CuI–Br Oligomers and Polymers Involving Cu–S(cystamine) Bonds

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Résumé en anglais	The syntheses, crystal structures, and thermal properties of five cuprous bromides derived from cystamine, [NH3(CH2)2SS(CH2)2NH3]2+, here denoted by (SS), are reported. Whereas (SS)2Cu4Br8 (1) is a polar tetramer and (SS)2Cu2Br6 (2) consists of [(SS)Cu2Br6]2– dimers, α1-(SS)Cu2Br4 (3), (SS)Cu3Br5 (4), and α2-(SS)Cu2Br4 (5) are polymers; 3 and 5 are one-dimensional and 4 has a corrugated 2D network. All the compounds contain corner-shared tetrahedra with Cu–Br–Cu connections, and in some cases, edge-shared with double bromine bridges. The copper coordination is tetrahedral, either CuBr4 or CuBr3S, except in one case, in which trigonal geometry was encountered. Compounds 1, 2, and 4, which are synthesized at 50 °C, display Cu–S bonds with the cystamine through either one or both sulfur atoms. On the other hand, 3 and 5, which are synthesized at 80 °C, do not have any. There is a high tendency to form hydrogen bonds between the polar ammonium heads of the cystamine with the bromine atoms. The range of phases experienced in this system is related to the bifunctional nature of cystamine, which is characterized by its primary ammonium ends and its disulfide bridge, and to the subtle competition between Br– and S–S ligands towards the CuI ions, which appears to be controllable by temperature. The presence of both chiral M- and P-helicoidal conformers of cystamine in 1–5 results in racemic compounds adopting centrosymmetric structures for 1, 3, 4, and 5 but 2 adopts a noncentrosymmetric structure (P212121) resulting from the coordination of copper ions to one conformer; the other conformer is noncoordinated and acts as the counterion.
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