Two Polymorphic Modifications of Dibromo-bis(acetonitrile-N)-zinc(II)

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Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70th birthday

Two polymorphic modifications of dibromo-bis(acetonitrile-N)-zinc(II) have been characterized by single crystal structure analysis and X-ray powder measurements. Form **I** cyrstallizes in the orthorhombic space group *Pnma* with $a = 13.101(2)$, $b = 10.210(1)$, $c = 6.8078(7)$ Å and $Z = 4$. The structure is composed of discrete molecular complexes in which each zinc cation is coordinated by two bromide anions and two acetonitrile ligands within distorted tetrahedra. Form **II** crystallizes in the orthorhombic space group *Cmcm* with $a = 8.0734(8)$, $b = 11.012(1)$, $c = 10.204(1)$ Å and $Z = 4$. In this compound also discrete complexes are found and the coordination of the zinc atoms is identical to that of form **I**. Two bromide atoms and two acetonitrile ligands coordinate to the zinc cations within distorted tetrahedra. The packing of the discrete molecular complexes in form **II** is completely different form that in form **I**. Form **I** was originally prepared in the presence of 2-chloropyrazine but can also be synthesized phase pure by crystallization from acetonitrile alone. In contrast, form **II** was only obtained in the presence of 2-chloropyrazine if the crystallization is performed under kinetic control but it immediately transforms into form **I**. Crystallization experiments reveal that form **I** is the thermodynamically most stable form between -40 °C and the boiling point of acetonitrile of 80 °C, whereas form **II** is metastable. On storing, the thermodynamically stable form **I** at room temperature decomposes into zinc(II) bromide within a few hours, but in a saturated acetonitrile atmosphere it is stable over a long period. On heating form **I** all ligands are liberated in one step leading to zinc bromide.

Key words: Polymorphism, Coordination Compounds, Zinc Bromide, Crystal Structures