NQR and Phase Transitions of Tetramethylammonium Tetrahalogenomercurates (II) *

Hiromitsu Terao[a], Tsutomu Okuda[b], Koji Yamada[d], Hideta Ishihara[c], and Alarich Weiss[d†]

[a] Faculty of Integrated Arts and Sciences, Tokushima University, Minamijosanjima-cho, Tokushima 770, Japan
[b] Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama, Higashihiroshima 739, Japan
[c] Department of Chemistry, Faculty of Education, Saga University, Honjo-machi 1, Saga 840, Japan
[d] Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstr. 20, D-64287 Darmstadt, Germany

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NQR and DTA revealed phase transitions in $[(CH_3)_4N]\ _2HgBr_4$ and $[(CH_3)_4N]\ _2HgI_4$ at 272 K and 264 K, respectively. The NQR resonance lines faded out with increasing temperature. From preliminary measurements of ^{81}Br NQR spin-lattice relaxation times and ^{199}Hg NMR a reorientational motion of $HgBr_4^-$ ions around one of their pseudo C_3 axes in the room temperature phase of $[(CH_3)_4N]\ _2HgBr_4$ is suggested.

Key words: $[(CH_3)_4N]\ _2HgX_4$, Phase transitions, Halogen NQR; ^{199}Hg NMR

Introduction

$[(CH_3)_4N]\ _2HgCl_4$ undergoes a ferroelastic phase transition at 279 K [1], the nature of which was investigated by a single crystal X-ray analysis [2]. $[(CH_3)_4]\ _2HgBr_4$ and $[(CH_3)_4N]\ _2HgI_4$ are isostructural with the chloride [3]. We have investigated $[(CH_3)_4N]\ _2HgX_4$ (X = Cl, Br, I) in the course of a halogen NQR study for a series of the complex compounds of mercury (II) halides with substituted alkylammonium halides.

Experimental

$[(CH_3)_4N]\ _2HgCl_4$ was prepared by mixing stoichiometric amounts of $HgCl_2$ and $(CH_3)_4NCl$ in ethanol [3]. The very small crystals were extracted by the same solvent in a Soxhlet extractor for improvement of the crystal quality. $[(CH_3)_4N]\ _2HgBr_4$ was prepared by cooling a 1:2 solution of $HgBr_2$ and $(CH_3)_4NBr$ in concentrated HBr [3]. $[(CH_3)_4N]\ _2HgI_4$ was prepared by cooling a 1:2 solution of HgI_2 and $(CH_3)_4NI$ in concentrated HI. C, H, N analyses confirmed the chemical formula of the compounds ($[(CH_3)_4N]\ _2HgCl_4$: Found C = 19.66, H = 4.65, N = 5.71%, Calcd C = 19.58, H = 4.93, N = 5.71%; $[(CH_3)_4N]\ _2HgBr_4$: Found C = 14.60, H = 3.66, N = 4.43%, Calcd C = 14.37, H = 3.62, N = 4.19%; $[(CH_3)_4N]\ _2HgI_4$: Found C = 11.10, H = 2.62, N = 3.22%, Calcd C = 11.22, H = 2.82, N = 3.27%).

NQR signals were observed by using super-regenerative spectrometers and a Matec pulsed spectrometer. ^{81}Br NQR spin-lattice relaxation times were measured by observing the free induction decays following to $90°-\tau-90°$ pulse sequences or the echo signals following to $90°-\tau-90°-180°$ pulse sequences. ^{199}Hg NMR spectra of $[(CH_3)_4N]\ _2HgBr_4$ were recorded below and above the phase transition temperature at 6.37 T. For the DTA measurements a homemade apparatus was used. The accuracy of the temperature measurements was ±1 K.

Results

The ^{35}Cl and ^{81}Br NQR frequencies for representative temperatures are listed in Table 1. At low temperatures $[(CH_3)_4N]\ _2HgCl_4$ gave four resonance lines as shown in Figure 1. With increase in temperature three of these faded out around 245 K, while the remaining

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Reprint requests to Dr. Hiromitsu Terao.

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Table 1. The ^{35}Cl and ^{81}Br NQR frequencies in $[(CH_3)_4N]_2HgCl_4$ and $[(CH_3)_4N]_2HgBr_4$.

Compound	Isotope	ν/MHz[a]		
		77 K	200 K	298 K
$[(CH_3)_4N]_2HgCl_4$	^{35}Cl	13.90(10)[bc]	13.55(12)	
		13.84(10)[c]	13.66(15)	13.43(6)[d]
		13.84(10)[c]	13.25(11)	
		12.69(13)	12.52(17)	
$[(CH_3)_4N]_2HgBr_4$	^{81}Br	91.91(100)	89.56(100)	
		90.42(180)	86.55(100)	
		88.16(130)	87.56(130)	85.88(100)
		84.02(240)	83.01(140)	

[a] The estimated accuracies of frequencies are ±0.01 MHz for ^{35}Cl and ±0.02 MHz for ^{81}Br.
[b] The numbers in parentheses are signal to noise ratios observed on a recorder.
[c] The estimated accuracies ±0.05 MHz.
[d] At 270 K.

one was followed up to 276 K near $T_c = 279$ K. No signal was detected above T_c.

Four lines exist also in $[(CH_3)_4N]_2HgBr_4$ at low temperatures (Figure 2). Three of these faded out around 266 K. The remaining one could be observed until ca. 358 K with a characteristic change at $T_c = 272$ K.

The temperature dependence of ^{127}I NQR lines due to the $m = \pm 1/2 \leftrightarrow \pm 3/2$ transitions in $[(CH_3)_4N]_2HgI_4$ is shown in Figure 3. Below $T_c = 264$ K eight lines were observed. Above T_c three resonance lines were observed, two of which faded out around 325 K. The remaining one was recorded until 368 K, where the signal intensity was still strong enough.

The DTA results for the respective compounds are shown in Figure 4. The curve of $[(CH_3)_4N]_2HgCl_4$ exhibits a small anomaly at $T_c = 279$ K. The anomaly may indicate a 2nd-order type phase transition. The DTA curve of $[(CH_3)_4N]_2HgBr_4$ shows an anomaly at $T_c = 277$ K, which may also indicate a 2nd-order type phase transition. On the other hand, the DTA curve of $[(CH_3)_4N]_2HgI_4$ may indicate a 1st-order type phase transition whose sharp peaks occur at 264 and 260 K on cooling and heating, respectively.

The temperature dependence of the ^{81}Br NQR spin-lattice relaxation times T_1 was measured for two lines of $[(CH_3)_4N]_2HgBr_4$ as shown in Figure 5. With increasing temperature, T_1 of both lines began to decrease steeply around 200 K and ceased to be observable around 250 K, which is below $T_c = 272$ K. That is, T_1 and also T_2^* became shorter than the dead time of

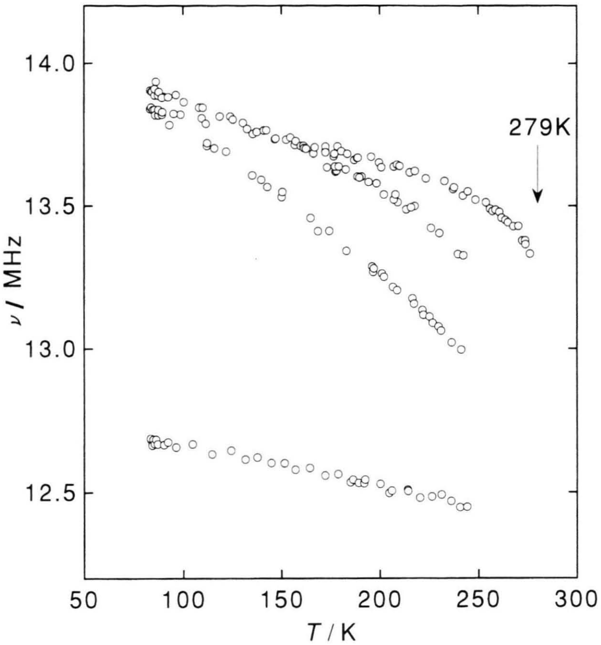

Fig. 1. Temperature dependence of ^{35}Cl NQR frequencies in $[(CH_3)_4N]_2HgCl_4$.

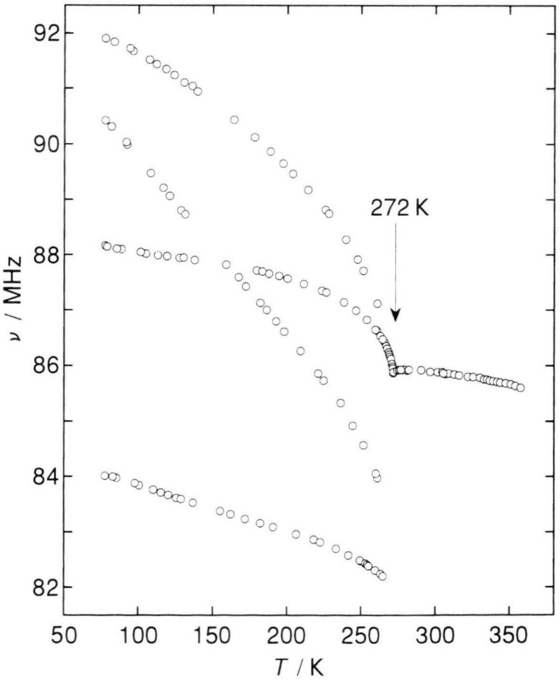

Fig. 2. Temperature dependence of ^{81}Br NQR frequencies in $[(CH_3)_4N]_2HgBr_4$.

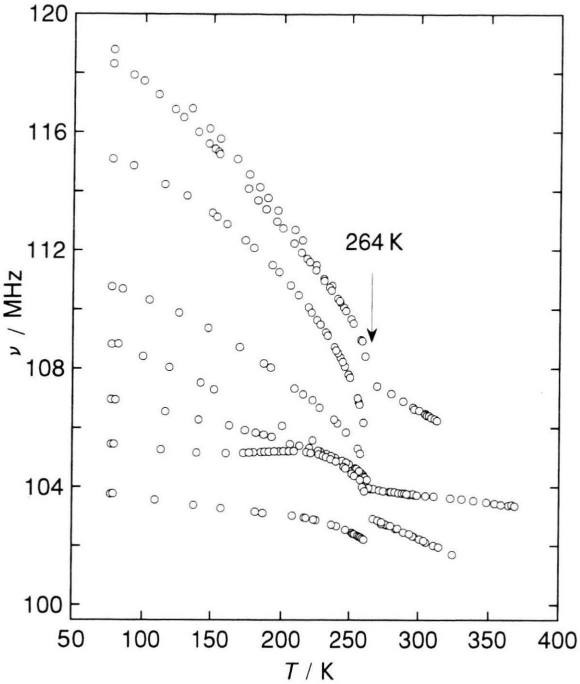

Fig. 3. Temperature dependence of ^{127}I ($m = \pm 1/2 \leftrightarrow 3/2$) NQR frequencies in $[(CH_3)_4N]_2HgI_4$.

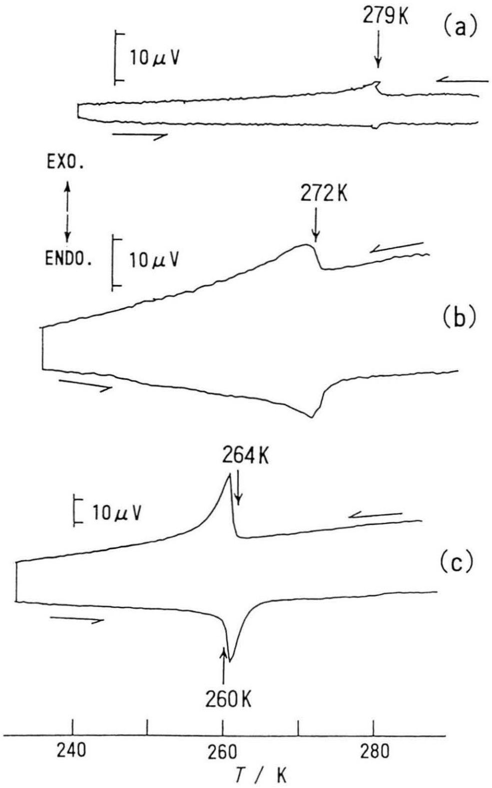

Fig. 4. DTA curves for $[(CH_3)_4N]_2HgX_4$. (a) X=Cl, (b) X=Br, (c) X=I.

the receiver (ca. 10 μs). Above T_c we could again get FID signals for the remaining line. Unfortunately, however, T_1 measurements were impossible because of the very short relaxation times, $T_1 < 20$ μs. On the other hand, one line could be observed continuously through T_c by the super-regenerative spectrometer, as shown in Figure 2. This may imply that the super-regenerative spectrometer is more applicable than the pulsed one for the detection of signals with $T_1 < 20$ μs.

The ^{199}Hg ($I = 1/2$) NMR spectra of $[(CH_3)_4N]_2HgBr_4$ recorded at 150 K and room temperature are shown in Figure 6. The line width at room temperature decreased to about 1/3 of that at 150 K.

Discussion

Kamenar and Nagl [3] have determined the structure of the room temperature phase (phase I) of $[(CH_3)_4N]_2HgBr_4$: Orthorhombic, Pnma with $Z = 4$, as shown in Figure 7. Br(2) and Br(2)′ are related by the mirror plane at $y = 1/4$. Therefore three crystallographically nonequivalent Br atoms exist in the unit

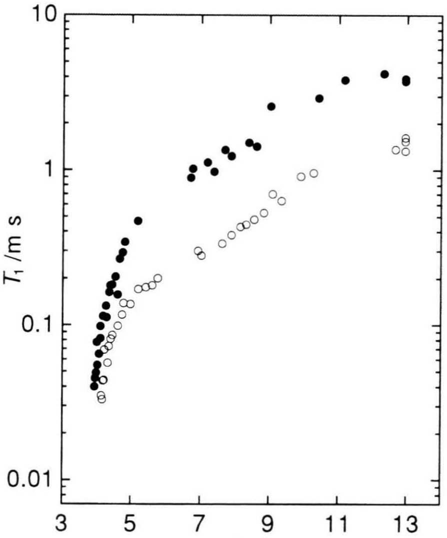

Fig. 5. Temperature dependence of the spin-lattice relaxation time (T_1) of ^{81}Br NQR resonance lines in $[(CH_3)_4N]_2HgBr_4$. Filled and open circles denote the 88.16 MHz and 84.02 MHz lines at 77 K, respectively.

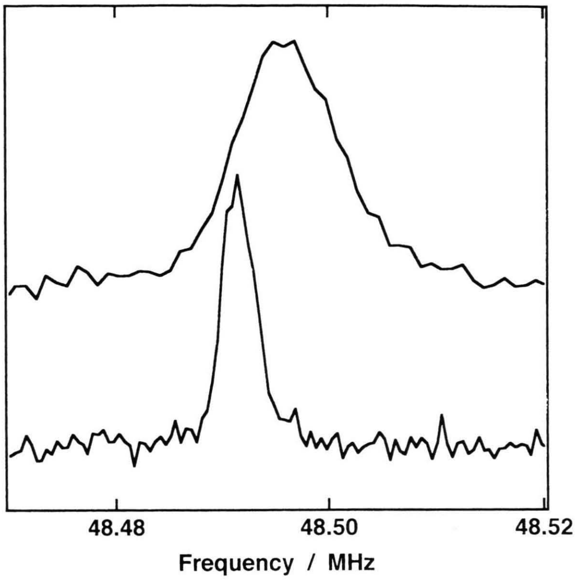

Fig. 6. ^{199}Hg NMR spectra in $[(CH_3)_4N]_2HgBr_4$. Above: 150 K; below: room temperature.

Table 2. The ^{127}I NQR frequencies, asymmetry parameters (η), and nuclear quadrupole coupling constants (e^2qQ/h) in $[(CH_3)_4N]_2HgI_4$.

T/K	ν/MHz[a]		e^2qQ/h/MHz	η
	$m=\pm 1/2$ $-\pm 3/2$	$m=\pm 3/2$ $-\pm 5/2$		
77	118.80(90)[b]	235.56(10)	786.26[785.56][c]	0.0818[0.0867]
	118.31(120)	235.31(10)	785.04[785.75]	0.0655[0.0589]
	115.10(120)	228.10(15)	761.42	0.0843
	110.77(250)	219.69(40)	733.26	0.0807
	108.82(160)	217.35(20)	724.64	0.0320
	106.97(280)	213.13(36)	710.85	0.0541
	105.46(130)	207.32(18)	692.94[688.13]	0.1160[0.1417]
	103.76(240)	205.61(25)	686.36[691.16]	0.0847[0.0272]
298	106.62(9)	n.d.[d]	–	–
	103.73(70)	207.41(17)	691.39	0.0136
	102.28(19)	n.d.	–	–

[a] The estimated accuracies of frequencies are within ±0.02 MHz and ±0.03 MHz for the transitions of $m=\pm 1/2-\pm 3/2$ and $m=\pm 3/2-\pm 5/2$, respectively.
[b] The numbers of parentheses are signal to noise ratios observed on a recorder.
[c] The numbers in brackets are values obtained by a possible alternative choice.
[d] Not detected.

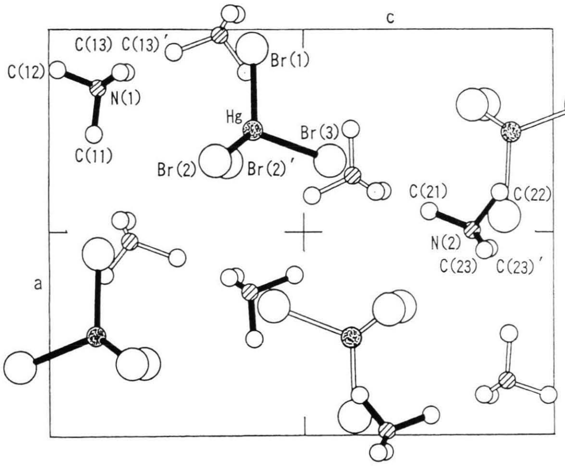

Fig. 7. The crystal structure of $[(CH_3)_4N]_2HgBr_4$ at room temperature (after [3]). The crystal belongs to Pnma; $a=1280.1$, $b=930.9$, $c=1614.8$ pm.

cell. However, only one ^{81}Br NQR line has been observed in phase I (Figure 2). A very similar temperature dependence has been observed for the ^{79}Br NQR of $[(CH_3)_4N]_2ZnBr_4$ by Perret et al. [4]. $[(CH_3)_4N]_2ZnBr_4$ has a phase transition at 287 K. Three of its four resonance lines in the low temperature phase II became unobservable above 260 K, while the remaining one could be followed up to 325 K in phase I. The same number of lines and the similar temperature dependences may suggest that the monoclinic phases II of both compounds are also isostructural. However, a recent structure refinement for phase I of $[(CH_3)_4N]_2ZnBr_4$ [6] has shown that a disordered structure is more plausible than an ordered one. Its mean structure is isostructural with that of $[(CH_3)_4N]_2HgBr_4$ [3]. A similar disordered structure has been considered for $[(CH_3)_4N]_2HgCl_4$, as described later.

The existence of only one signal from the three chemically different Br atoms in phases I of the above bromides is quite curious. The same situation appears in the $\nu-T$ curves of $[(CH_3)_4N]_2HgI_4$ (Fig. 3) and $[(CH_3)_4N]_2ZnI_4$[5]. The existence of three resonance lines on the low temperature side in phase I of both compounds is consistent with their β-K_2SO_4 structure. However, with increasing temperature two of them become unobservable above ca. 325 and ca. 284 K in $[(CH_3)_4N]_2HgI_4$ and $[(CH_3)_4N]_2ZnI_4$, respectively.

The above discrepancy between the number of resonance lines and that of chemically different halogen atoms has been explained by dominant torsional vibrations of MX_4 tetrahedra around the special bonds M–X(1) [4, 5]. Such vibrations would leave the EFG tensors of X(1) atoms almost invariant, while producing much larger effects on all other atoms whose bonds make large angles with the M–X(1) bond. In $[(CH_3)_4N]_2HgBr_4$, the Hg–Br(1) bond makes only 2.5° with the a-axis. Dominant torsional lattice vibrations around the a-axis would therefore bring the situation described above. Thus, the EFG tensors of the Br(1) would be left almost unchanged, while those of Br(2), Br(2)′, and Br(3) would suffer big fluctuations. As the amplitude of vibrations increases, the line widths of all Br atoms other than Br(1) may broaden beyond the limit of observation, resulting in a single line. The same argument may explain the partial disappearance in $[(CH_3)_4N]_2HgI_4$. In $[(CH_3)_4N]_2HgCl_4$ three lines disappear prior to the remaining one. Pirnat et al. [5] have added a further explanation by considering T_2^* for the extinction of the resonance lines. Now we may assign the 85.88 MHz line at 298 K to the Br(1) atom of $[(CH_3)_4N]_2HgBr_4$, and the 103.73 MHz line at 298 K to the I(1) atoms in $[(CH_3)_4N]_2HgI_4$. Further, in the latter compound we may assign the 106.62 MHz line to I(3) and the 102.28 MHz line to I(2) and I(2)′ by considering that the former line exhibits about half the signal intensity of the latter one.

On the other hand, in contrast to the above compounds, Cs_2CdBr_4 [7] and Cs_2HgBr_4 [8] give three Br NQR lines throughout the observed temperature range of the room temperature phases with the β-K_2SO_4 structure. On considering this difference we should pay attention to a possible correlation in the rotational motions between cations and anions in the crystals of the tetramethylammonium salts. Such a correlation has been suggested in the crystals of $[(CH_3)_4N]_2ZnBr_4$ [6] and $[(CH_3)_4N]_2HgCl_4$ [2].

The structure refinement phases I and II of $[(CH_3)_4N]_2HgCl_4$ by Asahi et al. [2] has shown that one anion and two kinds of cations are in disorder in the crystal. In phase I, $HgCl_4^-$ ions as well as $(CH_3)_4N^+$ ions occupy two sites related by the mirror plane in equal probability such that the mean structure is isostructural with that given in [3]. In phase II, ordering of ions takes place such that the ions are almost ordered below 233 K. One may think that the disordering of $HgCl_4^-$ ions causes the extinction of ^{35}Cl NQR lines as seen in Figure 1. However, Asahi et al. [6] have proposed a disordered structure also for phase I of $[(CH_3)_4N]_2ZnBr_4$, which is almost equal to that of $[(CH_3)_4N]_2HgCl_4$. In contradiction, a single NQR line has been observed in $[(CH_3)_4N]_2ZnBr_4$ and $[(CH_3)_4N]_2HgBr_4$, while no line in $[(CH_3)_4N]_2HgCl_4$.

It seems important to investigate the motional states of anions to avoid the above contradiction. Thus, we did the preliminary measurements of ^{81}Br NQR spin-lattice relaxation times T_1 and ^{199}Hg NMR spectra of $[(CH_3)_4N]_2HgBr_4$. A steep decrease of T_1 of both resonance lines above ca. 200 K may indicate the increasing activation of large torsional vibrations of anions as well as cation motions (Figure 5). A more remarkable observation is that the line width of the ^{199}Hg NMR spectrum at room temperature is decreased to almost 1/3 of that at 150 K (Figure 6). By considering the possible large contribution from neighboring Br atoms to the line width, such a decrease may suggest the existence of a reorientational motion of $HgBr_4$ tetrahedra around one of the pseudo C_3 axes in phase I of $[(CH_3)_4N]_2HgBr_4$. If these axes coincide with the Hg–Br(1) bonds, this motion does not contradict the observation of a single ^{81}Br NQR line for the reason described above. In the DTA curves, the anomaly in the bromide is rather large compared to that in the chloride. This may be consistent with the extra motion of anions in the bromide. Note also that the ^{81}Br NQR frequency differences in $[(CH_3)_4N]_2HgBr_4$, $\Delta\nu = \nu(T = T_c) - \nu(T)$, follow to the equation $\Delta\nu \propto (T_c - T)^{0.63}$ in the range of ca. 10 K below T_c. This critical exponent deviates a little from 1/2 [9].

In summary, T_c and the fade-out temperatures of NQR resonance lines are listed in Table 3. The existence of T_{f1}, at which the resonance lines become unobservable, is explained by the dominant torsional vibrations of HgX_4 tetrahedra around one of Hg–X bonds. On the other hand the fade-out of the remaining lines may result from the increasing thermal motions of cations and/or the anions in addi-

Table 3. Phase transition temperatures and fade-out temperatures.

Compound	T_{f1}/K [a]	T_{f2}/K [b]	T_c/K
$[(CH_3)_4N]_2HgCl_4$	245	276	279 ± 1 (2nd) [c]
$[(CH_3)_4N]_2HgBr_4$	266	358	272 ± 1 (2nd)
$[(CH_3)_4N]_2HgI_4$	325	> 368	264 ± 2 (1st)

[a] Temperatures at which some resonance lines fade out.
[b] Temperatures at which the last line fades out.
[c] Plausible orders of phase transitions.

tion to the above dominant motions. Phase II of $[(CH_3)_4N]_2HgI_4$ would be isostructural with phase III of $[(CH_3)_4N]_2ZnI_4$. The missing ^{35}Cl NQR in $[(CH_3)_4N]_2HgCl_4$ at high temperatures may be ascribed to the disordering of cations and anions. It seems that the phase transitions of $[(CH_3)_4N]_2HgBr_4$ is connected with the onset of a reorientational motion of $HgBr_4^-$ ions around their pseudo C_3 axis.

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