New Supramolecular Heterosynthon [C-I···O=C(carboxylate)] at Work:

Engineering of the Copper Acetates Cocrystals.

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Figure S1. Showing the energy framework of the native crystal of [Cu(OAc)₂·MeOH]₂ as the intersection of three planes (a, only half of each plane is shown for clarity), and its extended side projections (b) and (c). Intermolecular interactions are given in kJ/mol.
Figure S2. Showing the intermolecular interaction energies (in kJ/mol) in the fragment of cocrystal 2 packing,

(a) Selected intermolecular distances (Å): O(8)-I(4) 3.46(1), I(4)-O(9) 3.090(4)

(b) Selected intermolecular distances (Å): O(3)-I2 3.032(3), I(2) O(2) 3.748(3), I(1) O(6) 2.917(3)
(c) Selected intermolecular distances (Å): I3---O12 2.911(3), C19-I3---O12 176.2(1), C12-O12—I3 120.0(3)

**Figure S3.** Fragments of crystal packing of 2, showing three independent molecules of 1,4-DITFB bridging (a) two [Cu(OAc)₂MeOH]₂ molecules, (b) [Cu(OAc)₂MeOH]₂ molecule and MeOH solvate, and (c) two MeOH solvates.

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**Figure S4.** Showing the intermolecular interaction energies in the ([Cu(OAc)₂MeOH]₂ 2MeOH)ₙ chain of cocrystal solvate 2. Intermolecular interactions are given in kJ/mol. (CE-B3LYP / DGDZVP).
Figure S5. Showing the energy framework of 2 along the c-axis (cutoff 20 kJ/mol). Notice the absence of planar homomolecular energy frameworks.
Figure S6. Showing (a) the energy framework of the native [Cu(OAc)₂(4CNpy)]₂ crystal (notice the intersection of three planes) and its side projections (b) and (c). Cutoff 5 kJ/mol. Intermolecular interactions are given in kJ/mol.
**Figure S7.** Distribution of O-H---O=C distance in AcOH dimers in the structures, deposited in CCDC CSD (Release 2020.0) [1].

**Figure S8.** AA dimers shown in the fragments of the crystal packing of bis(acetylacetonato)-platinum(II) acetic acid solvate [2]. Packing pattern along the a axis (a) and packing pattern of the AA sublattice (b). Dotted lines shows H---O HBs at a distances shorter than sum of vDW radii. Bis(acetylacetonato)-platinum(II) are displayed in wireframe style for clarity.

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References on the theoretical and experimental studies of AA supralomolecular structure:


Jones, R. E., & Templeton, D. H. The crystal structure of acetic acid. Acta Crystallogr. 1958, 11, 484


