Synthse und Kristallstrukturen von $N$-[ω-(Dimethylammonio)alkyl]-$N',N',N''$-tetramethylguanidinium-Chlorid-tetraphenylboraten

Synthesis and Crystal Structures of $N$-[ω-(Dimethylammonio)alkyl]-$N',N',N''$-tetramethylguanidinium Chloride Tetraphenylborates

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Dicationic $N,N',N'',N''$-pentasubstituted guanidinium dichlorides 4a, b are obtained from the chloroformamidinium salt 2 and diamines 3a, b. $N$-[2-(Dimethylammonio)ethyl]-$N',N',N'',N''$-tetramethylguanidinium chloride tetraphenylborate (5a) and $N$-[3-(dimethylammonio)propyl]-$N',N',N'',N''$-tetramethylguanidinium chloride tetraphenylborate (5b) were synthesized from 4a, b by anion metathesis with one equivalent of sodium tetraphenylborate. The thermal properties of the salts 5a, b were studied by means of DSC methods, and their crystal structures were determined by single-crystal X-ray diffraction analysis. For 5a a solid-solid phase transition is observed at $-156 \, ^\circ\mathrm{C}$ to a low-temperature structure. The room-temperature modification (α-5a) crystallizes in the centro-symmetric orthorhombic space group $Pbca$ ($a = 13.1844(4)$, $b = 13.8007(4)$, $c = 34.7537(11)$ ˚A). The guanidinium ions are interconnected via chloride ions through bridging N–H···Cl hydrogen bonds, providing isolated units. The tetraphenylborate ions show some dynamic disordering in the crystal structure. The low-temperature modification (β-5a) also crystallizes orthorhombically, but in the non-centrosymmetric space group $Pna2_1$ ($a = 13.1099(4)$, $b = 69.1810(11)$, $c = 13.5847(5)$ ˚A) and consists of four crystallographically independent cations and anions in the unit cell. Compared with the room-temperature structure, a similar N–H···Cl hydrogen bond pattern is observed in the β-phase, but the tetraphenylborate ions are now completely ordered. 5b crystallizes in the monoclinic space group $P2_1/c$ ($a = 10.8010(3)$, $b = 14.1502(5)$, $c = 20.9867(9)$ ˚A, $\beta = 94.322(1)^\circ$). In the crystal structure the guanidinium ions are linked via chloride ions through N–H···Cl hydrogen bonds, but in contrast to 5a two infinite strands are formed along the $a$ axis with the tetraphenylborate ions interspersed between them for charge compensation.

Keywords: $N,N,N',N''$-Pentasubstituted Guanidinium Salts, Mixed Chloride Tetraphenylborate Salts, Thermal Analysis, Phase Transition, X-Ray Crystal Structures