

Isolated versus Condensed Anion Structure VI: X-ray Structure Analysis and ^{81}Br NQR of Guanidinium Pentabromodicadmate(II), $[\text{C}(\text{NH}_2)_3]\text{Cd}_2\text{Br}_5$, *tris*-Hydrazinium Pentabromocadmte(II), $[\text{H}_2\text{NNH}_3]_3\text{CdBr}_5$, and *bis*-Hydrazinium Tetrabromocadmte(II)-Tetra Hydrate, $[\text{H}_2\text{NNH}_3]_2\text{CdBr}_4\cdot 4\text{H}_2\text{O}$

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The structure of the condensed bromocadmte anions in $[\text{C}(\text{NH}_2)_3]\text{Cd}_2\text{Br}_5$ (**1**) and $[\text{H}_2\text{NNH}_3]_3\text{CdBr}_5$ (**2**) were studied at room temperature by X-ray diffraction. (**1**) crystallizes with double-chains bridged by Br atoms (orthorhombic, Pmmn, $Z = 2$, $a = 1394.0(5)$, $b = 394.5(1)$, $c = 1086.9(5)$ pm). This chain structure was not described previously. (**1**) shows three ^{81}Br NQR lines at temperatures between 77 and 323 K. Structural phase transitions take place at 283 K and at 535 K. (**2**) crystallizes with Br bridged zigzag-chains (monoclinic, $P2_1$, $Z = 2$, $a = 943.1(1)$, $b = 778.8(2)$, $c = 942.0(2)$ pm, $\beta = 102.10(2)^\circ$) and shows a first-order phase transition around 304 K with a large thermal hysteresis. Below the transition point five ^{81}Br NQR lines are observed at temperatures between 122 and 304 K, and above the transition point four ^{81}Br NQR lines at temperatures between 288 and 353 K. Two ^{81}Br NQR lines are observed in $[\text{H}_2\text{NNH}_3]_2\text{CdBr}_4\cdot 4\text{H}_2\text{O}$ (**3**) at temperatures between 77 and around 320 K with positive temperature coefficients.

Key words: NQR; DSC; Crystal Structure; Phase Transition; Bromocadmte.