Self-assembly of 1D- and 3D-Networks Through Non-coordination Intermolecular Forces: Synthesis and Crystal Structures of Copper(I) Complexes Based on Pyridazine-type Ligands

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Reaction of $[Cu_2(H_3CCN)_2(\mu\text{-pydz})_3][PF_6]_2$ (**1**) with an excess of pyridazine or phthalazine yielded the novel dinuclear complexes $[Cu_2(\mu\text{-pydz})_3(pydz)_2][PF_6]_2$ (**2**) and $[Cu_2(\mu\text{-pydz})(\mu\text{-phtz})_2(phtz)_2][PF_6]_2$ (**5**), respectively. Depolymerisation of the coordination polymer $^1_\infty\{[Cu(\mu\text{-pydz})_2][PF_6]\}$ (**3**) in dichloromethane by addition of an excess of benzo[c]cinnoline afforded the dinuclear copper(I) salt $[Cu_2(\mu\text{-pydz})_2(pydz)_2(benzo[c]cinnoline)_2][PF_6]_2$ (**4**). Furthermore, a new route for the preparation of bis(benzonitrile)tris(μ-phthalazine)dicopper(I) bis(trifluoromethanesulfonate), $[Cu_2(C_6H_5CN)_2(\mu\text{-phtz})_3][CF_3SO_3]_2$ (**7**), was established from $\{[Cu(CF_3SO_3)]_2 \cdot C_6H_5Me\}$, phthalazine and benzonitrile *via* the very air-sensitive intermediate $[Cu_2(CF_3SO_3)_2(\mu\text{-phtz})_3]$ (**6**). Copper(I) compounds **2**, **4**, and **7** were completely characterised and the molecular structures confirmed in the solid state by single-crystal X-ray structure determination. The analysis of the packing of the molecules in crystals of **4** and **7** revealed a self-assembly of one- and three-dimensional frameworks, respectively, resulting from intermolecular π-π stacking interactions between pyridazine-type ligands.

Key words: Copper(I), Pyridazine, Phthalazine, Benzo[c]cinnoline, Self-assembly