

Synthese und Kristallstrukturen von N -[ω -(Dimethylammonio)alkyl]- N',N',N'',N'' -tetramethylguanidinium-chlorid-tetraphenylboraten

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

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Dicationic N,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 $-156\text{ }^\circ\text{C}$ to a low-temperature structure. The room-temperature modification (α -**5a**) crystallizes in the centrosymmetric orthorhombic space group $Pbca$ ($a = 13.1844(4)$, $b = 13.8007(4)$, $c = 34.7537(11)$ Å). The guanidinium ions are interconnected *via* chloride ions through bridging N–H \cdots 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 $Pna2_1$ ($a = 13.1099(4)$, $b = 69.1810(11)$, $c = 13.5847(5)$ Å) and consists of four crystallographically independent cations and anions in the unit cell. Compared with the room-temperature structure, a similar N–H \cdots 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 $P2_1/c$ ($a = 10.8010(3)$, $b = 14.1502(5)$, $c = 20.9867(9)$ Å, $\beta = 94.322(1)^\circ$). In the crystal structure the guanidinium ions are linked *via* chloride ions through N–H \cdots 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.

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