

## $^{35}\text{Cl}$ Zeeman quadrupole spectra in $\text{CoHgCl}_4 \cdot 4\text{H}_2\text{O}$

V RAMAKRISHNA, G SATYANANDAM, B V R R K MURTY  
and C R K MURTY

Department of Physics, Nagarjuna University, Nagarjunanagar 522 510

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**Abstract.** A new  $^{35}\text{Cl}$  nuclear quadrupole resonance was reported at room temperature for the first time in  $\text{CoHgCl}_4 \cdot 4\text{H}_2\text{O}$  at 20.583 MHz. The results of the Zeeman effect revealed that the principal  $Z$ -direction is parallel to  $b$  axis and the value of the asymmetry parameter  $\eta$  is 0.042. The estimated covalency is found to be 0.38.  $^{35}\text{Cl}$  resonance was also observed at room temperature in deuterated crystal  $\text{CoHgCl}_4 \cdot 4\text{D}_2\text{O}$  at 20.598 MHz. No new results were observed from the Zeeman effect studies in this crystal. The line widths, substitutional effects and covalency of the bond are also discussed.

**Keywords.** Nuclear quadrupole resonance; Zeeman effect; asymmetry parameter; deuterated crystal; covalency.

### 1. Introduction

Nuclear quadrupole resonance (NQR) is becoming increasingly useful in the study of coordination compounds. Chlorine in mercuric chloride has a strong absorption at about 22 MHz at room temperature. Several mercury complexes were tested to see whether the resonance line shifts upon complex formation. In majority of the organic complexes of  $\text{HgCl}_2$ ,  $^{35}\text{Cl}$  NQR frequencies only were reported in literature (Ramakrishnan *et al* 1977). Temperature variation of  $^{35}\text{Cl}$  NQR frequency was investigated (Ramakrishnan *et al* 1975) in  $\text{HgCl}_2 \cdot 4$ -methylpyridine-1-oxide. Further there is only one inorganic tetrachloromercurate ( $\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$ ) in which chlorine resonances were reported at room temperature and high temperature phases (Saife 1971).

A programme of NQR studies was taken up in a series of inorganic and organic mercuric chloride complexes. The present work essentially deals with observing new chlorine resonance lines in  $\text{CoHgCl}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{CoHgCl}_4 \cdot 4\text{D}_2\text{O}$  and study of the Zeeman effect in single crystals of both the compounds. The results of Zeeman effect and the hydrogen-deuterium substitutional effects are discussed.

### 2. Theory

For nuclei of half integral spin, all NQR levels are doubly degenerate. In particular for  $I = 3/2$ , only one resonance line can be observed corresponding to the transi-

tion  $3/2 \leftrightarrow 1/2$ . The frequency for this line is given by

$$\nu = \frac{e^2 qQ}{2h} \left( 1 + \frac{\eta^2}{3} \right)^{1/2}, \quad (1)$$

where the parameters have their usual meanings. In this case a study of NQR Zeeman effect in single crystal is essential to evaluate the quadrupole coupling constant  $e^2 qQ$ , the asymmetry parameter  $\eta$  of the electric field gradient and the orientations of the principal field gradient axes. The equation of the zero-splitting locus obtained from the Zeeman study is given by (Das and Hahn 1958).

$$\sin^2 \theta_0 = \frac{2}{3 - \eta \cos 2\phi_0}. \quad (2)$$

where  $\theta_0$  and  $\phi_0$  are the polar and azimuthal angles of the magnetic field direction with respect to the principal field gradient system.

### 3. Experimental

The chlorine NQR spectrometer used in the present work is a self-quenched super-regenerative oscillator working in the frequency range 15–50 MHz. The frequencies were measured with a heterodyne frequency meter type 121-b (German make) and an electronic frequency counter type FM 800 B (Southern Electronics, Bangalore). Oscilloscope detection and recording technique were used for observing the signals.

For studying Zeeman effect, the magnetic field required was provided by a pair of Helmholtz coils, capable of rotation about the vertical axis. The corresponding angle of rotation ( $\theta$ ) can be measured to an accuracy of half a degree. The crystal fixed in a suitable crystal holder can be rotated ( $\phi$ ) about the r.f. axis with an accuracy of  $1/2^\circ$ .

Sufficiently large size single crystals of the system  $\text{CoCl}_2 \cdot \text{HgCl}_2 \cdot 4\text{H}_2\text{O}$  (Linke 1958) with well-defined faces were grown from an aqueous solution of  $\text{CoCl}_2$  and  $\text{HgCl}_2$  in the approximate ratio 1 : 2.5 by weight at  $25^\circ\text{C}$ . The crystals thus obtained were deep pink in colour. Care was taken to preserve the crystals as they are highly hygroscopic. These crystals were also chemically analysed and the molecular formula  $\text{CoCl}_2 \cdot \text{HgCl}_2 \cdot 4\text{H}_2\text{O}$  was confirmed. Similarly crystals of  $\text{CoHgCl}_4 \cdot 4\text{D}_2\text{O}$  were grown using heavy water.

The morphology of the crystal (Leelananda Rao, private communication) revealed that the crystal belongs to either orthorhombic or monoclinic and the long axis of the crystal was identified as the crystallographic  $c$  axis. Preliminary x-ray data on this crystal (Spence, private communication) confirmed that the crystal belongs to orthorhombic system with the unit cell dimensions

$$a = 7.82 \text{ \AA}, \quad b = 15.57 \text{ \AA}, \quad c = 8.17 \text{ \AA} \quad \text{and} \quad Z = 4.$$

The morphological structure of the crystal (Spence, private communication) is shown in figure 1.

#### 4. Results

A single NQR line for  $^{35}\text{Cl}$  in  $\text{CoHgCl}_4 \cdot 4\text{H}_2\text{O}$  was observed on the oscilloscope at 20.583 MHz at 300 K which was confirmed by observing a very weak  $^{37}\text{Cl}$  resonance at 16.22 MHz. The  $^{35}\text{Cl}$  resonance line was moderately intense which was almost half the intensity of any of the  $^{35}\text{Cl}$  resonance lines in mercuric chloride. In  $\text{CoHgCl}_4 \cdot 4\text{D}_2\text{O}$  also, a single  $^{35}\text{Cl}$  NQR line was observed at 20.598 MHz at 300 K. The signals were recorded with a strip chart recorder and lock-in amplifier. The spectra in  $\text{CoHgCl}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{HgCl}_2$  (low frequency line) are given in figure 2 for comparison of line widths. New resonance, below 15 MHz were not observed as the condition of the oscillator was not satisfactory. The error in all the frequency measurements was  $\pm 5$  kHz.

Zeeman effect studies in  $\text{CoHgCl}_4 \cdot 4\text{H}_2\text{O}$  single crystal had been carried out for two axes of rotations of the crystal. Based on morphology, all the three crystallographic axes were identified in the grown crystal. Two thin coatings of adhesives were given to the crystal. The  $c$  axis had been chosen as the first axis of rotation and fixed parallel to r.f. axis. The  $bc$  plane was taken as  $\phi = 0$  plane. The crystal in the holder was set so that no eccentric motion resulted during its rotation in the r.f. coil. Data on the Zeeman effect for this rotation gave only one locus as shown in figure 3. The search for other loci was carried out about a second axis of rotation, namely  $a$  axis parallel to r.f. axis and  $ba$  plane as  $\phi = 0$  plane. The intensity of the line being the same, this axis confirmed the presence of a single locus for this crystal. Data collected for various crystal rotations ( $\phi$ ) had been refined by least square analysis (Bucci and Cecchi 1964). The results thus obtained gave the principal  $Z$ -direction as parallel to  $b$  axis within experimental error and

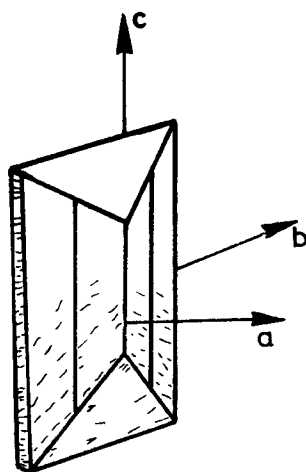


Figure 1. Morphological structure of  $\text{CoHgCl}_4 \cdot 4\text{H}_2\text{O}$ .

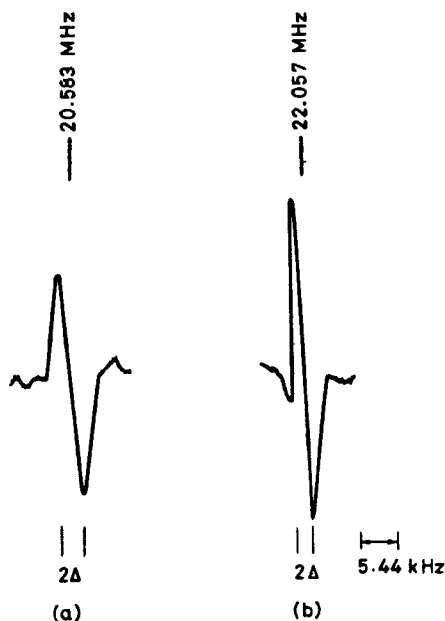


Figure 2.  $^{35}\text{Cl}$  NQR spectra in (a)  $\text{CoHgCl}_4 \cdot 4\text{H}_2\text{O}$  and (b)  $\text{HgCl}_2$  (low frequency line).  $\Delta$  is the line width.

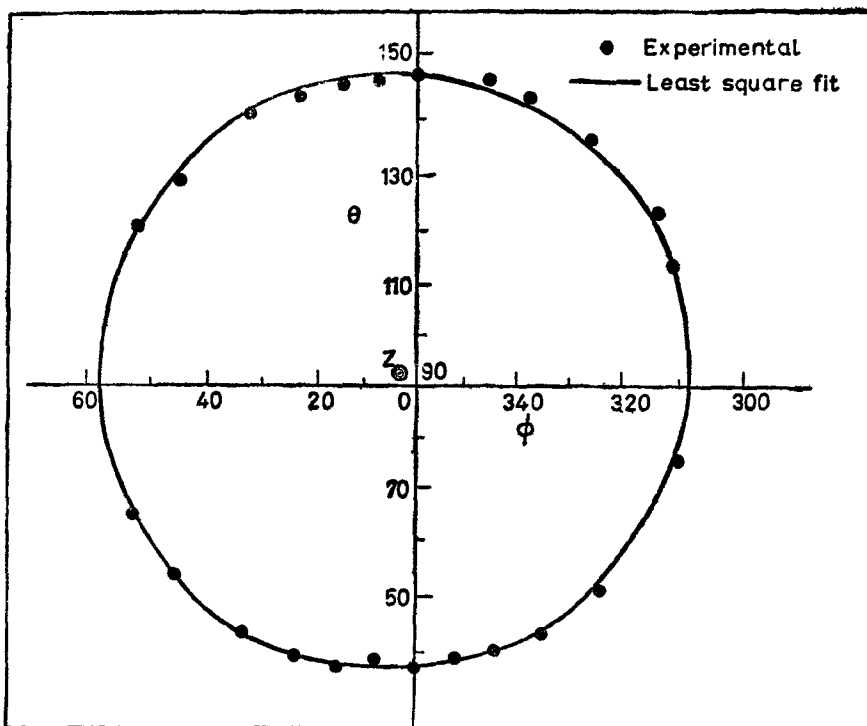


Figure 3. Zero splitting locus for  $^{35}\text{Cl}$  resonance line in  $\text{CoHgCl}_4 \cdot 4\text{H}_2\text{O}$  with  $c$  axis parallel to  $rf$  axis and  $bc$  plane as  $\phi = 0$  plane.

the value of the asymmetry parameter  $\eta$  as  $0.042 \pm 0.006$ . The same experiment was repeated for  $\text{CoHgCl}_4 \cdot 4\text{D}_2\text{O}$  for the same two axes of rotation. Within the limits of experimental accuracy, results identical to hydrated crystal were obtained.

## 5. Discussion

Scaife (1971) gave a detailed account of chlorine NQR in mercury chlorides and complex chlorides. In majority of the mercuric chloride complexes, specific structural principles laid down by Damm and Weiss (1955) revealed how compounds of the required stoichiometry were built up by the joining of distorted octahedra, each of which contains two short ( $2.25\text{--}2.40 \text{ \AA}$ ) and four longer ( $2.70\text{--}3.50 \text{ \AA}$ ) Hg-Cl bonds. In accordance with this principle, infinite chains of composition  $\text{HgCl}_4$  result if octahedral  $\text{HgCl}_6$  groups share opposite edges in  $\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$ . These chains are held together by  $\text{K}^+$  ions and the water molecules are found in the tunnels between these chains. Further, the short Cl-Hg-Cl bonds are perpendicular to the plane containing the bridging chlorines. In such compounds,  $\text{HgCl}_4$  units exist in the lattice with increased bond lengths to a greater or lesser extent compared with those in  $\text{HgCl}_2$  compound itself. As  $\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$  is also orthorhombic having the unit cell dimensions

$$a = 8.27 \text{ \AA}, b = 11.63 \text{ \AA}, c = 8.89 \text{ \AA} \text{ with } Z = 4,$$

the present crystal can be viewed as possessing a similar structure as that of  $\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$ . Scaife (1971), in all the mercuric chloride complexes considered, assigned the chlorine resonances lying between 15 to 23 MHz to the chlorine atoms at short distances. Thus the resonance line can be classified into this category.

It had been observed that  $^{35}\text{Cl}$  resonance line in  $\text{CoHgCl}_4 \cdot 4\text{H}_2\text{O}$  has a noticeable broadening when compared with any of the  $^{35}\text{Cl}$  lines in  $\text{HgCl}_2$ . Only low frequency  $^{35}\text{Cl}$  line of  $\text{HgCl}_2$  is given in figure 2 for comparison. The line width  $\Delta$  of  $\text{CoHgCl}_4 \cdot 4\text{H}_2\text{O}$  is 1.8 kHz and that of  $\text{HgCl}_2$  is 1.3 kHz. The broadening of NQR line may be due to the presence of impurities, strains, dislocations and in general, any disorders in the crystal. The crystals were grown to be free from disorders. The main reason for the broadening may therefore be the presence of paramagnetic ions in the lattice. The same effect of broadening has also been observed in  $\text{CoHgCl}_4 \cdot 4\text{D}_2\text{O}$ .

An appreciable increase of 15 kHz was observed in  $^{35}\text{Cl}$  frequency in  $\text{CoHgCl}_4 \cdot 4\text{D}_2\text{O}$  due to the replacement of H by D. There is no other NQR frequency reported in compounds obtained from substitution of H by D in water molecules except in  $\text{Na}_2\text{ZnCl}_4 \cdot 3\text{D}_2\text{O}$  (Pies and Weiss 1974) in which a negligible decrease of 3.8 kHz is observed in  $^{35}\text{Cl}$  NQR frequency. Any change in frequency can be attributed to change in the electric field gradient contribution at the resonating nucleus. In the present case, the effect of intermolecular hydrogen bonds due to the water molecules situated in the lattice might have caused the change in the frequency. In any case, the substitution of H by D on the NQR spectrum is less pronounced though not insignificant in  $\text{CoHgCl}_4 \cdot 4\text{D}_2\text{O}$ . However, a better insight can be gained if neutron diffraction or NMR data on this compound are available.

The results of Zeeman effect show that in an orthorhombic crystal, one principal field gradient Z direction being parallel to *b* axis is consistent with group theoretical considerations. Therefore the four molecules suggested by Spence (private communication) will have all shorter Cl-Hg-Cl units parallel to *b* axis.

The small value,  $\eta = 0.042$  leads to the concept of 'tendency towards axial symmetry' in the distorted octahedral molecule. The electric field gradient at a given nucleus may be considered as contributions  $q_i$  from the charges inside the molecule and  $q_e$  from the point charges external to the molecule. If it is assumed that  $q_e$  is neglected the imbalance in the *p*-electron population on the chlorine atoms can be defined as

$$U_p = e^2 qQ / (e^2 qQ)_{\text{atom}}, \quad (3)$$

where  $(e^2 qQ)_{\text{atom}} = 109.476$  MHz for  $^{35}\text{Cl}$ . Then the treatment of Townes and Dailey for the weighted average of the contributions from the proposed resonance structures gives

$$U_p = (1 - s^2 + d^2 - i - \pi) + i(s^2 - d^2), \quad (4)$$

where  $s^2$  is the degree of *s*-hybridisation,  $d^2$  the degree of *d*-hybridisation,  $\pi$  the degree of  $\pi$  bonding on chlorine and *i* the degree of ionic character in the bond. Neglecting *s*, *d* and  $\pi$  contributions, one can from equations (3) and (4) arrive at

$$\sigma = 1 - i = e^2 qQ / (e^2 qQ)_{\text{atom}}, \quad (5)$$

where  $\sigma$  is the degree of  $p_\sigma$  covalent bonding. Assuming the values of  $\eta$  in various mercuric chloride complexes to be small neglecting  $\pi$  bond contribution, Scaife (1971) plotted the values of  $\sigma$  obtained from equation (5) against  $d = \text{Hg-Cl}$  distances available and fitted to an exponential curve

$$d = 2.01 - 0.60 \log \sigma, \quad (6)$$

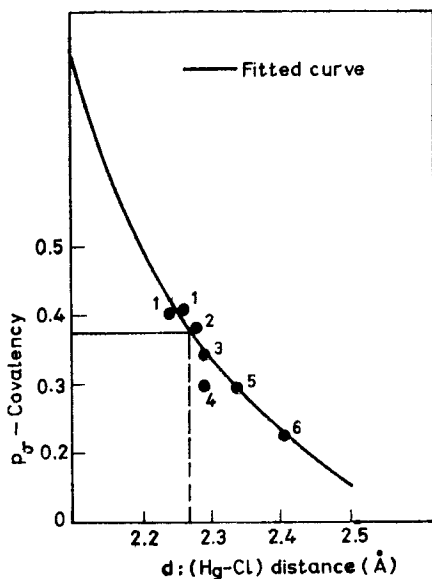
where 2.01 Å is the Hg-Cl distance extrapolated for diagonally coordinated mercury compounds. Following Scaife (1971), a list of diagonally coordinated mercury compounds in which experimental frequencies of  $^{35}\text{Cl}$  and  $d = \text{Hg-Cl}$  values available is given in table 1. The best fitted curve to the data is

$$d = 2.024 - 0.575 \log \sigma, \quad (7)$$

**Table 1.** Structural (Hg-Cl) distances, values of the covalency parameter ( $\sigma$ ), and  $^{35}\text{Cl}$  frequencies ( $\nu$ ) in certain mercury chlorides and complex chlorides as given by Scaife (1971).

Compound	$d$ (Hg-Cl) Å	$\nu$ ( $^{35}\text{Cl}$ ) MHz	$\sigma$
$\text{HgCl}_2$	2.24	22.06	0.40
	2.26	22.25	0.41
$\text{MeHgCl}$ (gas)	2.28	21.00	0.38
$\text{CsHgCl}_3$	2.29	*18.64	0.34
$\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$	2.29	16.24	0.30
$\text{NH}_4\text{HgCl}_3$	2.34	16.20	0.30
$\text{Hg}_2\text{Cl}_2$	2.41	12.34	0.23

\* Average of the three frequencies.



**Figure 4.** Variation of  $\sigma$ -covalency with  $d(\text{Hg-Cl})$  distance in various mercury chlorides and complex chlorides (see table 1). Solid curve represents equation 7 (see text). Dotted line corresponds to  $d$  value in  $\text{CoHgCl}_4 \cdot 4\text{H}_2\text{O}$ .

which is slightly different from (6). Data in table 1 and the fitted curve (7) are shown in figure 4. The point corresponding to  $\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$  is far away from the graph which may be due to high  $\eta$ .

For the compound under study, the covalent character  $\sigma$  estimated from (5) is 0.38 and the shorter Hg-Cl distance corresponding to the reported frequency is found to be 2.27 Å from the fitted curve. This distance is well within the range suggested by Damm and Weiss (1955).

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