased from 196 K, the high-frequency line gradually broadened and suddenly disappeared at 171 K and two broad new lines having equal intensity ($S/N \approx 3$) appeared at a slightly lower temperature. This indicates the existence of a phase transition as revealed previously.[1] The two new frequencies were observed above and below the resonance frequency of the high-frequency line of the high-temperature phase observed immediately above 171 K. The frequency of the broad high-frequency line newly recorded increased fairly sharply with decreasing temperature down to 98 K, where the signal disappeared. The broad low-frequency line increased its frequency almost linearly with decreasing temperature showing a mild gradient and also disappeared at 98 K. The low-frequency line of the high-temperature phase lowered its frequency slightly and discontinuously at 171 K and increased its frequency gently with decreasing temperature down to 98 K where the signal also disappeared. In the temperature range between 98 and 171 K, the lowest-frequency signal was also broad and the signal intensity was almost unchanged immediately above and below 171 K. Accordingly, three resonance lines having nearly the same intensity were observed in this temperature range. With increasing temperature, the same process of the temperature dependence of ^{35}Cl NQR frequencies could be followed exactly for this complex, indicating that the previously reported T_{tr}[1] of 169 K should be revised as 171 K.

At 77 K, four ^{35}Cl NQR frequencies having nearly equal intensity ($S/N \approx 4$) to each other could be clearly observed. A very weak ($S/N \approx 2$) and also very broad signal could be barely recorded near 15.95 MHz. However, the temperature dependence of this line could not be determined partly because this signal was too weak and broad to be measured accurately and partly because this line and another strong line with many side bands overlapped each other with increasing temperature. Two of the four lines lowered their frequencies very steeply with increasing temperature whereas the remaining two lines showed unusual positive temperature coefficients. The four lines disappeared just below 98 K, at which temperature three fairly strong signals appeared.

From the above observation of the temperature dependence of ^{35}Cl NQR frequencies, one can conclude that $(diMA)_2TeCl_6$ undergoes structural phase transitions at 98 and 171 K and two and three crystallographically nonequivalent chlorine atoms exist in the high and intermediate phases, respectively. The two and three nonequivalent chlorine atoms can be assigned to the single $[TeCl_6]^{2-}$ ion in the crystal by comparing these results with those of $(diMA)_2SnCl_6$ and by referring to the fact that the doubly strong line of the high-temperature phase is split into two with equal intensity. In the low-temperature phase, there exist at least five nonequivalent chlorine atoms. To confirm the existence of the phase transition at 98 K, we undertook the experiments of DTA. However, no heat anomaly could be observed. This may be due to the low sensitivity of our apparatus at lower temperatures and also possibly due to the small heat anomaly of this phase transition.

$[(CH_3)_2NH_2]_2PtCl_6$. At 77 K, two ^{35}Cl NQR frequencies were observed for this complex. The high-frequency line was moderately strong and also broad whereas the low-frequency line was weak and fairly sharp. With increasing temperature, the resonance frequency of both lines decreased almost linearly although the low-frequency curve was very slightly convex. The high-frequency line became gradually sharp and weak with increasing temperature, although it could be clearly observed even at room temperature. On the other hand, the low-frequency line decreased its intensity until it disappeared below room temperature. At 196 K, the intensity ratio of the high- to the low-frequency line was approximately 7:1.

Discussion

According to the X-ray analysis recently carried out,[2,6] $(diMA)_2SnCl_6$ forms orthorhombic crystals belonging to the space group Pnnm with Z=2. The structure consists of parallel sheets of almost regular $[SnCl_6]^{2-}$ octahedra held together by hydrogen bonds formed between cationic NH_2^+ groups and chlorine atoms. Each NH_2^+ group is symmetrically H-bonded to the two nearest neighbor complex anions in a sheet and each complex anion is the recipient of H-bonds from four cations. Each N–H vector lies nearly along the pseudo-threefold axis of the anion but it deviates in such a way that the N–H···Cl H-bonds are described as asymmetrically trifurcated or close to out-of-plane bifurcated. Short H-bonds having the distance of 2.6 Å are formed between N–H hydrogen and equatorial chlorine atoms which have a shorter Sn–Cl bond distance, while the axial chlorine atoms form longer H-bonds (3.0 Å). Accordingly, each chlorine atom has N–H···Cl type H-bonds, the hydrogen atom of which exists nearly on the plane including the chlorine atom and perpendicular to the Sn–Cl bond axis.

The present NQR results completely agree with the above crystal structure especially in the features that the tin complex yields two ^{35}Cl NQR lines attributable to two nonequivalent chlorine atoms in the single anion and that the high- and low-frequency lines are assignable to the equatorial and axial chlorine atoms, respectively. This assignment is compatible with the foregoing Sn–Cl bond distance discussion.

By referring to the above X-ray results, the unusual temperature dependence of the ^{35}Cl NQR frequencies observed particularly for the low-frequency line and the phase transition suggested can be explained as follows.[7] Let an Sn–Cl bond axis be the z axis of the chlorine atom. Then, two hydrogen atoms forming H-bonds with the chlorine atom lie nearly along the x- and y-axes of the chlorine atom. This suggests that the p_x and p_y electrons of the chlorine atom are polarized and that the population of these electrons decreases to some extent. This results in a decrease in the ^{35}Cl NQR frequency.[7–9]

Here, we assume that the H···Cl distances involving the equatorial and the axial chlorine atoms are longer and shorter, respectively, at 77 K than the corresponding values determined at room temperature. This is achieved by widening the H–N–H angle which is reported to be 84° at room temperature although this value is exceptionally small. With increasing temperature, the equilibrium position of the hydrogen atoms moves to that determined at room temperature through the excitation of unharmonic deformation vibrations of NH_2^+ groups. This may result in an increase and a sharp decrease in the ^{35}Cl NQR frequencies of the low- and high-frequency lines, respectively. In this phase, two slightly nonequivalent NH groups, as pointed out its existence by Knop *et al.*[2] from the IR study of the stretching vibration of partially deuterated NHD^+ groups in the cation, can be allowed to exist in the crystal without changing the number of nonequivalent chlorine atoms in each complex anion. At 102 K, the slightly nonequivalent NH groups become equivalent forming symmetrical NH_2^+ groups in the crystal. However, the equilibrium positions of the H atoms are still near those of the low-temperature phase. With increasing temperature furthermore, the equilibrium positions move slightly and gradually to those determined at room temperature. The high-frequency line of the partially deuterated analog $[(CH_3)_2ND_2]_2SnCl_6$ also shows a discontinuous change in the temperature coefficient of ^{35}Cl NQR frequencies near 102 K. This provides strong evidence for the existence of the phase transition suggested.

The NQR results of the high-temperature phase of $(diMA)_2TeCl_6$ can be explained along the same line as those obtained for $(diMA)_2SnCl_6$ at higher temperatures. In the intermediate phase, three broad NQR lines were observed suggesting the existence of strong dipolar interactions through N–H···Cl type H-bonding and/or the presence of some slight disorder in the position of CH_3 groups. In the low-temperature phase, more than four crystallographically nonequivalent chlorine atoms which presumably belong to the same complex anion exist, suggesting the presence of nonequivalent cations in the crystal in agreement with the results of our previous ^{1}H T_1 study.[1]

For $(diMA)_2PtCl_6$, two ^{35}Cl NQR lines having signal intensity greatly different from each other were observed. According to Ries,[10] this complex shows polymorphism and crystallizes in two morphologically different forms. In fact, the complex prepared in the present investigation yielded complicated X-ray powder patterns which are completely different from those of $(diMA)_2SnCl_6$ and $(diMA)_2TeCl_6$. The elementary analysis of the complex prepared exhibits perfect agreement with the theoretical value for $(diMA)_2PtCl_6$. Therefore, the two lines observed can be assigned to two different crystal forms. Although both forms have the same point-group symmetry D_{2h}, one form is easily crystallized with the bigger abundance ratio. Accordingly, the high-frequency line may be attributed to this crystalline form. No further discussion can be made of this complex because of the above ambiguity in the crystals prepared.

The ^{35}Cl NQR frequencies of $(diMA)_2SnCl_6$ and $(diMA)_2TeCl_6$ disappear in the noise level around 270 and 240 K, respectively. Each signal loses its intensity fairly quickly from the temperature lower by *ca.* 15 K than each fade-out temperature. The characteristic appearance of these temperature dependence curves below each fade-out temperature is that each ν *vs.* T curve decreases almost linearly with increasing temperature.

The fade-out phenomenon of NQR signals is usually interpreted in terms of a large fluctuation of the electric field gradient (EFG) produced at resonant nuclei by appropriate molecular motions such as molecular reorientation and molecular self-diffusion.[11] Brown *et al.*[12] observed the nuclear quadrupole relaxation time T_1 in $CaSnCl_6 \cdot 6H_2O$ and found a fairly sharp decrease in T_1 above 250 K, which was attributed to the reorientational motions of the complex anions. However, the ^{35}Cl NQR frequency could be observed up to 390 K. This suggests that the reorientational motion of the anions does not affect drastically the EFG of the chlorine atoms. Furthermore, the reorientation of octahedral hexachloro complex anions in various K_2PtCl_6 type complexes including $(NH_4)_2MCl_6$ is known usually to start far above room temperature.[13–15] Therefore, the fade-out of ^{35}Cl NQR signals in $(diMA)_2SnCl_6$ and $(diMA)_2TeCl_6$ which was observed below room temperature may not be explained by the fluctuation of EFG due to the motion of the complex anions.

From our ^{1}H NMR measurements previously carried out,[1] the 180 ° flip motion of the whole cation about its twofold pseudo-symmetry axis accompanying a large amplitude libration or small angle reorientation of the cation was detected above *ca.* 300 and 260 K for $(diMA)_2SnCl_6$ and $(diMA)_2TeCl_6$, respectively. These motions of the cations are expected to generate a large fluctuation of EFG produced at the chlorine nuclei of these complex anions, because the cation has two nonequivalent CH_3 groups and each chlorine atom has two H-bonded hydrogen atoms carrying a partial positive charge. The 180 ° flip motion of the cation results in a positional disorder of the CH_3 groups and the slow motion of NH_2^+ hydrogen atoms will disturb EFG at the chlorine nuclei and broaden the NQR signals. Therefore, one can conclude that the disappearance of the ^{35}Cl NQR signals of these complexes below room temperature is solely attributable to the motion of the cation as a whole.

References

1) H. Ishida, R. Ikeda, and D. Nakamura, *Ber. Bunsenges. Phys. Chem.*, **88**, 546 (1984).

2) O. Knop, T. S. Cameron, M. A. James, and M. Falk, *Can. J. Chem.*, **61**, 1620 (1983).

3) K. B. Dillon, J. Halfpenny, and A. Marshall, *J. Chem. Soc., Dalton Trans.*, **1983**, 1091.

4) D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, *J. Am. Chem. Soc.*, **82**, 5783 (1960).

5) Y. Kume, R. Ikeda, and D. Nakamura, *J. Magn. Reson.*, **33**, 331 (1979).

6) M. H. B. Ghozlen, A. Daoud, and J. W. Bats, *Acta Crystallogr., Sect. B*, **37**, 1415 (1981).

7) D. Nakamura, R. Ikeda, and M. Kubo, *Coord. Chem. Rev.*, **17**, 281 (1975).

8) A. Sasane, T. Matsuo, D. Nakamura, and M. Kubo, *Bull. Chem. Soc. Jpn.*, **43**, 1908 (1970); *J. Magn. Reson.*, **4**, 257 (1971).

9) C. W. Fryer and J. A. S. Smith, *J. Chem. Soc. A*, **1970**, 1029.

10) A. Ries, *Z. Kristallogr.*, **36**, 321 (1902).

11) H. Chihara and N. Nakamura, *Adv. Nucl. Quad. Reson.*, **4**, 1 (1980).

12) R. J. C. Brown, B. K. Hunter, M. Mackowiak, and S. Segel, *J. Magn. Reson.*, **50**, 218 (1982).

13) K. R. Jeffrey and R. L. Armstrong, *Phys. Rev.*, **174**, 359 (1968).

14) R. L. Armstrong and H. M. van Driel, *Adv. Nucl. Quad. Reson.*, **2**, 179 (1975).

15) C. Dimitropoulos and J. Pelzl, *J. Mol. Struct.*, **58**, 107 (1980).