Studies of Structure and Phase Transition in $[C(NH_2)_3]HgBr_3$ and $[C(NH_2)_3]HgI_3$ by Means of Halogen NQR, ^{1}H NMR, and Single Crystal X-Ray Diffraction

Hiromitsu Terao, Masao Hashimoto[a], Shinichi Hashimoto[a], and Yoshihiro Furukawa[b]

Department of Chemistry, Faculty of Integrated Arts and Sciences, Tokushima University, Minamijosanjima-cho, Tokushima 770-8502, Japan

[a] Department of Chemistry, Faculty of Science, Kobe University, Nadaku, Kobe 657-8501, Japan

[b] Faculty of School Education, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8524, Japan

Reprint requests to Dr. H. T.; E-mail: terao@ias.tokushima-u.ac.jp

Z. Naturforsch. **55 a,** 230–236 (2000); received August 23, 1999

Presented at the XVth International Symposium on Nuclear Quadrupole Interactions, Leipzig, Germany, July 25 - 30, 1999.

The crystal structure of $[C(NH_2)_3]HgBr_3$ was determined at room temperature: monoclinic, space group C2/c, $Z = 4$, $a = 775.0(2)$, $b = 1564.6(2)$, $c = 772.7(2)$ pm, $\beta = 109.12(2)^\circ$. In the crystal, almost planar $HgBr_3^-$ ions are connected via Hg···Br bonds, resulting in single chains of trigonal bipyramidal $HgBr_5$ units which run along the c direction. $[C(NH_2)_3]HgI_3$ was found to be isomorphous with the bromide at room temperature. The temperature dependence of the halogen NQR frequencies ($77 < T/K <$ ca. 380) and the DTA measurements evidenced no phase transition for the bromide, but a second-order phase transition at (251 ± 1) K (T_{c1}) and a first-order one at (210 ± 1) K (T_{c2}) for the iodide. The transitions at T_{c2} are accompanied with strong supercooling and significant superheating. The room temperature phase (RTP) and the intermediate temperature phase (ITP) of the iodide are characterized by two $^{127}I_{(m=1/2\leftrightarrow3/2)}$ NQR lines which are assigned to the terminal and the bridging I atoms, respectively. There exist three lines in the lowest temperature phase (LTP), indicating that the resonance line of the bridging atom splits into two. The signal intensities of the $^{127}I_{(m=1/2\leftrightarrow3/2)}$ NQR lines in the LTP decrease with decreasing temperature resulting in no detection below ca. 100 K. The $^{127}I_{(m=1/2\leftrightarrow3/2)}$ NQR frequency vs. temperature curves are continuous at T_{c1}, but they are unusual in the LTP. The T_1 vs. T curves of ^{1}H NMR for the bromide and iodide are explainable by the reorientational motions of the cations about their pseudo three-fold axes. The estimated activation energies of the motions are 35.0 kJ/mol for the bromide, and 24.1, 30.1, and 23.0 kJ/mol for the RTP, ITP, and LTP of the iodide, respectively.

Key words: $[C(NH_2)_3]HgX_3$; Crystal Structure; Phase Transition; NQR; ^{1}H NMR.