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TEMPERATURE DEPENDENCE OF THE ^{35}Cl NQR FREQUENCIES OF SOME TRICHLOROACETATES

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The ^{35}Cl NQR frequencies of magnesium trichloroacetate hexahydrate, sodium trichloroacetate trihydrate, and anhydrous sodium trichloroacetate were measured in the temperature region of 77-230 K. It was found that each of the two hydrated salts contains two thermally different non-equivalent trichloromethyl groups. The non-equivalence may be due to some intermolecular interaction.

It is well known that the ^{35}Cl NQR signals of trichloromethyl group ($-CCl_3$) fade out quite often. In order to investigate the nature of the fade-out phenomena from the structural point of view, we studied the temperature dependence of ^{35}Cl NQR frequencies of about thirty compounds having $-CCl_3$. In this communication, we wish to report the results obtained for three trichloroacetates; magnesium trichloroacetate hexahydrate ($Mg(TCA)_2.6H_2O$), sodium trichloroacetate trihydrate ($NaTCA.3H_2O$), and anhydrous sodium trichloroacetate (NaTCA).

The ^{35}Cl NQR spectra were observed by using a super-regenerative spectrometer. The experimental procedures of the NQR measurements have been reported previously.[1,2] The magnesium and sodium salts were prepared by neutralizing trichloroacetic acid with corresponding metal carbonates. Crystals of $Mg(TCA)_2.6H_2O$ and $NaTCA.3H_2O$ were obtained by recrystallizations from water. Polycrystalline NaTCA was obtained by dehydration of $NaTCA.3H_2O$. The observed ^{35}Cl NQR frequencies of these trichloroacetates at various temperatures are given in Table 1. Biedenkapp and Weiss reported the resonance frequencies of these compounds at 77 K.[3] The present results at the same temperature are in good agreement with their results.

In Fig.1 is shown the temperature dependence of the resonance frequencies of $Mg(TCA)_2.6H_2O$. At 77 K this salt gives six NQR signals, each of which decreases its frequency with an increase of temperature and fades out at a certain temperature below room temperature. The fade-out temperature (T_f) of ν_1, ν_2, and ν_5 is about 215 K. On the other hand, that of ν_3, ν_4, and ν_6 is about 120 K. As can be seen in Fig.1, the slopes of ν_3, ν_4, and ν_6 are steeper than those of ν_1, ν_2, and ν_5.

In Fig.2 is shown the temperature dependence of the resonance frequencies of $NaTCA.3H_2O$ and NaTCA. At 77 K the trihydrate gives six NQR signals. Three of them, ν_1, ν_2, and ν_4, fade out at about 155 K, but others, ν_3, ν_5, and ν_6, at about 205 K. The three resonance signals of NaTCA decrease their frequencies

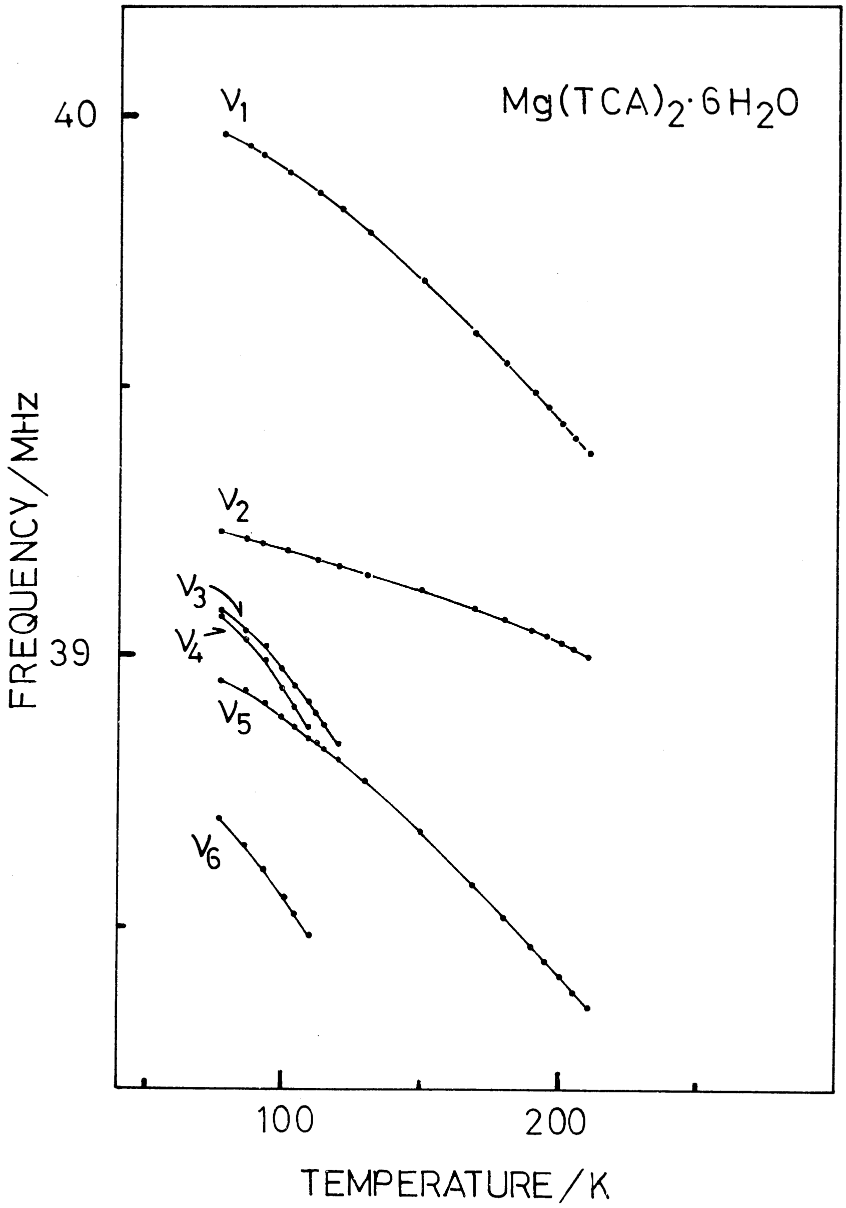

Fig.1. Temperature dependence of the resonance frequencies of magnesium trichloroacetate hexahydrate ($Mg(TCA)_2 \cdot 6H_2O$).

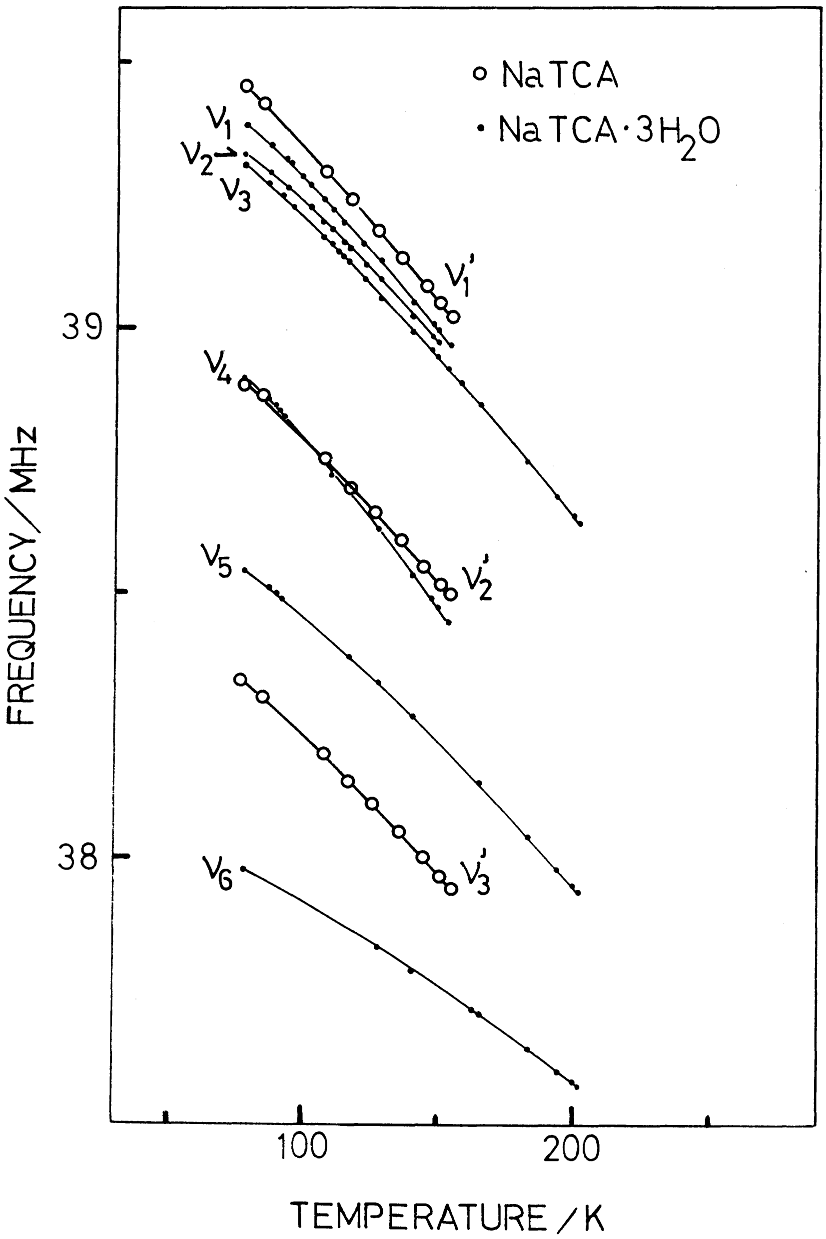

Fig.2. Temperature dependence of the resonance frequencies of sodium trichloroacetate trihydrate (NaTCA.$3H_2O$) and anhydrous sodium trichloroacetate (NaTCA).

in a manner similar to ν_1, ν_2, and ν_4 of NaTCA.$3H_2O$ and fade out at about 155 K.

As can be seen in Figs. 1 and 2, the results of the NQR measurements indicate that each of the two hydrated salts contains two types of $-CCl_3$.[4,5] That is, ν_1, ν_2, and ν_5 of $Mg(TCA)_2.6H_2O$ seem to belong to one type of $-CCl_3$, which will be referred to as Type-R, and ν_3, ν_4, and ν_6 to the other type, Type-F. Here, the "R" is to mean "reorientation-restricted" and the "F" "reorientation-free". In the case of NaTCA.$3H_2O$, ν_1, ν_2, and ν_4 are considered to belong to the $-CCl_3$ of Type-F and ν_3, ν_5, and ν_6 to that of Type-R. The temperature dependence of the resonance frequencies of NaTCA suggests that this salt contains the $-CCl_3$ of Type-F.

If the p-π orbital of a chlorine atom of a $-CCl_3$ participates in an intermolecular bond formation, the magnitude of the temperature coefficient of the resonance frequency of the chlorine atom is expected to be smaller than those of the other two chlorine atoms of the $-CCl_3$.[6,7] Since the magnitudes of the temperature coefficients found for ν_2 of $Mg(TCA)_2.6H_2O$ and ν_6 of NaTCA.$3H_2O$ are much smaller than those of others, these signals can be assigned to the chlorine atoms participating in the intermolecular interaction. It is well known that the fade-out of the resonance signals of $-CCl_3$ is due to the reorientation of the group.[8,9] If there is some interaction between $-CCl_3$ and surrounding molecule, its reorientation is expected to be hindered. It is reasonable, therefore, that the observed T_f value of the $-CCl_3$ of Type-R is higher than that of Type-F.

The two hydrated salts contain both types of $-CCl_3$. On the other hand, the anhydrous salt contains only that of Type-F. These facts suggest that the difference between Type-R and Type-F is associated with the hydrogen bond formation. However, because of the lack of the x-ray study of crystal structure, it is difficult to discuss in detail about the nature of the interaction.

Table 1. The observed ^{35}Cl NQR frequencies of magnesium trichloroacetate hexahydrate ($Mg(TCA)_2.6H_2O$), sodium trichloroacetate trihydrate ($NaTCA.3H_2O$), and anhydrous sodium trichloroacetate (NaTCA) at various temperatures

Compounds	Temperature K	Frequency MHz					
$Mg(TCA)_2.6H_2O$	77	39.963	39.227	39.088	39.075	38.954	38.700
	100	39.897	39.196	38.977	38.941	38.885	38.553
	150	39.694	39.122			38.675	
	200	39.430	39.021			38.407	
$NaTCA.3H_2O$	77	39.374	39.322	39.299	38.897	38.538	37.975
	140	39.047	39.022	38.994	38.533	38.263	37.792
	200			38.644		37.948	37.580
NaTCA	77	39.452	38.892	38.332			
	117	39.238	38.697	38.144			
	150	39.044	38.512	37.966			

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