cm^{-2} for the equivalent conductance was obtained for the related compound $(CH_3)_4NBrCl_2$ while a value of 201 ohm^{-1} cm^{-2} has been reported for $(CH_3)_4NNO_3$.[13]

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Zeeman Effect on the Pure Quadrupole Resonance of Mercuric Chloride

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A study of the Zeeman effect of the ^{35}Cl pure quadrupole resonance was carried out on a single crystal of mercuric chloride at about 23°. The mercuric chloride molecule is thought to be linear, because the bond angle deduced from the maximum field gradients of the two chlorine atoms is 179° 54′ ± 6′. The angle between the Hg–Cl bonds of neighboring molecules is 77° 0′ ± 5′. This result agrees with that of the X-ray diffraction by Braekken, *et al.*, better than that by Grdenić. The asymmetry parameters for the higher and lower resonance lines are found to be 0.087 ± 0.005 and 0.085 ± 0.005, respectively. The corresponding coupling constants are 44.445 and 44.073 Mc/sec, respectively. From these values, the ionic character and double bond character of the Hg–Cl bond for the higher line are calculated to be 52.2 and 2.1%, whereas those for the lower line are 52.6 and 2.0%. Therefore, the present results show that there is no so significant difference in bond nature between the two bonds as might be expected from arrangement of the chlorine atoms in the crystal.

Introduction

The pure quadrupole resonance frequencies for ^{35}Cl of mercuric chloride ($HgCl_2$) and their temperature dependence was investigated by Buyle-Bodin and Monfils,[1] using a powder sample. On the other hand, pressure shifts of resonance frequencies were studied by Dautreppe and Dreyfus.[2] In this connection, the studies of the Zeeman effect on the resonance of its single crystal will bring about some additional information.

The quadrupole interaction for ^{35}Cl with no external magnetic field gives rise to doubly degenerate levels as follows[3]

$$E_{\pm 1/2} = -(eQq_{zz}/4)(1 + \eta^2/3)^{1/2} \tag{1}$$

$$E_{\pm 3/2} = (eQq_{zz}/4)(1 + \eta^2/3)^{1/2} \tag{2}$$

where η is an asymmetry parameter defined as

$$\eta = (q_{xx} - q_{yy})/q_{zz} \tag{3}$$

and q_{xx}, q_{yy}, and q_{zz} are the electric field gradients in the direction of the x, y, and z axes, respectively, representing the largest for the z axis and the smallest for the x axis. When a magnetic field is applied, each doubly-degenerate level splits into two levels and four resonance lines are to be observed as shown in Figure 1. Obviously, the splitting of the level depends on the orientation of the magnetic field relative to the principal axes of the field gradient. For special orientations of the magnetic field, the resonance frequency corresponding to the transition from $E_{-1/2}$ to $E_{-3/2}$ is equal to that of $E_{+1/2}$ to $E_{+3/2}$. That is, the inner two lines coalesce to a single line. This condition is satisfied, when the following relation is satisfied[4]

$$\sin^2 \theta = 2/(3 - \eta \cos 2\phi) \tag{4}$$

where θ and ϕ are the coordinates of the magnetic field with respect to the principal axes. In this way, a cone about the z axis can be drawn by the θ and ϕ which satisfy eq 4. This is the so-called zero-splitting cone and is circular when $\eta = 0$, but roughly elliptical when $\eta \neq 0$. So the Zeeman study allows one to determine both the value of η and the direction of the principal axes of the field gradient.

The crystal structure of mercuric chloride has been determined from X-ray diffraction.[5,6] It was found to be orthorhombic with four molecules in its unit cell, and two chloride atoms in a molecule are crystallographically nonequivalent. The structural parameters showed the mercuric chloride molecule to be linear.

The purpose of the present investigation is to obtain some structural data for the mercuric chloride molecule in the crystalline state such as the bond character of Hg–Cl and the bond angle ∠Cl–Hg–Cl.

Experimental Section

Commercial mercuric chloride was purified by recrystallization and sealed in a glass cylinder (inner diameter 2.0 cm), the bottom of which was tapered to a capillary with a length of 15 cm. The single crystal was prepared by lowering the container slowly (at about 0.2 cm/hr) through a vertical furnace which had a proper temperature gradient.

The spectrometer consisted of a super-regenerative oscillator and a detector. The resonance lines were observed on an oscilloscope. The Zeeman field of about 150 gauss was furnished by

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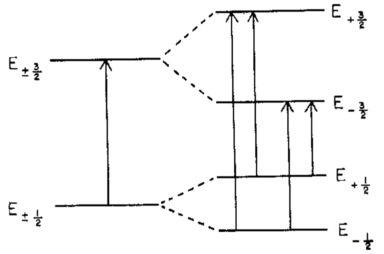

Figure 1.—Splitting of the energy levels for $I = {}^3/_2$ by the Zeeman effect.

the Helmholtz coil. The crystal could be rotated about the rotational axis which fixed the crystal, and the angle Φ could be measured with the error ±0.1°. On the other hand, the magnetic field could be rotated in a horizontal plane, and the angle Θ could be measured with the error ±1′.

The present experiment was performed at about 23°.

Results and Discussion

The pure quadrupole resonance lines for ^{35}Cl in mercuric chloride were observed at $\nu_1 = 22.251$ Mc/sec and $\nu_2 = 22.064$ Mc/sec at room temperature. The patterns of the zero-splitting direction were obtained by the measurement of the Zeeman effect for each resonance line. The Zeeman patterns for the ν_1 resonance line were found to be quite similar to those for ν_2. Thus it is shown that the lines ν_1 and ν_2 are due to two kinds of chlorine atoms Cl_1 and Cl_2 in the molecule $HgCl_2$. The Zeeman patterns are reproduced in Figure 2.

The directions of the principal axes of the field gradient were determined from these Zeeman patterns by the method used by Shimomura.[7] Since the z axis of the field gradient at a chlorine atom is considered to be coincident with the direction of the Hg–Cl bond, the angle between any two Hg–Cl bonds can be calculated. The results are listed in Table I, where $\angle Cl_{1A}$–Hg–Cl_{2A} and $\angle Cl_{1B}$–Hg–Cl_{2B} are intramolecular bond angles.

TABLE I

THE ANGLES BETWEEN Hg–Cl BONDS

	$Hg-Cl_{1A}$	$Hg-Cl_{2A}$	$Hg-Cl_{1B}$
$Hg-Cl_{2A}$	179° 56′		
$Hg-Cl_{1B}$	77° 0′	76° 59′	
$Hg-Cl_{2B}$	77° 1′	77° 0′	180° 0′

The values of the asymmetry parameter η are determined by the equation[4]

$$\eta = 3(\sin^2\theta_{\max} - \sin^2\theta_{\min})/(\sin^2\theta_{\max} + \sin^2\theta_{\min}) \quad (5)$$

Consequently, the quadrupole coupling constants are calculated by the equation

$$\nu = (eQq_{zz}/2h)(1 + \eta^2/3)^{1/2} \quad (6)$$

These values of η and eQq_{zz} are listed in Table II.

The bond angles obtained from the Zeeman analysis are given in Table III together with those calculated from the atomic coordinates determined by the X-ray analysis in the solid state[5,6] and the electron diffraction in the gaseous state.[8] The bond angle deduced from the Zeeman analysis is in good agreement with those of the X-ray analysis. This shows that the mercuric chloride molecule in the crystal is linear. The angles between Hg–Cl bonds in a molecule and its neighbor are listed in Table IV, where the numbering of atoms for the Zeeman results may be reversed, because the two cases cannot be distinguished. Whichever case may be adopted, the present results are in good agreement with those by Braekken and Scholten.[5] However, the angles obtained from Grdenić's data are larger than our values by about 9°, which is beyond our experimental error.

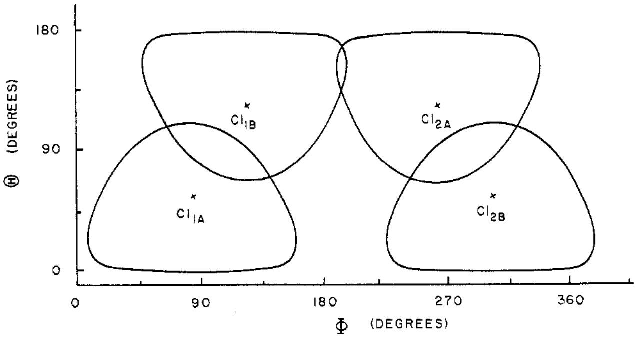

Figure 2.—Zero-splitting direction patterns of the Zeeman lines of $HgCl_2$. The axis of $\Theta = 0$ is taken as the rotational axis of the sample tube. The plane of $\Phi = 0$ is arbitrarily chosen.

TABLE II

THE VALUES OF η AND eQq_{zz} OF CHLORINE ATOMS IN Hg–Cl BONDS

	ν, Mc/sec	η	eQq_{zz}, Mc/sec
$Hg-Cl_1$	22.251	0.087 ± 0.005	44.445
$Hg-Cl_2$	22.064	0.085 ± 0.005	44.073

TABLE III

THE Cl–Hg–Cl BOND ANGLE IN MERCURIC CHLORIDE

	Zeeman anal	X-ray anal[5]	X-ray anal[6]	Electron diffraction
Bond angle	179° 54′ ± 6′	177° 48′	179° 59′	180°

Since it is known from the X-ray analysis that the a axis is perpendicular to all Hg–Cl bonds, the direction of the single crystal prepared in the present experiment can be determined. In this way, it was found that the c axis of the crystal deviated from the rotational axis of the sample container by about 27.5°. This means that the direction of the crystal might be governed by the orientation of the crystallite formed initially in the capillary. The angles between the principal axes of the field gradients x, y, and z and the crystal axes a, b, and c are given in Table V. It is noted that the x axis is along the a axis, that the y and z axes are in the bc plane, and that the present results agree with those of Braekken, *et al.*, better than those of Grdenić.

The ionic character and the double bond character

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