NQR & Coordination Chemistry—Investigations on Certain Mercury(II) Chloride Complexes

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The 35Cl NQR frequencies in five HgCl₂ complexes, viz. HgCl₂·DMSO, 3HgCl₂·2DMSO, HgCl₂·DMF, HgCl₂·THF and HgCl₂·4MePyO (4MePyO is 4-methylpyridine 1-oxide) have been studied and the results discussed in terms of possible structures.

**Material and Methods**

The complexes studied are HgCl₂·DMSO, 3HgCl₂·2DMSO, HgCl₂·DMF, HgCl₂·THF and HgCl₂·4MePyO, where DMSO = dimethylsulphoxide; DMF = dimethylformamide; THF = tetrahydrofuran; and 4-MePyO = 4-methylpyridine 1-oxide. The complexes were prepared by the usual procedures which generally involved the mixing of the reactants in hot methanol followed by stirring. The solvent was slowly evaporated at room temperature to get crystals, in all the cases except HgCl₂·THF which was obtained by recrystallising HgCl₂ in THF.

The spectra were recorded using a super regenerative NQR spectrometer built in the laboratory and employing a home-made lock-in-amplifier. The complexes were finely powdered and tightly packed into the sample tubes. For HgCl₂·THF it was necessary to keep 0.5 ml of THF above the sample as the complex was unstable in the absence of the excess THF.

**Results and Discussion**

The 35Cl NQR frequencies observed in the present investigation are presented in Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp. (K)</th>
<th>35Cl resonances (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgCl₂·DMSO</td>
<td>298</td>
<td>20.718, 21.349, 19.680, 19.461</td>
</tr>
<tr>
<td>HgCl₂·2DMSO</td>
<td>299</td>
<td>19.678, 19.588, 19.461</td>
</tr>
<tr>
<td>HgCl₂·DMF</td>
<td>298</td>
<td>20.273, 20.033</td>
</tr>
<tr>
<td>HgCl₂·THF</td>
<td>299</td>
<td>21.042, 19.724</td>
</tr>
<tr>
<td>HgCl₂·4MePyO</td>
<td>296</td>
<td>21.538, 20.112</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>21.740, 20.230</td>
</tr>
</tbody>
</table>

Two resonances for HgCl₂·DMSO at 21.184 and 20.075 MHz at room temperature; these could be observed only for a five-month old compound, while Maksyutin et al. reported the resonances at 19.878 and 19.494 MHz. Ryan could not observe the 35Cl NQR in this compound. This compound was, therefore, reinvestigated and four resonances have been observed, two in the region reported by Brill et al. and two in the region reported by Maksyutin et al.

Three resonances have been observed at room temperature for 3HgCl₂·2DMSO for the first time. Of these resonances, two (19.678 and 19.461 MHz) have frequencies similar to those of a pair of resonances observed in HgCl₂·DMSO. 3HgCl₂·2DMSO
exhibits only one resonance at 77K. This may be due to a phase transition occurring between the room temperature and 77 K.

The molecular structure (I) of 3HgCl₂.2DMSO is known. The structure (I) of 3HgCl₂.2DMSO consists of two types of HgCl₂ units. Hg(I), situated on a centre of symmetry, shows a two coordinated linear structure [Hg(I)–Cl(I)=2.306 Å, Cl–Hg–Cl=180°]. Two pairs of chlorine atoms belonging to adjacent dimeric groups (at \( \sim 3.0 \) Å) complete the coordination sphere to form an oblate octahedron. This kind of coordination with four long and two short contacts corresponding to covalent bonds is typical of Hg(II). Hg(2) is covalently coordinated by two chlorine atoms (Hg–Cl=2.309 Å, 2.320 Å, Cl–Hg–Cl=166.0°) and weakly coordinated by two oxygen atoms (Hg–O=2.52 Å and 2.56 Å) of the sulphoxide group. These ligands are arranged in a highly distorted tetrahedral configuration with angles ranging from 75.3° to 166.0°. The configuration may also be considered as a highly distorted octahedron, if two chlorine atoms from two adjacent HgCl₂ molecules are regarded as a part of the Hg(2) environment. The values of these Hg...Cl distances (3.302 and 3.372 Å) are very close to the sum of the Van der Waal radii (3.30 Å). In simpler terms, the structure can be regarded as consisting of HgCl₂ molecules and dimetric (HgCl₂.DMSO)₂ units (with oxygen bridges) bridged by chlorines. Thus, there are two types of HgCl₂ units.

From the similarity of the resonances observed for HgCl₂.DMSO and two of those observed for 3HgCl₂.2DMSO, it may be suggested that these resonances may be due to chlorines in the (HgCl₂.DMSO)₂ dimer. The separation of these frequencies (220 KHz) may be attributed to the two different bond lengths exhibited by two chlorines covalently bound to Hg(2). One may attribute the resonance at 19.460 MHz to the chlorine bound to Hg(2) at a distance of 2.320 Å. The higher frequency resonance at 19.680 MHz is then attributed to the other chlorine at a distance of 2.309 Å from Hg(2). Similar assignments based on the metal halogen distance have been made in a few complexes of CuCl₂ (ref. 11). The third resonance of 3HgCl₂.2DMSO occurring at 19.588 MHz is assigned to the chlorines attached to Hg(1) (i.e., belonging to HgCl₂). The appearance of only one resonance for these chlorines is consistent with the structure of the complex, as these two chlorines are at the same distance from Hg(1) and have similar interactions with the neighbouring mercury as well as chlorine atoms. The shifts in the resonance frequencies of 3HgCl₂.2DMSO from those of HgCl₂ a e towards the lower frequency region. This is due to the coordination of the ligand to the metal. The interaction between the HgCl₂(1) molecule and the (HgCl₂.DMSO)₂ dimer seems to be relatively strong so as to bring down the resonance frequency of HgCl₂ to 19.588 MHz.

Based on the assignment of frequencies for 3HgCl₂.2DMSO, the resonances of HgCl₂.DMSO have been assigned. As already pointed out, the resonances at 19.680 and 19.460 MHz in HgCl₂.DMSO indicate the presence of chlorines with interactions similar to those observed in 3HgCl₂.2DMSO. Thus, these two resonances may be attributed to those chlorines which have interactions with the neighbouring Hg(II) ions (so as to satisfy the coordination requirement of a hexa-coordinated mercury), apart from covalently bonding to a Hg(II). The appearance of resonances at higher frequencies (20.718 and 21.249 MHz) and their separation indicate that the structure consists of at least two more chlorine atoms which differ from the above mentioned chlorines in their interaction with the neighbouring Hg(II) and that these two chlorines differ in their Hg–Cl bond lengths. Keeping the above considerations in view, structure (II) based on (HgCl₂.DMSO)₂ dimers (oxygen-bridged) bridged by halogens may be suggested.

HgCl₂.DMF — The two resonances at 20.273 and 20.033 Hz with a separation of 240 KHz for HgCl₂.DMF indicate that the structure of this complex at room temperature is different from that of HgCl₂.DMSO. Among the complexes which exhibit 35Cl NQR in this region, the structure of only HgCl₂.Dioxane is known. The structure of HgCl₂.Dioxane is shown to contain infinite chains of alternating HgCl₂ and dioxane molecules. Each mercury atom is surrounded by two chlorines and two other oxygens such that all five atoms are in the same plane. HgCl₂.DMF may also have such a structure with two differing Hg–Cl distances.

HgCl₂.THF and HgCl₂.4MePyO — Two resonances are observed in each case, at about 19.5 and 21.00 MHz. Considering the structures of the complexes which exhibit resonances in these regions it seems possible that a dimer structure(III) with halogen bridges as suggested by Brill et al. adequately describes these complexes. Brill et al. have assigned the low frequency signal to the bridging chlorine and the high frequency one to the terminal one. This assignment is consistent with the assignments made for similar compounds of Pt(II) and Pd(II)12. Photoelectron spectroscopic studies13 on
Further, the low values of \( \frac{\partial v}{\partial T} \) for both the resonances in \( \text{HgCl}_2.4\text{MePyO} \) compared to the value of \( \frac{\partial v}{\partial T} \) for HgCl\(_2\) indicate a damping of the internal motions on complex formation (A report on the temperature dependence of NQR in HgCl\(_2.4\text{MePyO}\) has already appeared).\(^{14}\)

Thus NQR can provide an inexpensive analytical tool for studying structural aspects of molecules and also detect phase transitions if present.

Acknowledgement

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References