Isolated versus Condensed Anion Structure IV: An NQR Study and X-ray Structure Analysis of $[H_3N(CH_2)_3NH_3]CdI_4 \cdot 2H_2O$, $[H_3CNH_2(CH_2)_3NH_3]CdBr_4$, $[(CH_3)_4N]_2CdBr_4$, and $[(CH_3)_3S]_2CdBr_4$*

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The phase I of $[H_3N(CH_2)_3NH_3]CdI_4 \cdot 2H_2O$ (**1**) crystallizes with isolated $[CdI_4]^{2-}$ tetrahedra; monoclinic, C2/c, $Z = 8$, $a = 1702.6(3)$, $b = 1459.3(3)$, $c = 1555.5(3)$ pm, and $\beta = 120.32(3)°$ at 299 K. (**1**) shows a first-order phase transition at $T_{I \leftrightarrow II} = 245$ K. The eight ^{127}I (ν_1) NQR lines in phase II change discontinuously into four lines in phase I. The transition entropy from DSC measurements, $\Delta S = 5.0$ J K^{-1} mol^{-1}, shows that this transition is probably due to order-disorder of cations. $[H_3CNH_2(CH_2)_3NH_3]CdBr_4$ (**2**) crystallizes with isolated $[CdBr_4]^{2-}$ tetrahedra; orthorhombic $P2_12_12_1$, $Z = 4$, $a = 1447.8(5)$, $b = 1280.3(4)$, $c = 709.7(3)$ pm at 299 K. (**2**) shows four ^{81}Br NQR lines between 77 and around 325 K, above which temperature the lines disappear. $[(CH_3)_4N]_2CdBr_4$ (**3**) shows a second-order phase transition at $T_{I \leftrightarrow II} = 271$ K. Three of four ^{81}Br NQR lines in phase II disappear below this transition point, the other line can be observed up to 315 K. The transition entropy, $\Delta S = 9.01$ J K^{-1} mol^{-1}, indicates that the transition is an order-disorder type of the cations. $[(CH_3)_3S]_2CdBr_4$ (**4**) shows a first-order type phase transition at $T_{I \leftrightarrow II} = 304$ K. The four lines spectrum of ^{81}Br NQR is observed in phase II and disappears above the transition point. The transition entropy, $\Delta S = 46.8$ J K^{-1} mol^{-1} is abnormally large. The role of the hydrogen bond and the bridging power between the halogen and cadmium atoms upon the formation of the condensed anion structure is discussed.

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