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# Urea-based flexible dicarboxylate linkers for three-dimensional metal-organic frameworks

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Dedicated to Prof. Ionel Haiduc on the occasion of his 80<sup>th</sup> birthday.

**Keywords:** MOFs, metal-organic frameworks; urea function; 4,4'-(carbonylbis(azanediyl))dibenzoic acid; interpenetration, four-fold; diamondoid topology; hydrogen bonding

## Abstract

The metal-organic frameworks (MOFs) 3D-[Mn<sub>2</sub>(L1)<sub>2</sub>(DMF)]·2 DMF (**1**), 3D-[Cd<sub>2</sub>(L2)<sub>2</sub>(DMF)<sub>3</sub>] (**3**), [Zn<sub>2</sub>(L2)<sub>2</sub>(DMF)<sub>3</sub>] (**4**) and 3D-[Mn<sub>2</sub>(L2)<sub>2</sub>(DMF)<sub>3</sub>] (**5**) are the first examples of three-dimensional metal-organic networks constructed from a single ditopic dicarboxylate linker (i.e., without bridging co-ligands) with an urea group in the linker axis (L1<sup>2-</sup> = 4,4'-(carbonylbis(azanediyl))dibenzoate; L2<sup>2-</sup> = 4,4'-(carbonylbis(azanediyl))bis(3-methylbenzoate), DMF = dimethylformamide). From Cd<sup>2+</sup> and L1<sup>2-</sup> a 1D coordination polymer 1D-[Cd(L1)(DMF)<sub>3</sub>] (**2**) is formed. The urea group is engaged in hydrogen bonding with the C(4)[R<sup>1</sup><sub>2</sub>(6)] motif to an oxygen atom of a DMF solvent (in **1**) or a metal-coordinated carboxylate group (in **3-5**). Network **1** has infinite channels with parallelepiped cross sections and 30% solvent-filled volume. The 3D frameworks **3-5** are of diamond (6,6), **dia** topology with a single framework having large voids with 17.6 Å and 19.7 Å nodal separation. Thus, four symmetry-related nets interpenetrate, organized via H-bonds in the C(4)[R<sup>1</sup><sub>2</sub>(6)] motif, still leaving about 50% solvent-filled void volume in the four-fold interpenetrated structure.

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