Halogen NQR Studies in Certain Mercuric Halide-Polyether Complexes*

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The temperature variation of ^{35}Cl and ^{81}Br NQR frequencies are reported for mercuric chloride · triethylene glycol dimethyl ether ($HgCl_2$ · triglyme), mercuric chloride · diethylene glycol dimethyl ether ($HgCl_2$ · diglyme), and mercuric bromide · diethylene glycol dimethyl ether ($HgBr_2$ · diglyme). The frequencies have been assigned to the appropriate halogens using molecular models which take into account the various intra- and inter-molecular interactions in the solid state. The observed temperature variation of the NQR frequencies, in the range 77–300 K, has been analysed using the two torsional mode analysis in the framework of the Bayer-Kushida-Brown method with Tatsuzaki's correction to obtain the torsional frequencies and their average temperature coefficients.

Introduction

The structure and coordination environment of mercury in mercuric halide complexes have been studied using NQR in addition to other techniques like X-ray diffraction and IR [1, 2]. Wulfsberg [3] has analysed the NQR data of many mercuric halidepolyether complexes in this respect. $HgBr_2$ · triglyme is reported to undergo a phase transition [3]. The present NQR measurements have been carried out mainly to elucidate the electronic structure and motional aspects including phase transitions if any, in three mercuric halide complexes in the solid state, viz. (I) mercuric chloride · triglyme, (ii) mercuric chloride · diglyme, and (III) mercuric bromide · diglyme.

These compounds belong to the family of mercuric halide · polyether adducts whose general formula is $HgX_2 \cdot RO \cdot (CH_2CH_2O)_{n-1}-R$ where X=Cl, Br or I and R=CH_3, CH_3CH_2 etc. The HgX_2 · polyether complexes with $n = 2, 3, 4, 5$ are HgX_2 · glyme, HgX_2 · diglyme, HgX_2 · triglyme and HgX_2 · tetraglyme, respectively. The representative structure of one of them, viz. $HgCl_2$ · tetraglyme, is shown in Figure 1.

The NQR experiments were carried out using a home-made spectrometer with phase sensitive

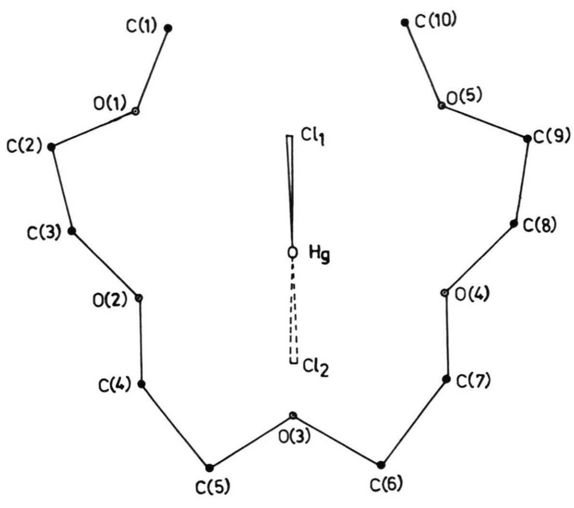

Fig. 1. Representative structure of $HgCl_2$ · tetraglyme complex.

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detection. The signals were about 3–4 kHz wide for ^{35}Cl and 15–20 kHz wide for ^{81}Br. The frequencies were measured with an accuracy of ±1 kHz using a BC-221 frequency meter for the ^{35}Cl resonances and a TS-175/U frequency meter for the ^{81}Br resonances. The temperature variation was carried out using a cryostat with an accuracy of ±0.5 K.

Results and Discussion

NQR frequencies and structural aspects

The NQR frequencies obtained for the three compounds are given in Table 1. The NQR frequencies at 77 K and room temperature from our data compare quite well with the literature [3]. The NQR spectrum of compound (I) consists of a single line throughout the temperature range studied whereas those of compounds (II) and (III) consist of two well separated frequencies throughout the temperature range. The frequency vs. temperature plots are given in Figures 2–4.

The halogen NQR frequency in mercuric halide complexes is affected by two factors [3]:

1) Increase in ligand to metal (Hg) co-ordination (n) increases the ionic character of the Hg ... X bond and lowers the NQR frequency.
2) Increase in the co-ordination number of halogens (additional Hg ... X contact) also should lower the NQR frequency by removing electrons from the p_x or p_y orbitals of the halogen or by polarising the Np_x and Np_y orbitals to higher $(N+1)\,p_x$ and $(N+1)\,p_y$ orbitals.

The reduction due to factors (1) and (2) can be understood from Townes and Dailey's theory [4]. Wulfsberg [3], using molecular models and comparing solid state NQR with solution IR studies in many of these adducts, has conjectured that complexes up to $n = 4$ could go into higher order of aggregation in the solid state due to additional Hg ... X contact (intermolecular). Any large difference in the NQR frequencies of the two halogens should be associated with their difference in co-ordination numbers whereas smaller differences should be attributed to their crystallographic inequivalences.

In compound (I) the observation of a single line in the NQR spectrum suggests that the two chlorines

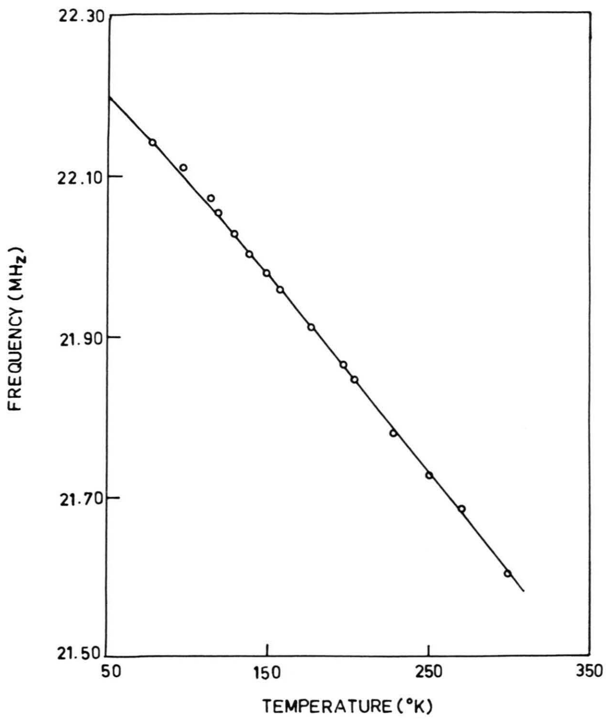

Fig. 2. Temperature dependence of ^{35}Cl NQR in $HgCl_2 \cdot$ triglyme.

Table 1. NQR frequences.

Compound		Resonance frequence (MHz)			
		[8]		[3]	
		77 K	R. T.	77 K	R. T.
(I) $HgCl_2 \cdot$ triglyme		22.142	21.605	22.144	21.603
(II) $HgCl_2 \cdot$ diglyme	line I	21.094	20.959	21.094	20.957
	line II	22.288	21.833	22.287	21.846
(III) $HgBr_2 \cdot$ diglyme	line I	140.675	138.875	–	138.700
	line II	146.250	143.180	–	143.100

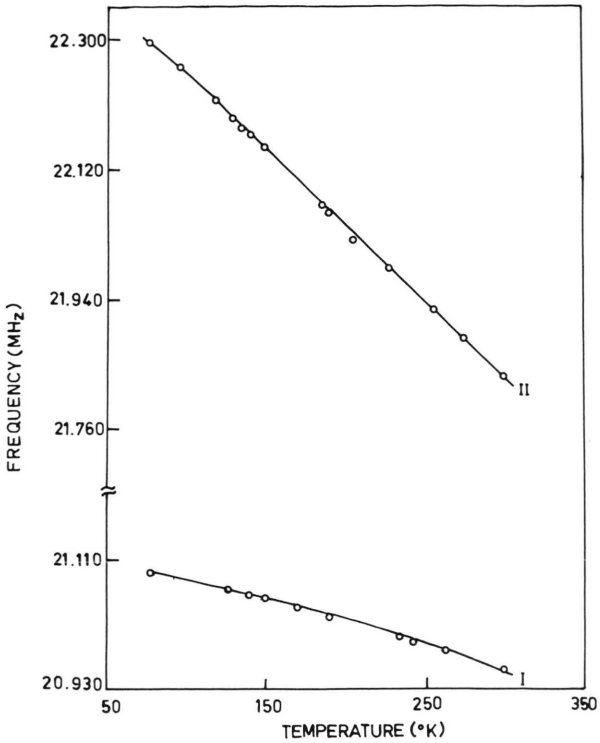

Fig. 3. Temperature dependence of ^{35}Cl NQR in $HgCl_2 \cdot$ diglyme.

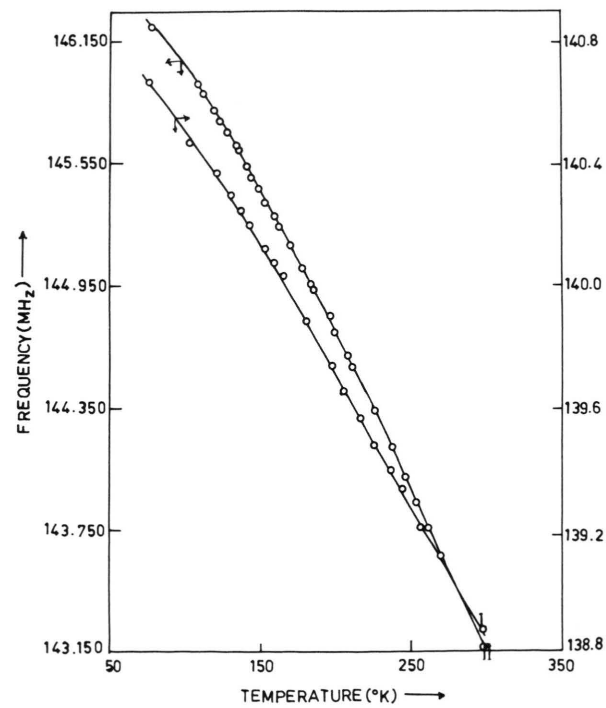

Fig. 4. Temperature dependence of ^{35}Cl NQR in $HgBr_2 \cdot$ diglyme.

are crystallographically equivalent. Further, the NQR frequency varies smoothly with temperature and the complex does not undergo any phase transitions.

The observation of two lines for compounds (II) and (III) indicates that the two halogens are inequivalent. The difference in the two NQR frequencies is 1.194 MHz and 5.575 MHz in (II) and (III), respectively, and is larger than could be expected from crystallographic inequivalences. It has been proposed [3] that the complexes exist as dimers in which one of the halogens is participating in intermolecular Hg ... X interaction.

Since each additional Hg ... X interaction lowers the NQR frequency, the low frequency line (line I) has been assigned to the bridging halogen (Cl, Br) which is participating in intermolecular Hg ... X bond, and the high frequency line (line II) has been assigned to the other halogen.

Temperature dependence of NQR and torsional mode analysis

The ν vs. T curves are shown in Figures 2–4. The signals vary smoothly with temperature. Further, the low frequency line I in compounds (II) and (III), shows lesser temperature variation than the high frequency line II. This may due to the lesser mobility of the halogen assigned to line I owing to its additional Hg ... X interaction (intermolecular). Hence, the observed temperature variation of the NQR lines is in keeping with the assignment of frequencies discussed earlier.

Also, the frequency shifts are less than 500 kHz (from 77 K–304 K) in the chlorine complex and around 2–3 MHz in the analogous bromine complex. The ratio of these shifts is in reasonable agree-

Table 2. Torsional frequencies.

Compound		Torsional frequencies ($C m^{-1}$)			
		f_1		f_2	
		77 K	R.T.	77 K	R.T.
(I) $HgCl_2 \cdot$ triglyme		20	18	26	24
(II) $HgCl_2 \cdot$ diglyme	line I	69	55	77	63
	line II	33	30	37	34
(III) $HgBr_2 \cdot$ diglyme	line I	38	31	41	34
	line II	33	27	35	29

Table 3. g values and least square fitting of experimental data.

Compound		4th Order polynomial			Brown		Kushida
		ν_0	$\langle g \rangle$	Δ (KHz^2)	$\langle g \rangle$	Δ (KHz^2)	Δ (KHz^2)
(I) $HgCl_2 \cdot$ triglyme		22.285	0.00013	31	0.00007	22.6	52.2
(II) $HgCl_2 \cdot$ diglyme	line I	21.125	0.00032	27.9	0.00028	5.7	63.2
	line II	22.414	0.000149	18.06	0.00006	18.07	12.3
(III) $HgBr_2 \cdot$ diglyme	line I	141.084	0.00031	264	0.00029	216	366
	line II	146.837	0.00067	453.8	0.00041	154.2	995.2

ment with the ratio of the quadrupole coupling constants of ^{35}Cl and ^{81}Br, viz. 0.171. This implies that the motional averaging of the NQR frequency in the chloro and bromo complexes is about the same suggesting similar molecular motions in them.

The temperature variation of NQR frequencies in molecular solids can be approximately described by Bayer's equation [5] as modified by Tatsuzaki [6] and given by

$$\nu(T) = \nu_0 \left[1 - \frac{3h}{8\pi^2 c} \cdot \sum_{i=1}^{3} \frac{\sin^2 \alpha_i}{A_i f_i} \left(\frac{1}{2} + \frac{1}{\exp(h f_i C/kT) - 1} \right) \right],$$

where ν_0 is the NQR frequency for the stationary molecule, α_i the angle between the axis of the i^{th} torsional mode and the principal z-axis of the EFG tensor, A_i the corresponding moment of inertia and f_i the corresponding frequency of the i^{th} torsional mode. The volume effects are taken into account by Brown [7].

The observed behaviour in the present compounds has been analysed numerically [8]. The torsional frequencies f_i and their temperature coefficients $\langle g \rangle$ are tabulated in Tables 2 and 3.

Acknowledgements

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