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THE STUDY OF COORDINATION STATE FOR 1:1 MOLECULAR COMPLEXES OF $AsCl_3$ AND $SbCl_3$ WITH DONORS CONTAINING NITROGEN OR SULPHUR BY MEANS OF NQR

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ABSTRACT

The ^{35}Cl, ^{75}As, and ^{121}Sb NQR spectra of MCl_3L (M = As, Sb; L = trimethylamine, aniline, tmtu(1,1,3,3,-tetramethylthiourea), dmit(1,3-dimethyl-2(3H)-imidazolethione) have been investigated. ^{35}Cl NQR signals were observed at room temperature in the separate regions of about 11 MHz, 15—16 MHz, and 23—25 MHz in $AsCl_3L$ and 8.8 MHz, 13—14 MHz, and 17—20 MHz in $SbCl_3L$. ^{75}As NQR lines were detected at 56—71 MHz in $AsCl_3L$. In $SbCl_3L$ the nuclear quadrupole coupling constant of ^{121}Sb is about 326 MHz and the asymmetry parameter is very small. The Zeeman effect on ^{35}Cl and ^{121}Sb NQR lines was examined for $SbCl_3 \cdot C_6H_5NH_2$ at room temperature and the electric field gradient at the Sb atom and its small asymmetry parameter is discussed using the Townes—Dailey treatment.

INTRODUCTION

In the 1:1 complexes of MCl_3L (M = As, Sb; L = ligand containing nitrogen or sulphur atom), a pseudo trigonal bipyramidal (TBP) arrangement of substituents about the central atom may be predicted on the basis of an idealized geometry for MCl_3LE (E = lone pair of electrons) assuming a stereoactive lone pair.

Figure 1 shows isomeric possibilities for an MCl_3LE system. According to the X-ray analysis [1], the structure of $AsCl_3 \cdot$dmit is well described as a dimer which consists of two square-pyramidal $AsCl_3 \cdot$dmit units sharing a

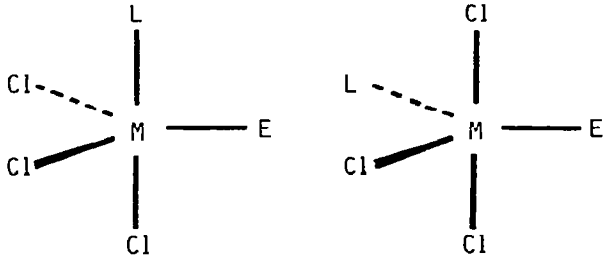


Fig. 1. Possible isomers of an MCl_3LE system.

common edge through long bridging chlorine atoms and in which the sulphur atoms occupy the apices of the two pyramids on the opposite sides of the plane formed by the six chlorine atoms. The monomeric unit of $AsCl_3 \cdot$dmit is regarded as a pseudo-TBP geometry if long bridging As · · · Cl bonds are ignored for simplicity. In this monomeric unit, the coordinated sulphur atom is at an equatorial position, whereas nitrogen atoms in $AsCl_3 \cdot N(CH_3)_3$ and $SbCl_3 \cdot C_6H_5NH_2$ occupy the axial positions [2, 3]. This difference in the position of the coordinated atom is considered to be reflected in the NQR frequencies of the chlorine and central atoms.

In this investigation, therefore, the ^{35}Cl, ^{75}As, and ^{121}Sb NQR spectra were observed for the MCl_3LE system. Furthermore, the Zeeman effect on ^{35}Cl and ^{121}Sb NQR lines was examined for $SbCl_3 \cdot C_6H_5NH_2$, in order to compare the orientation of the electric field gradient (efg) axes observed with that calculated by the Townes—Dailey treatment assuming sp^2 hybrid orbitals on the Sb atom.

Brill [4] has already observed a part of the NQR spectra in $SbCl_3 \cdot C_6H_5NH_2$ using polycrystalline samples and tried to explain the cause of the small asymmetry parameter of antimony in terms of the point-charge and tangential sphere—point charge models.

EXPERIMENTAL

Arsenic trichloride, antimony trichloride, trimethylamine, aniline, and tmtu were purchased from commercial sources and were used without further purification. Dmit was prepared by the method described in the literature [5].

The complexes of $AsCl_3 \cdot N(CH_3)_3$, $AsCl_3 \cdot$tmtu, $AsCl_3 \cdot$dmit, and $SbCl_3 \cdot$tmtu were prepared by the procedures in the literature [1, 2, 6]. The complex $SbCl_3 \cdot C_6H_5NH_2$ was obtained by melting stoichiometric amounts of $SbCl_3$ and $C_6H_5NH_2$ in a sealed glass tube. The single crystal of $SbCl_3 \cdot C_6H_5NH_2$ was grown by the Bridgman—Stockbarger method. These complexes were identified by CHN elemental analyses and measurement of melting point. Their analytical data are listed in Table 1.

TABLE 1

Melting points and analytical data

Compound	m.p. (°C)	Calculated (%)			Found (%)		
		C	H	N	C	H	N
$AsCl_3 \cdot N(CH_3)_3$		21.77	5.44	8.47	21.80	5.45	8.41
$AsCl_3 \cdot$tmtu	117—118	19.15	3.89	8.94	19.25	3.89	8.89
$AsCl_3 \cdot$dmit	147—150	19.41	2.59	8.94	19.50	2.58	9.08
$SbCl_3 \cdot C_6H_5NH_2$	100—101	22.43	2.19	4.36	22.45	2.28	4.26
$SbCl_3 \cdot$tmtu	189—191	16.67	3.36	7.78	16.56	3.27	7.74

The NQR spectrometers used were super-regenerative oscillators with frequency modulation or Zeeman modulation. Resonance lines were observed on an oscilloscope or a recorder. For $SbCl_3 \cdot C_6H_5NH_2$, the Zeeman effect on the resonance lines was observed using the magnetic field of about 25 mT and examined by means of the zero-splitting cone method at room temperature.

RESULTS AND DISCUSSION

Table 2 shows the ^{35}Cl and ^{75}As NQR frequencies of the $AsCl_3L$ complexes at room temperature and 77 K. In $AsCl_3 \cdot N(CH_3)_3$ and $AsCl_3 \cdot$dmit the axial As—Cl bond distances are longer than the equatorial ones as shown in Figs. 1 and 3. In general, the ^{35}Cl NQR frequency for the longer bond is lower than that for the shorter one. Therefore, these ^{35}Cl signals are assigned as in Table 2.

In $AsCl_3 \cdot N(CH_3)_3$ two ^{35}Cl NQR lines with an intensity ratio of 1:2 were observed at room temperature and dry ice temperature. The number of the observed ^{35}Cl NQR lines does not coincide with that expected from the crystal structure [2]. The temperature coefficient of the resonance line due to the axial ^{35}Cl atom was positive. It seems to be attributable to the motion of the trimethylamine at the *trans* position.

The molecular structure of $AsCl_3 \cdot$tmtu is assumed to be similar to that of $AsCl_3 \cdot$dmit, because tmtu resembles dmit very closely in ligand properties. Therefore, the ^{35}Cl NQR lines in $AsCl_3 \cdot$tmtu are assigned as listed in Table 2. In $AsCl_3 \cdot$dmit the ^{35}Cl NQR line corresponding to the chlorine atom in the longest axial As—Cl bond was not observed.

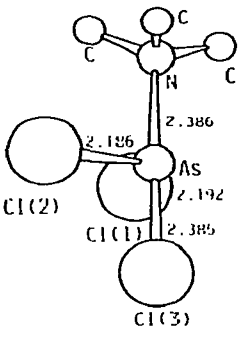
According to the Townes—Dailey treatment, the ionic character in these compounds is estimated to be 46—58% for the equatorial bonds and 71—78% for the axial ones, i.e. the electron density of the axial bonding orbital of the As atom is less than that of the equatorial one. As is obvious from Figs. 2 and 3, the nitrogen atom in $AsCl_3 \cdot N(CH_3)_3$ occupies an axial position *trans* to a chlorine atom, while the sulphur atom in $AsCl_3 \cdot$dmit occupies an

TABLE 2

The NQR frequencies for $AsCl_3L$

Compound	Temp. (K)	Frequency (MHz)			
		^{75}As	^{35}Cl	^{35}Cl	^{35}Cl
$AsCl_3 \cdot N(CH_3)_3$	~300	56.65	24.79(e)[a]	14.98(a)	
	195	58.76[b]	25.07(e)	14.45(a)	
$AsCl_3 \cdot$tmtu	~300	63.84	23.33(e)	16.08(a)	11.25(a)
	77	67.22	23.54(e)	16.50(a)	
$AsCl_3 \cdot$dmit	~300	71.05	23.34(e)	15.04(a)	
	77	75.34	23.94(e)	15.23(a)	

[a] e and a in parentheses stand for equatorial and axial chlorines. [b] Value at 77 K.



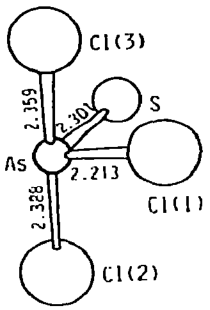


Fig. 2. The molecular structure of $AsCl_3{\cdot}N(CH_3)_3$.

Fig. 3. Atomic arrangement about As in $AsCl_3{\cdot}$dmit.

equatorial position. In $AsCl_3{\cdot}$tmtu, the sulphur atom is considered to occupy an equatorial position from the results of NQR. This arrangement is consistent with the concept of the valence shell electron repulsion (VSEPR) model suggested by Gillespie and Nyholm [7]. In other words, a lone pair or a strong donor occupies an equatorial position and a weak donor occupies an axial position, since the repulsion among the bonding pairs and unshared pairs of valence electrons are minimized in such a configuration.

Table 3 shows the ^{35}Cl and ^{121}Sb NQR parameters for both $SbCl_3{\cdot}C_6H_5NH_2$ and $SbCl_3{\cdot}$tmtu complexes. The ^{35}Cl NQR lines were assigned, referring to the results of the $AsCl_3L$ complexes. In the case of $SbCl_3{\cdot}C_6H_5NH_2$, the assignment of ^{35}Cl NQR lines was confirmed by the Zeeman effect. The nuclear quadrupole coupling constants (e^2Qq/h) of the Sb atoms are nearly equal in both complexes and asymmetry parameters of the Sb atoms are very small, particularly in $SbCl_3{\cdot}C_6H_5NH_2$, in spite of the asymmetric environment about the antimony atom as shown in Fig. 4.

TABLE 3

NQR parameters for $SbCl_3L$ at room temperature

Compound		Frequency (MHz)		η	e^2Qq/h (MHz)
		ν_1	ν_2		
$SbCl_3{\cdot}C_6H_5NH_2$	^{121}Sb	48.94	97.77	0.030	326.2
	^{35}Cl	20.39(e)[a]		0.188	40.54
		19.36(e)		0.142	38.46
		13.95(a)			
$SbCl_3{\cdot}$tmtu	^{121}Sb	49.36	97.61	0.093	326.0
	^{35}Cl	17.51(e)			
		13.01(a)			
		8.81(a)			

[a] e and a in parentheses stand for equatorial and axial chlorines.

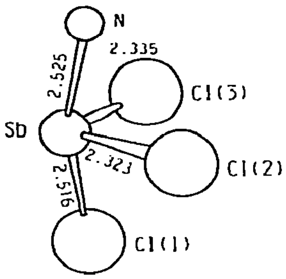


Fig. 4. Atomic arrangement about Sb in $SbCl_3 \cdot C_6H_5NH_2$.

The measurement of the Zeeman effect on ^{35}Cl and ^{121}Sb NQR lines was carried out for $SbCl_3 \cdot C_6H_5NH_2$ at room temperature in order to determine the orientations of the efg axes and to examine the cause of the small asymmetry parameter of the Sb atom. The zero-splitting patterns are reproduced in Fig. 5 for Cl(2), Cl(3), and ν_1 of ^{121}Sb NQR lines. Each resonance line gave two zero-splitting loci and the two-fold axis was determined from the symmetry of the observed patterns. Therefore, this crystal belongs to the monoclinic system and the two-fold axis obtained corresponds to the b-axis of the crystal. The orientations of the efg z-axis and the crystal b-axis are shown in Fig. 6. In order to determine the orientations of the efg axes of the Sb atom, angles between the z-axes of the Cl atoms and the two-fold axis were compared with those between the Sb—Cl bond directions and the b-axis from the results of the X-ray analysis. By this procedure, it was found that the ^{35}Cl signals at 20.39 MHz and 19.36 MHz correspond to Cl(2) and Cl(3) in Fig. 4, respectively. Figure 5 reveals that the efg z-axis of the Sb atom is directed toward the bisector of the Cl(2)—Sb—Cl(3) angle, i.e. the z-axis of Sb is coincident with the expected direction of the lone pair of electrons. Furthermore, the y- and x-axes are along the Sb—N bond direction and in the equatorial plane, respectively. The direction of the z-axis of Sb is compatible with that predicted in terms of the point charge and tangential sphere-point charge model calculations by Brill [4].

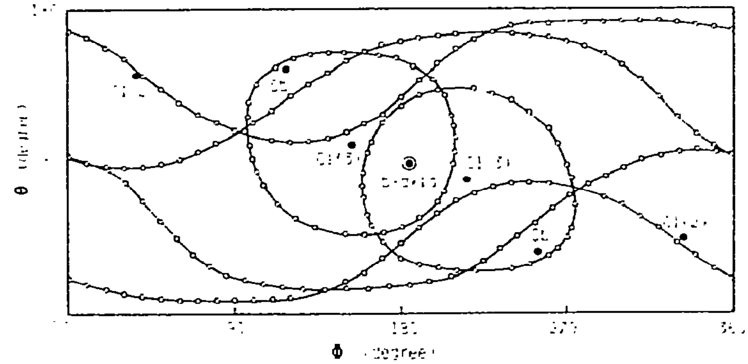


Fig. 5. The ^{35}Cl and ^{121}Sb zero-splitting patterns for $SbCl_3 \cdot C_6H_5NH_2$ at room temperature.

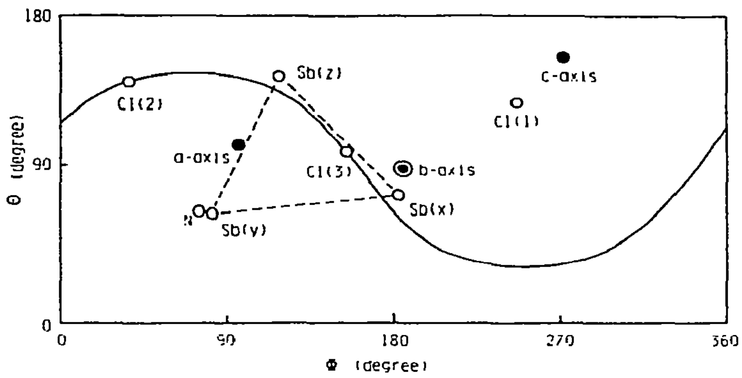


Fig. 6. The efg axes of ^{35}Cl and ^{121}Sb in $SbCl_3 \cdot C_6H_5NH_2$.

Generally, the trigonal-bipyramidal geometry of MX_5 complexes has been explained by assuming sp^3d hybrid orbitals on the central atom. In the case of the complexes studied in the present work, the central atoms are typical elements, so the contribution of the outer d-orbital is considered to be small. Therefore, we assumed the sp^2 hybrid and p_y orbitals for the bonding of the central atom. These orbitals on the central As and Sb atoms are given by

$$\begin{aligned}
\Psi_1 &= \phi_y \\
\Psi_2 &= (\cot\gamma)\phi_s + (1-\cot^2\gamma)^{1/2}\phi_z \\
\Psi_3 &= (1/2)^{1/2}\ [(1-\cot^2\gamma)^{1/2}\phi_s - (\cot\gamma)\phi_z + \phi_x] \\
\Psi_4 &= (1/2)^{1/2}\ [(1-\cot^2\gamma)^{1/2}\phi_s - (\cot\gamma)\phi_z - \phi_x]
\end{aligned} \qquad (1)$$

where ϕ_s, ϕ_x, ϕ_y, and ϕ_z are the s, p_x, p_y, and p_z orbitals of the central atoms respectively, and 2γ is the equatorial Cl—M—Cl angle. Both the Ψ_3 and Ψ_4 are used for the formation of the equatorial bonds with the chlorine atoms, and the Ψ_2 orbital is occupied by a lone pair of electrons. Furthermore, the Ψ_1 orbital which does not take part in the sp^2 hybridization, i.e. the p_y orbital of the central atom, is used for the formation of the axial bonds by three centre four electron bonds. The electron populations of both Ψ_3 and Ψ_4 orbitals are represented by b, which can be evaluated using the NQR frequencies of the equatorial chlorine atoms. The electron population of the Ψ_2 orbital is assumed to be 2, since it is occupied by a lone pair of electrons, and that of the Ψ_1 orbital is represented by a, which cannot be estimated because the NQR signal of the nitrogen atom *trans* to the chlorine atom was not detected. Then, the occupation numbers of p_x, p_y, and p_z orbitals on the central atom (designated as N_x, N_y, and N_z) are expressed by

$$\begin{aligned}
N_x &= b \\
N_y &= \mathrm{a} \\
N_z &= 2(1-\cot^2\gamma) + b\cot^2\gamma
\end{aligned} \qquad (2)$$

The quadrupole coupling constants for the central atom are expressed with respect to the x, y, and z components of the efg axes by the equations

$$e^2Qq_{xx}/e^2Qq_0 = -[(N_y + N_z)/2 - N_x] = [(b-a)/2 - (1-b/2)(1-\cot^2\gamma)]$$
$$e^2Qq_{yy}/e^2Qq_0 = -[(N_z + N_x)/2 - N_y] = [a - b - (1-b/2)(1-\cot^2\gamma)]$$
$$e^2Qq_{zz}/e^2Qq_0 = -[(N_x + N_y)/2 - N_z] = [(b-a)/2 + (2-b)(1-\cot^2\gamma)] \qquad (3)$$

where e^2Qq_0 is the quadrupole coupling constant due to one p electron of the central atom. Using eqns. (1—3) the asymmetry parameter, η and the values of e^2Qq_{ii}/e^2Qq_0 (ii = xx, yy and zz) were calculated as a function of N_y (= a) for both the complexes of $SbCl_3 \cdot C_6H_5NH_2$ and $AsCl_3 \cdot N(CH_3)_3$. The results are illustrated graphically in Figs. 7 and 8. In the case of $SbCl_3 \cdot C_6H_5NH_2$, the asymmetry parameter is found to be 0.03 for the ^{121}Sb NQR line. The values of N_y corresponding to η = 0.03 are about 0.35, 0.37, 0.66 and 0.68 from Fig. 7. However, at N_y = 0.66 and 0.68, the maximum value of $|e^2Qq_{ii}|$ changes from $|e^2Qq_{zz}|$ to $|e^2Qq_{xx}|$. Moreover, at N_y = 0.37,

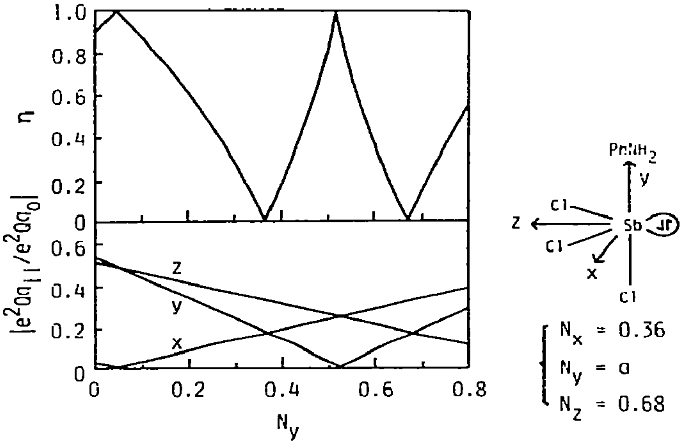


Fig. 7. Plots of $|e^2Qq_{ii}/e^2Qq_0|$ and η as a function of N_y in $SbCl_3 \cdot C_6H_5NH_2$.

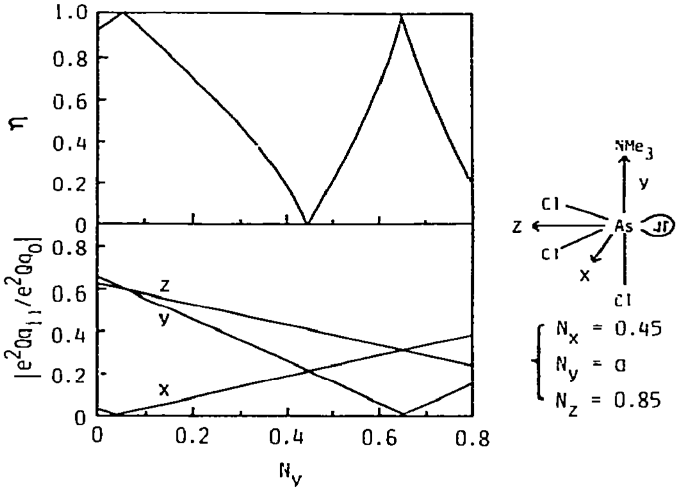


Fig. 8. Plots of $|e^2Qq_{ii}/e^2Qq_0|$ and η as a function of N_y in $AsCl_3 \cdot N(CH_3)_3$.

the values of $|e^2Qq_{ii}|$ are in the order of $|e^2Qq_{zz}| > |e^2Qq_{xx}| > |e^2Qq_{yy}|$. Therefore, the value of N_y should be 0.35 at which the order of $|e^2Qq_{ii}|$ is $|e^2Qq_{zz}| > |e^2Qq_{yy}| > |e^2Qq_{xx}|$ and the efg axes are coincident with the results of the Zeeman effect.

The contribution of the chlorine atom *trans* to the nitrogen atom to N_y is estimated to be 0.25 from ^{35}Cl NQR so that the contribution of the nitrogen atom to N_y is 0.10, since the total of N_y is 0.35. The bond distances of the axial Sb—N and Sb—Cl bonds are nearly equal (2.525 Å and 2.516 Å, respectively), but single bond radii for the nitrogen and chlorine atoms are 0.74 Å and 0.99 Å, respectively [8]. The Sb—N bond, therefore, seems to be fairly weak compared with the Sb—Cl bond. Consequently, the value of N_y calculated from this model seems to be reasonable.

The similar calculation was carried out for $AsCl_3 \cdot N(CH_3)_3$ although the asymmetry parameter and the directions of the efg axes were not obtained for the As atom. We assumed that the asymmetry parameter and the orientations of the efg axes of the As atom in this complex are similar to those of the Sb atom in $SbCl_3 \cdot C_6H_5NH_2$ since the molecular structures of both complexes are similar. The value of N_y is estimated to be about 0.43 at $\eta = 0.03$. The contribution of the nitrogen atom to N_y is 0.16, which was estimated from the NQR results of the *trans* chlorine atom. The contribution of the nitrogen atom in $AsCl_3 \cdot N(CH_3)_3$ is somewhat large compared with that in $SbCl_3 \cdot C_6H_5NH_2$. It may be explained in terms of the difference in the basicity between trimethylamine and aniline since the former is more basic than the latter.

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