The interest in functional coordination compounds is motivated by their potential applications in materials science associated with properties of both inorganic and organic constituents. The cyclic triimidazo[1,2-\(a\)',2'-c:1''',2'''-e][1,3,5] triazine, \(L_1\), emissive in the solid state due to stacking interactions and formation of H-aggregates, was documented as a multidentate ligand capable to assemble Cu(I) halide coordination networks with emissive and NLO behaviour (Licenti et al., 2017; 2019). Starting from copper(II) nitrate or acetate salts and four triimidazole ligands including \(L_1\), its positional isomer, triimidazo[1,2-\(a\)',2'-c:1''',5'''-e][1,3,5]triazine, \(L_2\), and two isomeric pyridine-substituted derivatives, \(L_3\) and \(L_4\), eight Cu(II) compounds are reported: four mono- ([\(\text{Cu}(L_2)_4\text{(NO}_3\text{)}_2\text{)]·dmf}, \(1\), [\(\text{Cu}(L_2)_4\text{(CH}_3\text{COO})_2\text{]}\), \(2\), [\(\text{Cu}(L_2)_2\text{(NO}_3\text{)}_2\text{(H}_2\text{O})_2\text{]}·\text{H}_2\text{O}, \(3\), [\(\text{Cu}(L_2)_2\text{(CH}_3\text{COO})_2\text{]}\), \(4\), two dinuclear ([\(\text{Cu}_2(L_1)_2\text{(CH}_3\text{COO})_4\text{]}\), \(5\), and [\(\text{Cu}_2(L_3)_2\text{(CH}_3\text{COO})_4\text{]}\), \(6\), complexes, and two 1D coordination polymers, ([\(\text{Cu}_2(L_2)(\text{CH}_3\text{COO})_4\text{]}\)]_{\text{n}} and ([\(\text{Cu}(L_3)(\text{NO}_3\text{)}_2]\), \(7\), and ([\(\text{Cu}(L_3)(\text{NO}_3\text{)}_2]\), \(8\). The Cu(II) atom in \(1-4\) has either \(\text{N}_4\text{O}_2\) or \(\text{N}_2\text{O}_4\) square-bipyramidal coordination cores. Complexes \(5-6\) include paddle-wheel acetate dimers capped by \(L_1\) or \(L_2\) in axial positions. In the zigzag-like coordination polymer \(7\) the acetate paddle-wheel dimers, interlinked by bridging \(L_2\) ligand, coordinate via axial positions to Cu(II) atoms by different N-binding sites, being associated in the crystal with discrete \(\text{Cu}_2(L_2)(\text{CH}_3\text{COO})_4\text{H}_2\text{O}\) dinuclear units. In \(8\), \(L_3\) coordinates the metal atom in a chelate mode, while nitrate anions coordinate the metal in a chelate and bidentate bridging modes. The ligands’ stacking motifs are traced and discussed. Studies on the emissive properties of selected compounds are currently underway.

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