Phase Transitions in Tetramethylammonium Hexachloroplatinate(IV), -tellurate(IV), and -stannate(IV) as Studied by ^{35}Cl NQR and Powder X-Ray Diffraction

Yoshihiro Furukawa,* Laxman S. Prabhumirashi,† Ryuichi Ikeda, and Daiyu Nakamura

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

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The ^{35}Cl NQR spectra of $[(CH_3)_4N]_2PtCl_6$, $[(CH_3)_4N]_2TeCl_6$, and $[(CH_3)_4N]_2SnCl_6$ were recorded in a temperature range between 77 and ca. 350 K. Below room temperature, the temperature dependence measurements of NQR frequencies for all of these complexes confirmed the presence of structural phase transitions reported very recently. From the experiments of DTA carried out above room temperature, structural phase transitions were located at 385, 351, and 365 K in the same order of the above complexes. The X-ray powder patterns taken in the highest-temperature phase of these complexes (at ca. 390 K) were well interpreted as arising from the K_2PtCl_6-type cubic structure with the lattice constant $a_0 = 12.82_8$, 13.05_3, and 12.97_5 Å for the Pt, Te, and Sn complexes, respectively. In this phase of each complex, however, no NQR spectra were observed. The mechanism of the phase transitions detected is discussed in connection with the structure of these complexes.

Recently, tetramethylammonium hexahalometallates-(IV), $(tetMA)_2MX_6$, have been extensively studied because of their interesting phase transitions observed at low temperatures.[1-5] In our previous paper,[6] we reported the accurate transition temperatures of $(tetMA)_2PtCl_6$, $(tetMA)_2TeCl_6$, and $(tetMA)_2SnCl_6$ determined from the experiments of differential thermal analysis (DTA) and of proton spin-lattice relaxation time (T_1) carried out below room temperature. However, the nature of these phase transitions is still unclear.

Berg and Søtofte[7] reinvestigated the room-temperature structure of $(tetMA)_2PtCl_6$ by using a single crystal X-ray diffraction method, and found that the structure could be approximately described in the cubic system belonging to the space group Fm3m. In a subsequent paper,[8] Berg and Nielsen also studied the room-temperature structure of $(tetMA)_2TeBr_6$ and found that the complex forms cubic crystals in the space group Fd3c. Based on this new result, they indicated in their paper that the room-temperature structure of $(tetMA)_2PtCl_6$ might be the same because some weak Fm3m-forbidden reflections had been detected in the previous X-ray study. In fact, Mackenzie et al.[9] found, very recently, from the neutron powder diffraction study of $[N(CD_3)_4]_2PtCl_6$ that the compound also forms Fd3c crystals. The three hexachlorometallates(IV) described above are known to have the room-temperature crystal structure being isomorphous with each other.[10,11] For these complexes, therefore, a phase transition from the Fd3c structure to the simple Fm3m one may be expected to take place at a higher temperature. The present investigation of ^{35}Cl NQR in these hexachlorometallates(IV) has been undertaken to clarify the nature of the phase transitions already located at lower temperatures, and also to detect another phase transition possibly existing at higher temperature.

Experimental

The NQR spectra of ^{35}Cl were observed by means of a modified Dean-type super-regenerative spectrometer already described.[12] A chromel-alumel thermocouple was used for the determination of temperature. Observed temperatures were estimated to be accurate within ± 1 K. The measurements of DTA were carried out by use of a home-made apparatus.[13] X-Ray powder patterns were taken by means of a Model D-3F diffractometer from Rigaku Denki Co. equipped with a copper anode. A goniometer was calibrated with the standard sample of silicon.

All the sample employed in the present investigation were the same as those prepared in the previous NMR and DTA experiments.[6]

Results and Discussion

Temperature Dependence of ^{35}Cl NQR Frequencies.
Figure 1 shows the temperature dependence of ^{35}Cl NQR frequencies in $(tetMA)_2PtCl_6$, $(tetMA)_2TeCl_6$, and $(tetMA)_2SnCl_6$. The resonance frequencies of these complexes determined at various temperatures are listed in Table 1.

At room temperature, a single ^{35}Cl NQR frequency was observed for $(tetMA)_2PtCl_6$ indicating that all the chlorine atoms are crystallographically equivalent in

TABLE 1. ^{35}Cl NQR FREQUENCIES IN $(tetMA)_2PtCl_6$, $(tetMA)_2TeCl_6$, AND $(tetMA)_2SnCl_6$

Compound	T/K	NQR line	ν/MHz
$(tetMA)_2PtCl_6$	286	a	26.627 ± 0.002
	170	a	26.774 ± 0.002
		b	26.88 ± 0.03
		c	27.00 ± 0.03
	77	b	27.00 ± 0.03
		c	27.12 ± 0.03
$(tetMA)_2TeCl_6$	293		16.300 ± 0.003
	77		16.52 ± 0.05
			16.60 ± 0.05
$(tetMA)_2SnCl_6$	292		16.683 ± 0.003
	77		16.70 ± 0.05
			17.51 ± 0.05

† Present address: Chemistry Department, Poona University, Pune 411007, India.
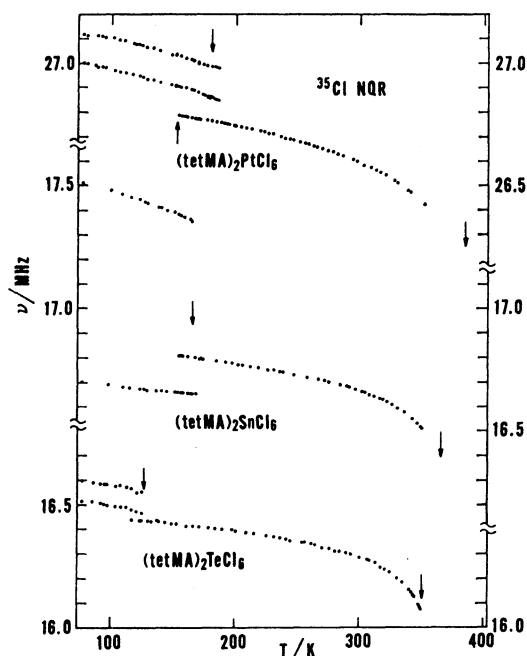
Fig. 1. Temperature dependence of ^{35}Cl NQR frequencies observed for (tetMA)$_2$PtCl$_6$, (tetMA)$_2$TeCl$_6$, and (tetMA)$_2$SnCl$_6$. Arrows indicate T_{tr} determined by the experiments of DTA.[6]

the crystal. With decreasing temperature, it was noticed that the resonance line became suddenly weak at 181 K. On further cooling, two very broad signals appeared at 178 K on the high-frequency side of the weak line labelled as **a**. These experimental facts indicate that (tetMA)$_2$PtCl$_6$ undergoes a structural phase transition at 181 K in good agreement with the previous DTA experiments.[6] In the temperature range between 181 and 178 K, only the weakened **a** line could be detected. This is presumably because the two new lines appearing at 178 K are too broad to be detected immediately below the transition temperature, T_{tr}. The two broad lines, the lower-frequency one (denoted as **b**) of which was about twice stronger than the higher-frequency one (**c**), could be observed continuously down to 77 K. However, the **a** line gradually weakened with decreasing temperature and disappeared in the noise level at 153 K, which agreed well with the second T_{tr} determined from the measurements of DTA.[6] The fact that three and two NQR lines were observed above and below the lower T_{tr}, respectively, indicates that the phase transition at 153 K is also a structural one. As in the previous paper,[6] we call the three phases determined below room temperature as α, β, and γ in the order of decreasing temperature. The above NQR results indicate that there exist at least three and two nonequivalent chlorine atoms in the β and γ phases, respectively. It is interesting to note that no discontinuity can be seen in the temperature dependence of the **a** line and also of the **b** and **c** lines at $T_{tr}(\alpha \rightarrow \beta)$ and $T_{tr}(\beta \rightarrow \gamma)$, respectively.

When the sample of (tetMA)$_2$PtCl$_6$ was warmed from 77 K, the **b** and **c** lines followed exactly the same temperature dependence curves obtained on the cooling

run. Although both lines became weak above ca. 180 K, they could be recorded up to ca. 190 K which is higher by ca. 10 K than $T_{tr}(\alpha \rightarrow \beta)$. On the other hand, the **a** line did not appear at $T_{tr}(\beta \rightarrow \gamma)$ but it became detectable again at 181 K which agreed well with $T_{tr}(\alpha \rightarrow \beta)$. These experimental facts indicate that, when the sample was heated from 77 K, no phase transition takes place at $T_{tr}(\beta \rightarrow \gamma)$ and both phases α and β may coexist in a narrow range of temperature above 181 K.

It is known from the previous DTA experiments[6] that, on heating (tetMA)$_2$PtCl$_6$ from a temperature below 107 K, heat anomaly corresponding to the phase transition $\beta \rightarrow \gamma$ disappears, but it reversibly appears unless the sample is once cooled down below 107 K. In the present NQR experiments, the same behavior in the temperature dependence of the NQR frequencies was observed, i.e., the **a** line appeared at 153 K [$T_{tr}(\beta \rightarrow \gamma)$] on heating the sample which was once cooled down to a temperature not lower than 107 K. This suggests that the phase obtained by cooling the sample to 77 K is different from that existing between 153 and 107 K when the sample was cooled and warmed to and from, respectively, a temperature above 107 K.

Although no heat anomaly could be detected below $T_{tr}(\beta \rightarrow \gamma)$ on both cooling and warming runs, we call the phase obtained by cooling (tetMA)$_2$PtCl$_6$ to 77 K as δ as was defined in the previous paper.[6] The reason why no heat anomaly corresponding to the phase transitions $\gamma \rightleftarrows \delta$ was observed is considered as that the transition $\gamma \rightarrow \delta$ may take place very gradually as already suggested by Berg,[5] and δ transforms directly into β or α at 181 K. The latter statement means that δ is the stable phase at lower temperatures than 181 K. In the T_1 experiments,[6] two phases γ and δ are clearly distinguishable from one another. However, they are almost indistinguishable in the present NQR experiments. Accordingly, it is thought that the change of the orientation of tetMA$^+$ cations in the crystal or the change of the orientation of methyl groups in a cation may be responsible for the transition $\gamma \rightarrow \delta$. Both changes of the orientations of the cations in the crystal of (tetMA)$_2$PtCl$_6$ are considered to give only minor influence on the electric field gradient of resonant chlorine nuclei (possibly a change in the NQR linewidth) because tetMA$^+$ is highly symmetric.

With increasing temperature above $T_{tr}(\delta \rightarrow \alpha)$, the frequency of the **a** line decreased quite normally and faded out in the noise level at ca. 350 K, indicating the absence of phase transition up to this temperature.

At room temperature, (tetMA)$_2$TeCl$_6$ yielded a single ^{35}Cl NQR line.[11] With decreasing temperature, the line became gradually weak from ca. 150 K and finally disappeared at 117 K. On cooling further, no resonance was observed until two broad signals appeared at 106 K. The two signals became gradually strong with decreasing temperature and could be detected down to 77 K. When (tetMA)$_2$TeCl$_6$ was heated from 77 K, on the other hand, the doublet lines could be observed up to 128 K, above which temperature a single line was observed at the same frequency as that detected on the cooling run. These experimental facts indicate that (tetMA)$_2$TeCl$_6$ undergoes a first-order structural phase

transition at 128 K in agreement with the previous DTA and NMR results,[6] and that all chlorine atoms are equivalent in the crystal of the high-temperature phase whereas two nonequivalent chlorine atoms exist in the low-temperature phase crystal.

With increasing the temperature above room temperature, the frequency of the single line of (tetMA)$_2$-TeCl$_6$ decreased unusually before it weakened and disappeared at *ca.* 350 K. This observation suggested the occurrence of another phase transition at a temperature immediately above 350 K.

For (tetMA)$_2$SnCl$_6$, a structural phase transition showing a thermal hysteresis was located at 168 K from the measurements of the temperature dependence of ^{35}Cl NQR frequencies. The results agree with those of the previous DTA experiments.[6] In the low-temperature phase, two largely separated very broad signals, the lower-frequency one of which was stronger, were observed suggesting that the crystalline lattice of (tetMA)$_2$SnCl$_6$ undergoes a tetragonal distortion below T_{tr}. With increasing temperature, the frequency of the high-temperature line decreased rather rapidly and the line disappeared at *ca.* 350 K.

DTA above Room Temperature. To locate another high-temperature phase transition expected for the present complexes from the temperature dependence measurements of ^{35}Cl NQR frequencies, we carried out DTA experiments above room temperature. The results were that thermal anomalies indicating the presence of phase transitions were found at 385, 351, and 365 K for the Pt, Te, and Sn complexes, respectively. Hereafter, the highest-temperature phase of these complexes is denoted as α'. It is worthwhile to note here that no ^{35}Cl NQR spectra were observed in the α' phase of these complexes although signals were searched carefully above T_{tr}.

Powder X-Ray Diffraction. The present study has revealed the presence of the high-temperature phase for the three hexachloro complexes. Therefore, we took X-ray powder patterns at various temperatures in order to obtain detailed information on the structure of the complexes in their high-temperature phase as well as on their room-temperature structure.
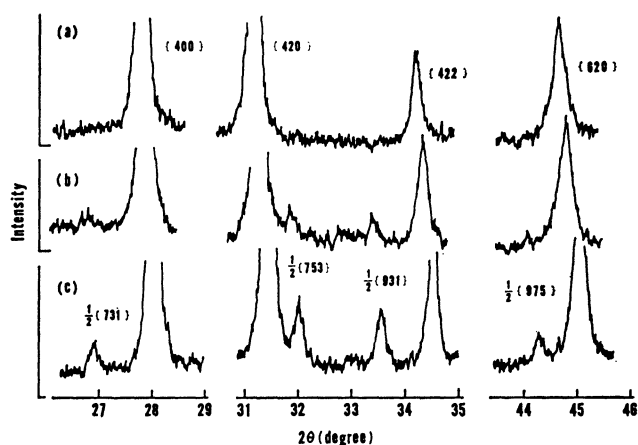
The diffraction patterns (below $2\theta=60°$) of (tetMA)$_2$-PtCl$_6$ recorded at room temperature could be attributed to the Fm3m cubic lattice with $a_0=12.73_1$ Å, in agreement with the results of Berg and Søtofte.[7] However, there remained four unassignable weak diffraction lines, the *d*-spacing values of which were 3.32$_0$, 2.79$_5$, 2.67$_1$, and 2.04$_4$ Å (see Fig. 2). These four reflections cannot be indexed by any Fm3m-allowed sets of integers along with $a_0=12.73_1$ Å. If we take a large cubic unit cell consisting of eight Fm3m units, however, the four reflections can be indexed by the following Miller indices, {731}, {753}, {931}, and {975} in the order of the above *d*-spacing values.

Berg and Nielsen reported that (tetMA)$_2$TeBr$_6$ has approximately the Fm3m structure but exactly it forms cubic crystals belonging to the space group Fd3c with $a_0=26.563$ Å and $Z=32$. The large unit cell is formed by doubling each edge of the Fm3m unit and, therefore, includes eight Fm3m units. Even in this structure, all the bromine atoms are crystallographically equivalent in agreement with the earlier NQR results.[14] Moreover, it is of interest to note that the Fm3m-forbidden reflections observed for (tetMA)$_2$PtCl$_6$ are allowed for the Fd3c system and are interpreted well. Accordingly, it can be concluded that, at room temperature, (tetMA)$_2$PtCl$_6$ forms cubic crystals belonging to the space group Fd3c with $a_0=25.46_2$ Å and $Z=32$. Very recently, Mackenzie *et al.* showed that [N(CD$_3$)$_4$]$_2$PtCl$_6$ also forms Fd3c cubic crystals at room temperature.[9] The diffraction patterns of (tetMA)$_2$TeCl$_6$ and (tetMA)$_2$SnCl$_6$ could be well described in the Fd3c cubic system with a_0 being 25.86$_8$ and 25.73$_6$ Å, respectively.

The diffraction patterns of the complexes studied were recorded at various temperatures above room temperature as shown in Fig. 2 for (tetMA)$_2$PtCl$_6$. When the temperature was raised, the Fm3m-forbidden reflections became weak and finally disappeared from the patterns taken in the α' phase of the complex. Therefore, the patterns of α'-(tetMA)$_2$PtCl$_6$ are completely interpreted in terms of the Fm3m lattice with a_0 being 12.82$_8$ Å at *ca.* 388 K. Similarly, the Fm3m lattice constant a_0 of α'-(tetMA)$_2$TeCl$_6$ and α'-(tetMA)$_2$SnCl$_6$ were determined as 13.05$_3$ Å at *ca.* 394 K and 12.97$_3$ at *ca.* 389 K, respectively. The lattice constants determined in the present study are estimated to be accurate to 0.010 Å.

Fig. 2. X-Ray powder patterns of (tetMA)$_2$PtCl$_6$ taken at (a) *ca.* 400 K, (b) *ca.* 370 K, and (c) *ca.* 300 K. Indices are referred to the Fm3m unit cell.

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