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Chlorine Nuclear Quadrupole Resonance in Some Nontransition Metal Inorganic Chloride Complexes[1]

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Chlorine-35 and chlorine-37 nuclear quadrupole resonances have been observed in polycrystalline PCl_5 (ionic), PCl_4PF_6, PCl_4SbCl_6, $(C_2H_5)_4NPCl_6$, $NOSbCl_6$, $(C_2H_5)_4NSbCl_6$, $AsCl_4AlCl_4$, and $PbCl_4$. The frequencies are discussed and assignments of the resonances to the PCl_4^+, $AsCl_4^+$, PCl_6^-, and $SbCl_6^-$ ions are made. The effects of thermal annealing and the size of the Zeeman modulating field magnitude on the resonances are discussed.

Introduction

We wish to report the detection of chlorine nuclear quadrupole resonance in a number of group V chloride complexes and in some related compounds. This work is part of a program to study the variation of chlorine nuclear quadrupole resonance (nqr) frequencies in sets of isoelectronic molecules and ions.

We have observed resonances in ionic PCl_5 ($PCl_4^+PCl_6^-$), PCl_4SbCl_6, PCl_4PF_6, $AsCl_4AlCl_4$, $(C_2H_5)_4NPCl_6$, $NOSbCl_6$, and $(C_2H_5)_4NSbCl_6$, as well as in the related compound $PbCl_4$.

The detection of three chlorine resonances in PCl_5 at liquid nitrogen temperatures was reported by McCall and Gutowsky[2a] and Holmes, *et al.*,[2b] have reported the chlorine resonances in PCl_2F_3, the molecular modification of PCl_4PF_6. Nakamura[3] has reported chlorine nqr in $(NH_4)_2PbCl_6$. The resonances in the compounds listed above are otherwise previously unreported.

Experimental Section

A. Preparation of Compounds.—PCl_4PF_6 (ionic),[4] $NOSbCl_6$,[5] PCl_4SbCl_6,[5] and $AsCl_4AlCl_4$[6] were prepared by the methods described in the references. Gutmann[7] reported the preparation of $(C_2H_5)_4NPCl_6$ in the course of conductometric titrations. We prepared the compound by dissolving 2.9 g of PCl_5 in 100 ml of CH_2Cl_2 and 2.3 g of $(C_2H_5)_4NCl$ in 30 ml of CH_2Cl_2. The PCl_5–CH_2Cl_2 was cooled to 0° and the $(C_2H_5)_4NCl$–CH_2Cl_2 added slowly with stirring. The solid obtained was filtered in a drybox and washed with dry CCl_4; the wash solvent was removed by pumping. A yield of 4.1 g of the dry product was obtained. *Anal.* Calcd for $(C_2H_5)_4NPCl_6$: C, 25.7; H, 5.39; N, 3.75; P, 8.28; Cl, 56.88. Found: C, 26.1; H, 5.08; N, 3.86; P, 8.53; Cl, 57.13.

$(C_2H_5)_4NSbCl_6$ was prepared by the same general method as described above for $(C_2H_5)_4NPCl_6$ using $SbCl_5$–CH_2Cl_2 (1.3 ml/10 ml) in place of the PCl_5–CH_2Cl_2 solution. *Anal.* Calcd for $(C_2H_5)_4NSbCl_6$: C, 20.7; H, 4.34; N, 3.01; Sb, 26.2; Cl, 45.8. Found: C, 20.8; H, 4.41; N, 3.20; Sb, 25.1 ± 1.2; Cl, 46.8 ± 0.9.

$(pyH)_2PbCl_6$ was prepared by the slow addition of 18 g of PbO_2 to 400 ml of concentrated HCl at 0° and the subsequent addition of 7 g of pyridine. The light yellow crystals were filtered and washed with ethanol. $PbCl_4$ was prepared from $(pyH)_2PbCl_6$ by the method described by Brauer.[8]

B. Apparatus.—The nuclear quadrupole resonance spectrometer incorporates a self-quenched superregenerative oscillator, with a coherence control described by Peterson and Bridenbaugh.[9] The Zeeman modulation utilized a clamped asymmetric 30-c square-wave signal with the field applied perpendicularly to the axis of the sample coil. We have no provision at present for external quenching of the oscillator. Spectra at 77°K were obtained in a cold finger dewar flask with the oscillator coil wrapped around the outside of the finger. The same dewar filled with a Dry Ice–methylene chloride slush was used for measurements at 195°K.

Frequency measurements were made with a calibrated Hammarlund SP-600-J receiver very loosely coupled to the oscillator. For *intense* close-lying multiplets, the side-band structure of the resonance was examined as a function of quench frequency and the center band was so identified. For the weak resonances, a possible error of ±0.05 MHz can result from misidentification of the center band.

The qualitative side-band structure of the observed resonances was found to be quite sensitive to the magnitude of the modulating field. For intense (presumably narrow) resonances, where relatively small modulation fields (3–5 gauss peak to peak) sufficed to make the resonance detectable, the normal alternation of first- and second-derivative signals in successive side bands obtained. For the weaker (presumably broad) resonances, larger fields (10–20 gauss peak to peak) were necessary for the observation of the resonance. At these fields the side-band structure approached a succession of "first-derivative" line shapes. At intermediate modulation fields, the patterns became a complex mixture of the above two varieties.

The range investigated for these compounds was 15–40 MHz in general. The range 10–15 MHz was also searched in the case of $PbCl_4$ and $AsCl_4AlCl_4$.

C. Thermal Annealing.—The signal to noise ratios observed for the resonances listed herein have been found to be extremely sensitive to the thermal history of the sample. We assume that this is principally due to lattice strains which develop under a fast cooling process. In several of the compounds studied, there is a likelihood of phase changes occurring between room temperature and liquid nitrogen temperatures. The annealing process at the low temperatures is very slow so that we have maintained our samples at liquid nitrogen temperatures for periods of up to 4 weeks. The frequency changes which occur during such a period are exemplified in the two sets of data for ionic PCl_5 at 77°K shown in Table I.

Our observation of four previously undetected resonances in ionic PCl_5, we believe, further substantiates the care which must be exercised in allowing polycrystalline samples to anneal at low temperatures.

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(1) Work supported by NSF Grant GP-3838.

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TABLE I

CHLORINE NQR FREQUENCIES IN IONIC PCl_5

Temp, °K	$\nu(Cl^{35})$, MHz	*S/N*	$\nu(Cl^{37})$, MHz	*S/N*	Designation[a]
			PCl_5 (ionic) (annealed)		
77	29.61 ± 0.03	5/1	23.35 ± 0.04	2/1	$\nu_1{}^{A}(PCl_6^-)$
	30.07 ± 0.03	3/1	23.75 ± 0.04	2/1	$\nu_2{}^{A}(PCl_6^-)$
	30.45 ± 0.03	3/1	24.00 ± 0.04	2/1	$\nu_3{}^{A}(PCl_6^-)$
	30.62 ± 0.03	3/1	24.15 ± 0.04	2/1	$\nu_4{}^{A}(PCl_6^-)$
	32.28 ± 0.03	20/1	25.42 ± 0.04	7/1	$\nu_1{}^{A}(PCl_4^+)$
	32.61 ± 0.03	8/1	25.68 ± 0.04	3/1	$\nu_2{}^{A}(PCl_4^+)$
195	29.27 ± 0.02	6/1	23.13 ± 0.03	2/1	$\nu_5{}^{A}(PCl_6^-)$
	29.93 ± 0.03	5/1	23.57 ± 0.03	2/1	$\nu_6{}^{A}(PCl_6^-)$
	31.96 ± 0.02	26/1	25.15 ± 0.02	8/1	$\nu_4{}^{A}(PCl_4^+)$
300	No resonance detected				
			PCl_5 (ionic) (unannealed)		
77	29.65 ± 0.03	7/1	23.41 ± 0.03	3/1	$\nu_1{}^{A}(PCl_6^-)$
	30.08 ± 0.03	5/1	23.75 ± 0.04	3/1	$\nu_2{}^{A}(PCl_6^-)$
	30.47 ± 0.03	4/1	24.00 ± 0.03	2/1	$\nu_3{}^{A}(PCl_6^-)$
	32.30 ± 0.03	30/1	25.29 ± 0.03	10/1	$\nu_3{}^{A}(PCl_4^+)$
	31.42 ± 0.03	25/1	25.59 ± 0.03	8/1	$\nu_1{}^{A}(PCl_4^+)$
	32.63 ± 0.03	10/1	25.77 ± 0.03	4/1	$\nu_2{}^{A}(PCl_4^+)$
195	29.28 ± 0.03	4/1	23.10 ± 0.03	3/1	$\nu_5{}^{A}(PCl_6^-)$
	29.93 ± 0.03	3/1	23.52 ± 0.03	3/1	$\nu_6{}^{A}(PCl_6^-)$
	31.95 ± 0.03	25/1	25.25 ± 0.03	6/1	$\nu_4{}^{A}(PCl_4^+)$
300	No resonance detected				

[a] In this and the following tables, in the designation of the resonances $\nu_n{}^{X}(Y)$, X denotes the particular compound, Y the particular species giving rise to the resonance, and *n* is an index which identifies a particular resonance due to that species.

D. Signal to Noise Ratios.—The signal to noise ratios (*S/N*) reported here are in no sense absolute or even comparable at very different frequencies. They represent the ratio of the peak to peak voltage of the most intense side band to the peak to peak noise voltage observed in the traces from which frequency measurements were made. No attempt at summing the intensities in the various side bands was made. In most cases the reported values were the maximum intensities observed, while in others (particularly those with larger *S/N*) slower scans might have produced increased intensity. Our sweep rates during frequency measurements were generally of the order of 10 kHz/min.

Crystal Structures

The crystal structures of the compounds studied in this work are for the most part unknown. None of the compounds has been examined structurally at 77 or 195°K. A small amount of data concerning the structures at room temperature is available.

Clark, Powell, and Wells[10] in their classic work on PCl_5 found the room-temperature form to be ionic with a crystal symmetry P4/n. Their work places the PCl_4^+ cations at sites of $\bar{4}$ symmetry and the PCl_6^- anions at sites of 4 symmetry. Such a crystal structure would provide field gradient tensors for each of the four chlorine atoms on the cation differing only in their spatial orientations but not in their principal values. The anion could give rise to two different field gradient tensors (one for the axial chlorines and a different one for the equatorial chlorines) depending on the extent of tetragonal distortion experienced by the anion.

Thus the predicted nuclear quadrupole resonance spectrum of a polycrystalline sample would show a single absorption due to PCl_4^+ at a frequency characteristic of the electronic environment of a Cl in the PCl_4^+ ion, and at a different (presumably lower) frequency, a pair of resonances due to PCl_6^- with an intensity ratio of 2:1 due, respectively, to the four equatorial chlorines and the two axial chlorines in the PCl_6^- ion.

The only available crystal structure data on the compound PCl_4PF_6 are the powder patterns given by Kolditz.[11] Our own[12] interpretation of the infrared and Raman spectra of the solid ionic form of this compound at room temperature have limited the possible site symmetry of PCl_4^+ to 222, $\bar{4}$, or $\bar{4}2m$, any one of which will provide symmetric equivalence of the four chlorine atoms in this ion. Such an analysis again allows for only a single chlorine quadrupole resonance to occur in a polycrystalline sample.

The only remaining structural information available to us is based on our[12] Raman investigations of $AsCl_4$-$AlCl_4$ which shows no evidence for distortion of the $AsCl_4^+$ ion from tetrahedral symmetry at room temperature, again implying only a single observable resonance.

Results

Our experimental results are summarized in Tables I–V. The tables give the measured frequencies of the chlorine-35 resonances, the corresponding chlorine-37 frequencies, and the signal to noise ratios as described above. In Table I, the data for annealed PCl_5 represent the spectrum observed after 2 weeks of immersion of the sample in liquid nitrogen. After that period of time, no further changes have been observed in samples maintained at 77°K for up to 4 weeks. The data for unannealed PCl_5 represent the spectrum observed after 2 hr of immersion in liquid nitrogen.

TABLE II

CHLORINE NQR FREQUENCIES IN PCl_4PF_6 AND $(C_2H_5)_4NPCl_6$

Temp, °K	$\nu(Cl^{35})$, MHz	*S/N*	$\nu(Cl^{37})$, MHz	*S/N*	Designation
			PCl_4PF_6		
77	32.46 ± 0.03	15/1	25.55 ± 0.03	5/1	$\nu_1{}^{B}(PCl_4^+)$
195	32.20 ± 0.03	8/1	24.35 ± 0.03	2/1	$\nu_1{}^{B}(PCl_4^+)$
300	No resonance detected				
			$(C_2H_5)_4NPCl_6$		
77	29.32 ± 0.03	15/1	23.07 ± 0.03	4/1	$\nu_1{}^{C}(PCl_6^-)$
	30.06 ± 0.02	25/1	23.66 ± 0.03	8/1	$\nu_2{}^{C}(PCl_6^-)$
	30.34 ± 0.02	13/1	23.89 ± 0.03	3/1	$\nu_3{}^{C}(PCl_6^-)$
195	29.01 ± 0.03	20/1	22.94 ± 0.03	7/1	$\nu_1{}^{C}(PCl_6^-)$
	29.66 ± 0.02	7/1	23.42 ± 0.02	3/1	$\nu_2{}^{C}(PCl_6^-)$
	29.76 ± 0.02	4/1	23.47 ± 0.02	2/1	$\nu_3{}^{C}(PCl_6^-)$
300	No resonance detected				

The Cl^{37} resonance corresponding to every Cl^{35} resonance with the exception of two in PCl_4SbCl_6 was sought and found. This is particularly important in the case of the arsenic and antimony compounds since isotopes of these elements (As^{75} (100%), Sb^{121} (57%), and Sb^{123} (43%)) can potentially give resonances in a sufficiently distorted environment. The detection of an Al^{27} resonance is extremely unlikely in the range of frequencies examined.

The measured frequency ratios $\nu(Cl^{35})/\nu(Cl^{37})$ are all within 0.4% of the ratio of the corresponding quadru-

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TABLE III

CHLORINE NQR FREQUENCIES IN PCl_4SbCl_6 AND $(C_2H_5)_4NSbCl_6$

Temp, °K	$\nu(Cl^{35})$, MHz	*S/N*	$\nu(Cl^{37})$, MHz	*S/N*	Designation
			PCl_4SbCl_6		
77	22.80 ± 0.05	2/1	...		$\nu_1^D(SbCl_6^-)$
	23.02 ± 0.05	2/1	...		$\nu_2^D(SbCl_6^-)$
	31.87 ± 0.03	5/1	25.15 ± 0.05	2/1	$\nu_1^D(PCl_4^+)$
	32.35 ± 0.03	12/1	25.50 ± 0.05	4/1	$\nu_2^D(PCl_4^+)$
	32.51 ± 0.03	20/1	25.63 ± 0.05	6/1	$\nu_3^D(PCl_4^+)$
195	22.80 ± 0.02	3/1	...		$\nu_3^E(SbCl_6^-)$
	31.90 ± 0.04	3/1	...		$\nu_4^D(PCl_4^+)$
	32.10 ± 0.04	6/1	25.24 ± 0.03	2/1	$\nu_5^D(PCl_4^+)$
300	No resonance detected				
			$(C_2H_5)_4NSbCl_6$		
77	24.01 ± 0.02	4/	18.89 ± 0.03	2/1	$\nu_1^E(SbCl_5^-)$
	24.21 ± 0.02	6/1	19.09 ± 0.03	2/1	$\nu_2^E(SbCl_6^-)$
	24.67 ± 0.02	8/1	19.45 ± 0.02	3/1	$\nu_3^E(SbCl_6^-)$
	24.86 ± 0.02	5/1	19.58 ± 0.02	2/1	$\nu_4^E(SbCl_6^-$
195	23.83 ± 0.02	7/1	18.77 ± 0.02	2/1	$\nu_5^E(SbCl_6^-)$
	24.02 ± 0.02	8/1	18.93 ± 0.02	2/1	$\nu_6^E(SbCl_6^-)$
	24.36 ± 0.02	5/1	19.21 ± 0.05	2/1	$\nu_7^E(SbCl_6^-)$
	300 No resonance detected				

TABLE IV

CHLORINE NQR FREQUENCIES IN $NOSbCl_6$

Temp, °K	$\nu(Cl^{35})$, MHz	*S/N*	$\nu(Cl^{37})$, MHz	*S/N*	Designation
77	22.35 ± 0.03	6/1	17.62 ± 0.03	3/1	$\nu_1^F(SbCl_6^-)$
	22.97 ± 0.03	5/1	18.09 ± 0.03	2/1	$\nu_2^F(SbCl_6^-)$
	23.15 ± 0.03	4/1	18.25 ± 0.03	2/1	$\nu_3^F(SbCl_6^-)$
	23.37 ± 0.03	3/1	18.40 ± 0.03	2/1	$\nu_4^F(SbCl_6^-)$
	25.03 ± 0.03	4/1	19.75 ± 0.02	2/1	$\nu_5^F(SbCl_6^-)$
	25.48 ± 0.03	4/1	20.15 ± 0.03	2/1	$\nu_6^F(SbCl_6^-)$
195	22.93 ± 0.04	6/1	18.14 ± 0.04	2/1	$\nu_7^F(SbCl_6^-)$
	23.78 ± 0.04	8/1	18.80 ± 0.04	3/1	$\nu_8^F(SbCl_6^-)$
	23.96 ± 0.04	5/1	18.94 ± 0.04	2/1	$\nu_9^F(SbCl_6^-)$
301	23.24 ± 0.03	5/1	18.40 ± 0.04	2/1	$\nu_{10}^F(SbCl_6^-)$
	23.45 ± 0.03	6/1	18.55 ± 0.04	2/1	$\nu_8^F(SbCl_6^-)$
	23.55 ± 0.03	5/1	18.60 ± 0.04	2/1	$\nu_9^F(SbCl_6^-)$

TABLE V

CHLORINE NQR FREQUENCIES IN $AsCl_4AlCl_4$ AND $PbCl_4$

Temp, °K	$\nu(Cl^{35})$, MHz	*S/N*	$\nu(Cl^{37})$, MHz	*S/N*	Designation
			$AsCl_4AlCl_4$		
77	36.82 ± 0.04	5/1	29.00 ± 0.04	2/1	$\nu_1(AsCl_4^+)$
	37.03 ± 0.04	7/1	29.25 ± 0.04	2/1	$\nu_2(AsCl_4^+)$
195	36.21 ± 0.05	12/1	28.45 ± 0.04	4/1	$\nu_1(AsCl_4^+)$
	36.50 ± 0.05	12/1	28.71 ± 0.04	4/1	$\nu_2(AsCl_4^+)$
300	No resonance detected				
			$PbCl_4$		
77	22.68 ± 0.05	3/1	17.84 ± 0.05	2/1	$\nu_1(PbCl_4)$

pole moments[13] (1.26878 ± 0.00015). The deviations from this ratio are presumed to represent experimental errors in the measurements of resonance frequencies rather than the more subtle variations (~0.02%) due to thermal vibrations discussed by Wang.[14]

Discussion

PCl_5 (Ionic).—We note that, as indicated in Table I, we have observed a multiplicity of resonances in annealed PCl_5 at 77°K. The room-temperature crystal structure of PCl_5 is consistent with only three chlorine quadrupole resonances. McCall and Gutowsky[2a] reported three resonances at 32.63, 32.384, and 32.282 MHz at 77°K. We observe four additional Cl^{37} resonances with a weighted (by relative intensities) average frequency of 30.11 MHz. (Table VI summarizes the average frequencies for all of the compounds studied in this work.) We associate these four resonances [$\nu_1^A(PCl_6^-)$, $\nu_2^A(PCl_6^-)$, $\nu_3^A(PCl_6^-)$, and $\nu_4^A(PCl_6^-)$] with the PCl_6^- ion. The three resonances reported above are observed in our unannealed sample but in our annealed PCl_5, only two of them persist [$\nu_1^A(PCl_4^+)$, $\nu_2^A(PCl_4^+)$]. These two we assign to the PCl_4^+ ion. The numbers of these resonances are not consistent with the predictions of the room-temperature crystal structure and we conclude that between 77 and 300°K a phase change must occur. Our data at 195°K are consistent with the room-temperature predictions so that the transition may well take place between 77 and 195°K. The fact that annealing is unimportant at 195°K is further evidence for the phase at 195°K being very similar to that at room temperature. Careful intensity measurements on the intensities of the PCl_6^- resonances at 195°K might allow the interpretation of those two resonances [$\nu_5^A(PCl_6^-)$ and $\nu_6^A(PCl_6^-)$] as arising from the equatorial and axial chlorines on the tetragonally distorted octahedral PCl_6^- ion.

PCl_4PF_6 and $(C_2H_5)_4NPCl_6$.—In these two compounds we have isolated the PCl_4^+ and PCl_6^- ions, respectively. The detection of a resonance (see Table II) at 32.46 MHz in PCl_4PF_6 confirms our assignment of the PCl_4^+ resonance in PCl_5. That the resonance is not multiple indicates that the PCl_4^+ ion contains four equivalent chlorine atoms, consistent with the site symmetry deduced from the vibrational spectrum and discussed above in the section on crystal structures.

In $(C_2H_5)_4NPCl_6$, a triplet with an average frequency of 29.92 MHz again confirms our assignment of the resonances due to PCl_6^- in PCl_5. In this compound, some distortion of the PCl_6^- ion is evident.

The regular temperature dependences of the resonances in both these compounds between 77 and 195°K suggest that no significant phase transitions occur in that temperature range.

PCl_4SbCl_6, $(C_2H_5)_4NSbCl_6$, and $NOSbCl_6$.—The data on these compounds given in Tables III and IV are less easily interpretable. The three resonances near 32 MHz in PCl_4SbCl_6 at 77°K [$\nu_1^D(PCl_4^+)$, $\nu_2^D(PCl_4^+)$, and $\nu_3^D(PCl_4^+)$] which average 32.37 MHz are almost certainly due to the PCl_4^+ ion. The remaining resonances in that compound and all the resonances in $(C_2H_5)_4NSbCl_6$ and $NOSbCl_6$ are due to antimony–chlorine-containing species. Table VI shows the average frequencies observed in these compounds (labeled $SbCl_6^-$). Unlike the observation made on the previous substances, large differences in the resonance frequencies from compound to compound are evident. Cation effects of the order of 0.7 MHz have been observed in the chlorine nqr in hexahalorhenates(IV)[15] and such effects may underlie the range observed for the resonances due to $SbCl_6^-$ in these three compounds. The multiplicities of the resonances observed, however, change between 77 and 195°K for each of the com-

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TABLE VI

AVERAGE CHLORINE-35 NQR FREQUENCIES (MHz) OF MCl_4 AND MCl_6 SPECIES AT VARIOUS TEMPERATURES

Compound	Temp, °K			$10^6(°K)^{-1}(-\Delta\bar{\nu}/\bar{\nu}\Delta T)$[d]
	77	195	300	
PCl_4^+ in PCl_4PCl_6[a]	32.45 ± 0.15 (2)[c]	31.96 ± 0.02 (1)[c]	...	128
PCl_4PF_6	32.46 ± 0.03 (1)	32.20 ± 0.03 (1)	...	68
PCl_4SbCl_6	32.37 ± 0.15 (3)	32.03 ± 0.09 (2)	...	89
PCl_6^- in PCl_4PCl_6[a]	30.11 ± 0.37 (4)	29.60 ± 0.33 (2)	...	143
$(C_2H_5)_4NPCl_6$	29.92 ± 0.34 (3)	29.25 ± 0.31 (3)	...	190
$SbCl_6^-$ in $(C_2H_5)_4NSbCl_6$	24.48 ± 0.30 (4)	24.04 ± 0.16 (3)	...	153
$NOSbCl_6$	23.60 ± 0.86 (6)	23.56 ± 0.40 (3)	23.42 ± 0.11 (3)	14
PCl_4SbCl_6	22.91 ± 0.11 (2)	22.80 ± 0.02 (1)	...	41
$AsCl_4^+$ in $AsCl_4AlCl_4$	36.94 ± 0.10 (1)	36.36 ± 0.15 (1)	...	133
$PbCl_4$	22.68 ± 0.05 (1)	...	...	...
$PbCl_6^{2-}$ in $(NH_4)_2PbCl_6$[b]	17.26 ± 0.05	17.142 ± 0.003	17.061 ± 0.002	59

[a] From data for annealed sample. [b] Data from D. Nakamura.[3] [c] The numbers in parentheses indicate the number of resonances included in averages. [d] At 77°K.

pounds studied. This would seem to indicate the occurrence of phase transitions in this temperature range. These phase changes may well involve significant chemical change, such as Sb–O bond formation in the case of $NOSbCl_6$. Antimony pentachloride forms addition compounds with a large variety of compounds[16] the characteristics of which in the solid state are not at all straightforward.[17] In PCl_4SbCl_6 and $(C_2H_5)_4NSbCl_6$ the likelihood of chemical rearrangement is small so that, in the absence of detailed structural information, we can only conclude that the average frequency corresponding to the $SbCl_6^-$ ion at 77°K should be 23.7 ± 0.7 MHz but that resonances as high as 25.5 MHz [$\nu_6^F(SbCl_6^-)$ in Table IV] may be due to that ion.

The temperature dependences of the average resonance frequencies in these compounds are not likely to be of help in identifying the resonances since lines do disappear as the temperature is raised, so that identification of an individual component of the multiplet is difficult if not impossible. One further point which bears mention is that the intensities of the resonances due to $SbCl_6^-$ are generally much lower than those corresponding to the other lines studied. This is particularly evident in the reported resonances in PCl_4SbCl_6 (Table III) where the total intensity of the PCl_4^+ resonance is approximately 10 times as large as the $SbCl_6^-$ resonance (the latter having been observed under conditions of maximum sensitivity, the former under much less than optimum conditions). We may therefore not be detecting weaker resonances due to $SbCl_6^-$.

$AsCl_4AlCl_4$.—The resonances observed in this compound are given in Table V. They are certainly due to the $AsCl_4^+$ ion. Extensive searches for the $AlCl_4^-$ resonance yielded no observable signal. Segel and Barnes[18] report four resonances in a compound characterized as $Ga(AlCl_4)$ in the frequency range 10.3–11.3 MHz at room temperature. We assume that these are characteristic of the $AlCl_4^-$ species in general so that our assignment is well justified. The detection of two resonances in this compound is inconsistent with the low distortion of this ion expected at room temperature from vibrational data and discussed above. We assume therefore that the phase studied at 77 and 195°K is different from the room-temperature phase (in which we observe no resonance).

$PbCl_4$.—The chlorine resonance in this compound (Table V) (reported only at 77°K) is included so as to complete the data on the chlorine quadrupole resonances in the group IV tetrachlorides first reported by Livingston.[19]

Interpretation

In the absence of Zeeman studies, no information about the asymmetry of the field gradient tensor at chlorine obtains. For that reason we cannot deduce quadrupole coupling constants from our observed frequencies withour further assumptions. Furthermore, since most of the compounds examined in this work are ionic, the field gradient at chlorine contains contributions from the field of the ions constituting the lattice. Bersohn[20] first showed that field gradients in ionic crystals are of long-range origin. Ikeda, *et al.*,[15] calculated the ionic contributions to field gradients at chlorine in some alkali hexachlororhenates and hexachloroplatinates. In these compounds, the calculated magnitudes of the field gradients due to direct and indirect ionic contributions tend to be small (less than 0.5%) compared to the total observed field gradients. The individual ions discussed in this work are inherently covalent and it is expected that ionic contributions to the field gradients are negligible compared to the bonding contributions.

Since an asymmetry parameter as large as 0.3 produces less than a 2% change in the absolute value of the quadrupole coupling constant derived from the assumption of axial symmetry ($|eqQ| = 2\nu$), we will assume for our purposes that asymmetry effects are negligible.

Therefore, we tabulate effective average quadrupole coupling constants in Table VII which we can compare with similar values obtained in other compounds of interest.

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TABLE VII

EFFECTIVE Cl^{35} QUADRUPOLE COUPLING CONSTANTS (MHz) IN SOME TETRAHEDRAL AND OCTAHEDRAL MOLECULES (AT 77°K)

$CCl_4{}^a$	81.9				
$SiCl_4{}^a$	40.8	$PCl_4{}^{+\,b}$	64.8	$AlCl_4{}^{-\,c}$	21.2
$GeCl_4{}^a$	51.3	$AsCl_4{}^{+\,b}$	73.9		
$SnCl_4{}^a$	48.2				
$PbCl_4{}^b$	45.4				
		$PCl_6{}^{-\,b}$	60.0		
$SnCl_6{}^{2-\,d}$	31.3	$SbCl_6{}^{-\,b}$	47.6		
$PbCl_6{}^{2-\,d}$	34.6				

[a] From Livingston.[19] [b] This work. [c] From Segel and Barnes.[18] [d] From Nakamura.[3]

We restrict our interpretation of the data presented here to qualitative generalizations. A more complete analysis will be appropriate when data on more extensive sets of isoelectronic molecules are available. Table VII includes only two pairs of isoelectronic species ($GeCl_4$ and $AsCl_4{}^+$, $SnCl_6{}^{2-}$ and $SbCl_6{}^-$) and one set of three ($AlCl_4{}^-$, $SiCl_4$, and $PCl_4{}^+$).

The anomalous behavior of the group IV tetrahalides at $SiCl_4$ and $SiBr_4$ is repeated in our data on $PCl_4{}^+$ and $AsCl_4{}^+$, the former having a chlorine quadrupole coupling constant 0.88 times as large as $AsCl_4{}^+$. (For $SiCl_4$ and $GeCl_4$ the analogous quantity is 0.80, and the ratio of the $SiBr_4$ to $GeBr_4$ Br^{81} quadrupole coupling constants is 0.84).

Schawlow[21] has interpreted this irregularity in the Townes and Dailey[22] framework as possibly arising from double-bond character in the silicon–chlorine bond (presumably of a Si-d—Cl-p π-bond type). In $PCl_4{}^+$ with a larger positive charge on the nucleus of the central atom, one might expect an enhancement of the lowering of the field gradient by that mechanism. Our observation is that the actual effect is to diminish the field gradient lowering compared to that observed for the third-row element. There is a possibility that $AsCl_4{}^+$ constitutes the anomaly rather than $PCl_4{}^+$ in this series, since chlorine compounds of As(V) have been difficult to prepare.

One can however see that a regular increase in eQq (Cl^{35}) accompanies an increase in the charge of the central atom in the tetrahedron.

The data on octahedral chloride ions given here are not extensive enough to draw any strong generalizations. We would rather note that, generally, the intensities of these resonances are weak in comparison to those of the neutral and cationic species studied. This may well reflect an inherent breadth in their resonances due to the presence of many low-frequency vibrational motions which serve to make vibrational effects on the field gradient tensor maximal in these anions.

Further work is presently in progress to detect resonances in other species isoelectronic with those given here in a hope that this direct property of molecular wave functions can become a useful diagnostic tool for bonding studies.

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Some Cobalt(III) Complexes Containing a Tetracoordinate Macrocyclic Schiff Base Amine Ligand: Preparation, Chemistry, and Infrared, Visible, and Ultraviolet Spectra[1]

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Several new complexes of the type $Co^{III}(C_{16}H_{32}N_4)L_2$ have been prepared, where $C_{16}H_{32}N_4$ is a macrocyclic Schiff base amine ligand and L = Cl^-, Br^-, OH^-, NCS^-, $N_3{}^-$, CN^-, $NO_2{}^-$, or OH_2. Two very closely related geometrical isomers of $[Co(C_{16}H_{32}N_4)Cl_2]ClO_4$ have been prepared and characterized. Analysis of infrared spectra, chemical properties, and especially of the visible spectra of the $Co^{III}(C_{16}H_{32}N_4)L_2$ complexes implies that the ligands L are *trans* to one another. Analysis of visible spectra of the $Co^{III}(C_{16}H_{32}N_4)L_2$ complexes indicates that the macrocyclic Schiff base amine ligand, $C_{16}H_{32}N_4$, has an appreciably higher crystal field strength (Dq) than one finds for related primary and secondary amine ligands.

Of the known coordination complexes of Co(III) only a relatively few involve a macrocyclic ligand. The known macrocyclic complexes of Co(III) include vitamin B_{12},[3] the porphyrin and the phthalocyanine[4] complexes, and four cyclic tetradentate secondary amine complexes.[5-8] The chemistry of the B_{12} series of compounds exhibits many unusual features,[3,9] at least

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