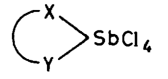
# The Chlorine-35 and Antimony-121 and -123 Nuclear Quadrupole Resonance Spectra of Five-membered Ring Chelate Derivatives of Antimony Pentachloride

**Claudine Gerard-Dion and Edwin A. C. Lucken** *
*Département de chimie physique, Section de Chimie de l'Université de Genève, Sciences II, 30, Quai E. Ansermet, 1211 Genève 4, Switzerland*

The $^{35}$Cl and $^{121,123}$Sb quadrupole resonance spectra of several five-membered ring chelate derivatives of antimony pentachloride are reported. Four of these are of known structure: the singly chelated derivatives of tropolone, *N*-methyloxamide, and *NN'*-dimethyloxadiamide, and the doubly chelated derivative of oxalic acid. The doubly chelated derivative of *NN'*-dimethyloxadiamide, of unknown crystal structure, has also been measured. The $^{35}$Cl resonance frequencies of the axial and equatorial chlorine atoms are quite distinct and, for the tropolone complex, imply a 10% difference between the ionicity of the axial and equatorial groups, and are affected to a different extent by the nature of the chelate group. The large value of the $^{121}$Sb asymmetry parameter of the oxalate complex is satisfactorily explained by the observed small angular deformations of the geometry from that of a regular octahedron.

It has been claimed that the values of $^{35}$Cl nuclear quadrupole resonance frequencies of the complexes of tin tetrachloride, $L_2SnCl_4$, may be used to determine the stereochemistry (*cis* or *trans*) of the complex.[1] Two recent studies[2,3] have cast doubt on this affirmation but it was nevertheless shown that some information on this question may be obtained from the temperature dependence of these frequencies.

The interpretation of the results for these tin tetrachloride complexes is hampered by the paucity of independent structural information. We have therefore undertaken a systematic study of a related series, the chelated compounds of the general formula (A). These compounds have the advantage that the chelate nature of the substituent imposes the *cis* geometry while the possibility of observing the $^{121}$Sb and $^{123}$Sb resonance frequencies adds yet another experimental parameter. Furthermore, *X*-ray crystal structures are available for a number of these derivatives, in particular for four related compounds in which the chelate ring has five members. Our initial studies therefore have concentrated on these and we report them here.



(A)

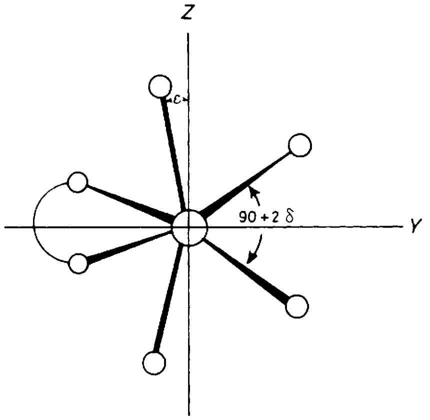


**Figure 1.** Idealised geometry and field-gradient axes of the chelated complexes

## Experimental

The complexes were all prepared according to published procedures.[4–7] N.q.r. spectra were measured on a Decca super-regenerative spectrometer, frequencies being compared with harmonics from an internal crystal-controlled oscillator. Temperatures were measured with a Hewlett–Packard 2802A digital thermometer and varied between 77 K and room temperature by using a cryostat controlled with an Artronix 5301-E temperature controller.

## Results and Discussion

The crystal structures of the compounds studied here all conform to the general scheme of Figure 1 and Table 1 shows the values of those structural parameters which are most relevant to the present discussion.

$^{35}$Cl *Frequencies*.—The $^{35}$Cl resonance frequencies at 77 K are shown in Table 2. In most cases the corresponding $^{37}$Cl resonances have also been observed.

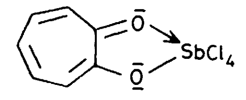
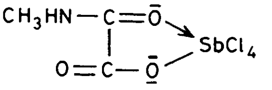
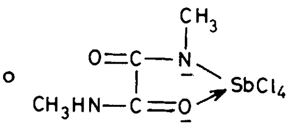
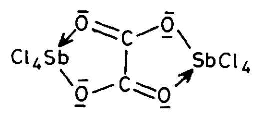
For most of the compounds shown here they fall into two distinct groups. It is most likely that one set of frequencies is to be associated with the chlorine atoms in the plane of the chelating group, the equatorial chlorine atoms, whereas the other set is to be associated with the axial chlorine atoms.

The temperature dependence of all these frequencies is perfectly normal and is illustrated by the data shown in Figure 2. In the range between 77 and 300 K the value of the resonance frequency can be fitted to a quadratic whose parameters are likewise given in Table 2. The relatively low degree of temperature dependence is consistent with the chlorine atoms responsible for the resonances being part of a relatively large and rigid molecule and thus is consistent with structure shown in Figure 1.

The structures shown in Table 1 are all such that the axial Sb–Cl bonds are longer than the equatorial Sb–Cl bonds. Both on general grounds and in the light of previous studies, for example for P–Cl bonds in chlorocyclophosphazenes[8] or Sb–Cl bonds in various $SbCl_3$ complexes,[9] it is to be expected that the longer Sb–Cl bonds are to be associated with the lower $^{35}$Cl resonance frequencies. This implies that the higher frequencies are due to the chlorine atoms in the equatorial position and the lower frequencies to those in the axial position. This attribution will be assumed from now on.

The correlation between frequency and bond length is shown in Figure 3. The slope (−0.010 Å per MHz) is slightly less than

**Table 1.** Structural parameters for chelated complexes

| | Compound | Ref. | $d(\text{Sb–Cl}_{eq})$/Å | $d(\text{Sb–Cl}_{ax})$/Å | $d(\text{Sb–O})$/Å | OSbO (°) (α) | $\text{Cl}_{eq}\text{SbCl}_{eq}$ (°) (β) | $\text{Cl}_{ax}\text{SbCl}_{ax}$ (°) (γ) |
|---|---|---|---|---|---|---|---|---|
| ● |  (I) | 4 | 2.308 (2) | 2.359 (2) | 2.030 (5) | 79.2 (3) | 100.2 (1) | 177 |
| ■ |  (II) | 5 | 2.324 (2)<br>2.324 (2) | 2.346 (2)<br>2.349 (2) | 2.067 (5)<br>2.102 (6) | 79.7 (2) | 100.4 (1) | 172.5 (1) |
| ○ |  (III) | 6 | 2.301 (5)<br>2.325 (5) | 2.340 (6)<br>2.356 (5) | 2.039* (12)<br>2.087 (10) | 79.5 (4) | 96.2 (4) | 175.4 (2) |
| ▲ |  (IV) | 7 | 2.293 (3)<br>2.297 (3) | 2.315 (4)<br>2.326 (4) | 2.170 (9)<br>2.173 (9) | 76.6 (3) | 103.2 (1) | 166.2 (1) |
| | | | 2.293 (3)<br>2.296 (3) | 2.318 (4)<br>2.325 (4) | 2.158 (8)<br>2.163 (8) | 76.6 (3) | 103.2 (1) | 166.3 (1) |

* Sb–N Bond.

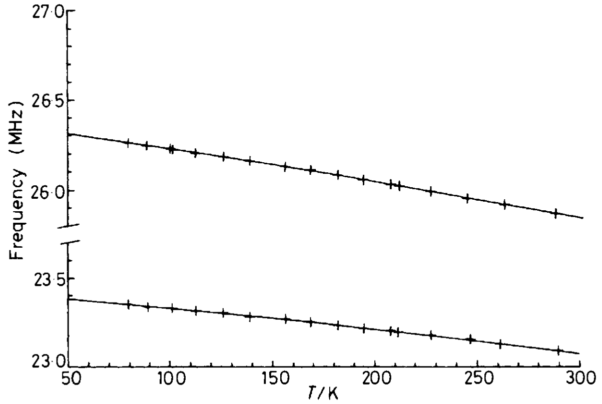


**Figure 2.** Temperature dependence of the $^{35}$Cl resonance frequencies of the tropolone–SbCl$_4$ complex

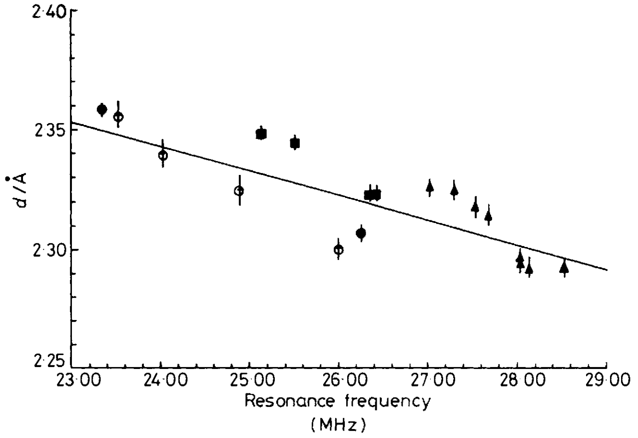


**Figure 3.** Correlation between Sb–Cl bond length and the corresponding $^{35}$Cl resonance frequency. The symbols are those shown for the compounds in Table 1

but of the same order of magnitude as that observed in the two investigations quoted above (−0.013 for the chlorocyclophosphazenes and −0.015 for the SbCl$_3$ complexes).

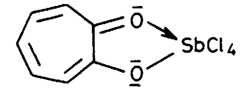
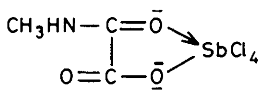
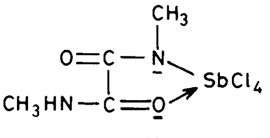
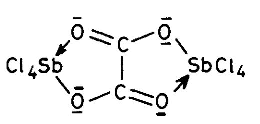
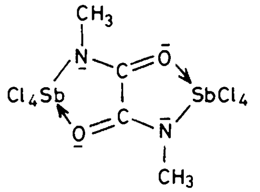
Implicit in the above argument is the assumption that the lengthening of Sb–Cl bonds is due to an increase in their polarity and that the lowering of the $^{35}$Cl resonance frequency is a further reflection of this increased polarity. This will be so if there is no significant conjugation between the chlorine and antimony atoms. If this is the case then the asymmetry parameter of the $^{35}$Cl quadrupole coupling tensors will be small and the coupling constant given by twice the resonance frequency. Furthermore, we can make the usual approximate analysis[10] of the coupling constant, $e^2Qq$, to yield the partial ionic character, $i$, of the Sb–Cl bond. It is assumed that, as usual, the $^{35}$Cl coupling constant is negative, leading to equation (1)

$$e^2Qq/e^2Qq_0 = 1 - i \qquad (1)$$

where $e^2Qq_0$ is the coupling constant of a chlorine atom forming a pure covalent bond (−110 MHz). The figures for the individual ionic characters of the Sb–Cl bonds together with the average ionic characters of the SbCl$_4$ fragment shown in Table 2 have been derived in this way.

Although the number of compounds described here is not large a number of tendencies are clear. For the tropolone complex there is a very well defined stereochemical effect on the Sb–Cl bonds, the quadrupole resonance spectra indicating a difference of 0.05 (10%) in the partial ionic characters of the axial and equatorial bonds. The other two compounds in which both atoms linked to antimony are oxygen atoms reveal that replacement of the seven-membered ring of tropolone by a

**Table 2.** $^{35}$Cl Resonance frequencies (MHz), temperature dependences, and Sb–Cl ionic characters

| Compound | Resonance frequency at 77 K (MHz) | Temperature dependence $\nu = \nu_0 + AT + BT^2$ | | | Ionic character of Sb–Cl bond | Average ionic character |
|---|---|---|---|---|---|---|
| | | $\nu_0$/MHz | $A$/kHz/K$^{-1}$ | $B$/Hz/K$^{-2}$ | | |
|  (I) | 23.350 | 23.43 | −9.59 | −0.7 | 0.575 | 0.549 |
| | 26.259 | 26.39 | −14.8 | −1.1 | 0.523 | |
|  (II) | 25.128 | 25.30 | −20.9 | −1.6 | 0.543 | 0.530 |
| | 25.505 | 25.62 | −12.7 | −2.8 | 0.536 | |
| | 26.356 | 26.48 | −13.8 | −2.4 | 0.521 | |
| | 26.420 | 26.55 | −14.8 | −2.5 | 0.520 | |
|  (III) | 23.531 | 23.63 | −10.8 | −2.1 | 0.572 | 0.552 |
| | 24.028 | 24.16 | −14.1 | −2.6 | 0.563 | |
| | 24.886 | 24.97 | −8.09 | −2.5 | 0.548 | |
| | 26.012 | 26.15 | −15.6 | −2.1 | 0.527 | |
|  (IV) | 27.022 | 27.13 | −11.6 | −3.4 | 0.509 | 0.495 |
| | 27.300 | 27.43 | −14.8 | −2.7 | 0.504 | |
| | 27.543 | 27.71 | −19.2 | −2.2 | 0.499 | |
| | 27.679 | 27.82 | −14.9 | −3.2 | 0.497 | |
| | 28.044 | 28.16 | −12.5 | −2.6 | 0.490 | |
| | 28.044 | 28.22 | −18.9 | −2.9 | 0.490 | |
| | 28.142 | 28.28 | −15.4 | −2.3 | 0.488 | |
| | 28.537 | 28.69 | −16.2 | −3.2 | 0.481 | |
|  (V) | 24.716 | 24.83 | −13.8 | −1.6 | 0.551 | 0.530 |
| | 25.619 | 25.73 | −12.7 | −2.1 | 0.534 | |
| | 26.539 | 26.66 | −13.9 | −1.8 | 0.517 | |
| | 26.573 | 26.65 | −8.81 | −1.0 | 0.517 | |

more electron-attracting fragment decreases the average ionic character and decreases the spread in ionic character, the axial chlorine atoms being more affected than the equatorial chlorine atoms. In the two remaining compounds one of the donor oxygen atoms has been replaced by the less electronegative methylamino group. Comparison of the analogous pairs, (**II**) + (**III**) and (**IV**) + (**V**), shows that this substitution increases the average ionic character by *ca.* 0.035, the main effect once again being manifested by the lower frequency axial chlorine atoms.

All these observations are, no doubt, manifestations of the various stereochemical phenomena usually known as the *trans*-effect. They provide a possible explanation of the observation [11] that in the complexes of SbCl$_5$ the frequency of the chlorine atom *trans* to the ligand is sometimes lower and at other times higher than the resonances of the four chlorine atoms *cis* to the ligand. To test this it would be necessary to study a closely related series of ligands where the local environment of the SbCl$_5$ group is as close to one having four-fold symmetry as possible.

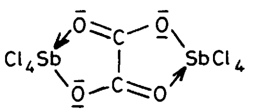
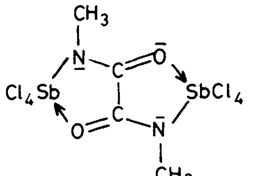
$^{121,123}$Sb *Frequencies.*—Of the five compounds reported here only two have shown any signs of the antimony resonances, despite repeated efforts at finding them. Furthermore, one of these two compounds is precisely the one for which structural data are not available. The results at 77 K are shown in Table 3 The coupling constants are assumed to be positive.

For the oxalate, where, in agreement with the crystal structure which reveals the presence of two non-equivalent molecules in the unit cell there are ten antimony resonances, the antimony parameters could be followed over the whole range between 77 K and room temperature. The temperature dependence of both the coupling constant and the asymmetry parameter could be satisfactorily fitted to a quadratic. The coefficients of these quadratics are likewise given in Table 3 and do not call for any particular comment.

The coupling constants themselves are in the same range as those of other six-co-ordinated derivatives of pentavalent antimony, for example the various donor–acceptor complexes of SbCl$_5$ [11,12] but the large asymmetry parameters call for some comment. For polyco-ordinated nuclei such as these the partial field gradient model is more appropriate than one using specific hybrid orbitals.[13] If all the bond angles in these compounds were 90° then a model based on the placing of three pairs of equivalent partial field gradient tensors on each of the pairs of equivalent ligands predicts an asymmetry parameter, $\eta$, identical to zero. Quite small deformations of the bond angles from 90° lead however at once to quite appreciable values of $\eta$.

The dependence of the asymmetry parameter on the deformation from octahedral geometry may be quantified with the aid

**Table 3.** $^{121}$Sb Resonance frequencies, quadrupole coupling constants, and asymmetry parameters

| Compound | Frequency (MHz) at 77 K | Attribution | η | Coupling constant (MHz) | Temperature dependences | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $e^2Qq_0$ | + | $AT$ | + | $BT^2$ |
| | | | | | $\eta_0$ | + | $AT$ | + | $BT^2$ |
|  (IV) | 23.03 | $^{123}$Sb ($1/2 \longleftrightarrow 3/2$) | | | | | | | |
| | 26.78 | $^{123}$Sb ($3/2 \longleftrightarrow 5/2$) | | $^{121}$Sb: 158.4 | 159.6 | | $-1.36 \times 10^{-2}$ | | $-1.72 \times 10^{-5}$ |
| | 28.98 | $^{121}$Sb ($1/2 \longleftrightarrow 3/2$) | 0.473 | | 0.472 | | $2.0 \times 10^{-5}$ | | $4.5 \times 10^{-8}$ |
| | 42.27 | $^{123}$Sb ($5/2 \longleftrightarrow 7/2$) | | $^{123}$Sb: 201.9 | | | | | |
| | 45.67 | $^{121}$Sb ($3/2 \longleftrightarrow 5/2$) | | | | | | | |
| | 24.94 | $^{123}$Sb ($1/2 \longleftrightarrow 3/2$) | | | | | | | |
| | 25.32 | $^{123}$Sb ($3/2 \longleftrightarrow 5/2$) | | $^{121}$Sb: 151.9 | 152.7 | | $-1.13 \times 10^{-2}$ | | $2.4 \times 10^{-5}$ |
| | 29.78 | $^{121}$Sb ($1/2 \longleftrightarrow 3/2$) | 0.573 | | 0.581 | | $-1.11 \times 10^{-4}$ | | $1.0 \times 10^{-7}$ |
| | 40.07 | $^{123}$Sb ($5/2 \longleftrightarrow 7/2$) | | $^{123}$Sb: 193.6 | | | | | |
| | 43.11 | $^{121}$Sb ($3/2 \longleftrightarrow 5/2$) | | | | | | | |
|  (V) | 16.44 | $^{121}$Sb ($1/2 \longleftrightarrow 3/2$) | 0.67 | $^{121}$Sb: 78 | | | | | |
| | 21.82 | $^{121}$Sb ($3/2 \longleftrightarrow 5/2$) | (±0.01) | (±1) | | | | | |

of a simple model. Based on the typical structure shown in Figure 1 together with the data of Table 1 we use an ideal structure which has $C_{2v}$ symmetry and where the closing of the XSbY angle with respect to 90°(2δ) is equal to the corresponding opening of the $Cl_{eq}SbCl_{eq}$ angle. Furthermore each of the axial Cl–Sb bonds is inclined by an angle ε towards the chelating group. Partial field gradients $P_1$—$P_3$ are associated with the equatorial chlorine atoms, the axial chlorine atoms, and the chelating oxygen atoms respectively. Straightforward manipulation then yields relationships (2) and (3) between these parameters, the field gradient, and the asymmetry parameter.

$$e^2Qq = e^2Q\left[2P_2(1 - \frac{3}{2}\sin^2\varepsilon) - (P_1 + P_3)\right] \quad (2)$$

$$e^2Qq{\cdot}\eta = e^2Q{\cdot}3\left[(P_1 - P_3)\sin 2\delta - P_2\sin^2\varepsilon\right] \quad (3)$$

In labelling the axes (Figure 1) it was assumed that the partial field gradients, $P_1$ and $P_2$, due to the chlorine atoms are, in accordance with the electronegativity scale, greater than the partial field gradient associated with the oxygen atoms.

To obtain any further information concerning the angles we need independent estimates of the partial field gradients $P_1$—$P_3$. For $P_1$ and $P_2$ we may use the $^{35}$Cl resonances to obtain the ionicity of the Sb–Cl bonds *via* the usual analysis[10] and hence equate $P_1$ and $P_2$ to the appropriate fraction of the field gradient, $P_0$, arising from a completely homopolar distribution of electrons in the antimony ligand bond where $\nu_{ax}$, $\nu_{eq}$ are measured in MHz and 54.5 MHz is the $^{35}$Cl resonance frequency of molecular chlorine.

The partial field gradients at the antimony atom are then given by equations (4) and (5). Equation (2) may then be used to derive the value of $P_3$ if a value is assumed for $P_0$. The term in $\sin^2\varepsilon$ may here be safely neglected since the experimental values of ε are less than 7°. If the orbitals used by the antimony atoms are assumed to be $sp^3d^2$ hybrids then $P_0$ is one-half that of a single electron in an antimony 5*p* orbital. For the corresponding $^{121}$Sb coupling constant we assume $e^2QP_0$ to have the value 830 MHz.[14] The value of $P_3/P_0$ so obtained may be substituted in equations (2) and (3), together with the experimental values of δ and ε for the oxalate complex (6.7 and 6.9° respectively for both sites). The four lowest $^{35}$Cl frequencies are attributed to the axial chlorine atoms while the four highest are attributed to the equatorial chlorine atoms. In this way average values of $P_1/P_0$ and $P_2/P_0$ of 0.513 and 0.498 are obtained, thus yielding *via* equation (2) the value of 0.293 for $P_3/P_0$. Equation (3) then gives the value of η equal to 0.7. It is clear that these small angular deformations are quite sufficient to account for the large values of η which are observed. As for the value of $P_3/P_0$, the effective population of the antimony orbitals bonded to the oxygen atom, we may compare it with the values 0.282 and 0.267 obtained in the same way for the corresponding Sb–O bond in the complexes formed by $SbCl_5$ with acetophenone and diethyl ether respectively.[12,15]

$$P_1 = (1 - i_{eq})P_0 = \frac{\nu_{eq}^{Cl}}{54.5}{\cdot}P_0 \quad (4)$$

$$P_2 = (1 - i_{ax})P_0 = \frac{\nu_{ax}^{Cl}}{54.5}{\cdot}P_0 \quad (5)$$

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