Synthesis, Thermal Properties and Crystal Structure of Twinned Crystals of the New Coordination Polymer Poly[$(CuBr)_2$(μ_2-pyrimidine-N,N')]

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Dedicated to Professor Hans Bock on the occasion of his 75th birthday

Reaction of copper(I) bromide with pyrimidine in acetonitrile leads to the formation of crystals of the new coordination polymer poly[$(CuBr)_2$(μ_2-pyrimidine-N,N')]. Indexing of the reflections yields a monoclinic primitive cell with $a = 3.9119(2)$, $b = 13.525(1)$, $c = 15.346(1)$ Å, $\beta = 97.29(1)^\circ$ and $V = 805.4(1)$ Å^3. Inspection of the reciprocal space shows weak reflections which might be indicative of a superstructure leading to a doubling of the crystallographic *c*-axis. The structure can be solved in space group $P2_1/m$ but the refinement leads to very poor reliability factors (*wR*2 for all refl.: 62.57%, R_1 for all $Fo > 4\sigma(Fo) = 27.84\%$). A twin refinement assuming merohedral twinning drastically reduces the *R*-values (*wR*2 for all refl.: 7.27%, R_1 for all $Fo > 4\sigma(Fo) = 2.64\%$) and a structure model is obtained which consists of two crystallographically independent copper and bromine atoms and two pyrimidine ligands in the asymmetric unit. However, carefull inspection of this structure shows that the two crystallographically independent layers formed by the connection of the building blocks are very similar and that they are related by a translation by half of the crystallographic *c*-axis. As a result of that, the crystal is just a partial merohedral twin and the reflections which led to the assumption that the *c*-axis is twice as long are generated by the second twin domain. The structure was refined with the correct twin law (*wR*2 for all refl.: 6.70%, R_1 for all $Fo > 4\sigma(Fo) = 2.57\%$). By this procedure a reasonable structure model is obtained which consists of one crystallographically independent copper and bromine atom and one pyrimidine ligand. In the crystal structure CuBr double chains are formed which are connected into layers *via* μ-N,N' coordination by the N-donor ligands. On heating, the compound loses all of the ligands and transforms into CuBr within only one single step in an exothermic reaction.

Key words: Coordination Polymers, Crystal Structures, Partial Merohedral Twinning