**Electronic**
**Supplementary**
**Information**

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

# Engineering of the Copper Acetates Cocrystals.

**Yury V. Torubaev, Ivan V. Skabitsky**

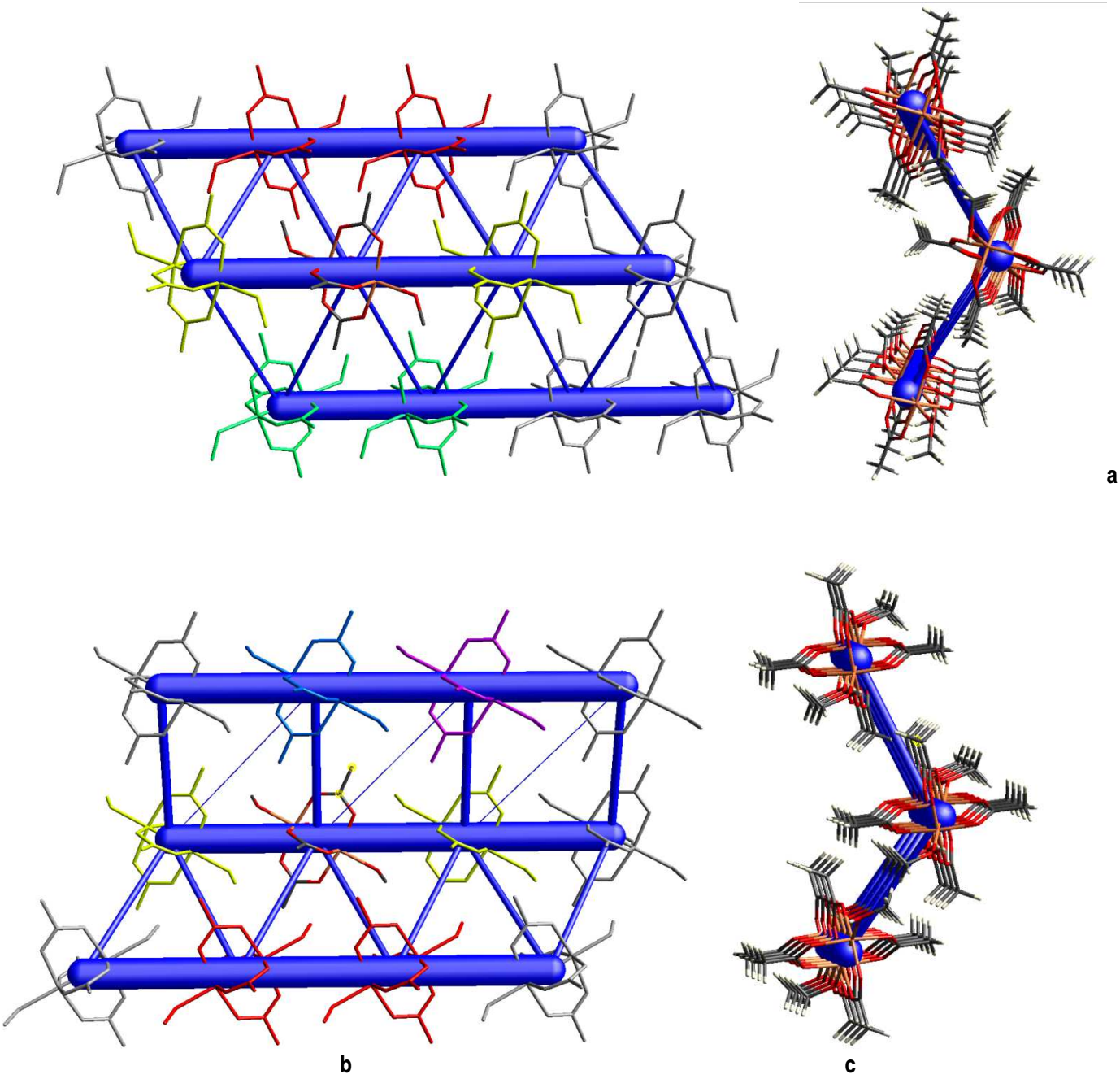



**Figure S1.** Showing the energy framework of the native crystal of $[Cu(OAc)_2MeOH]_2$ as the intersection of three planes (**a**, only half of each plane is shown for clarity), and its extended side projections (**b**) and (**c**). Intermolecular interactions are given in kJ/mol

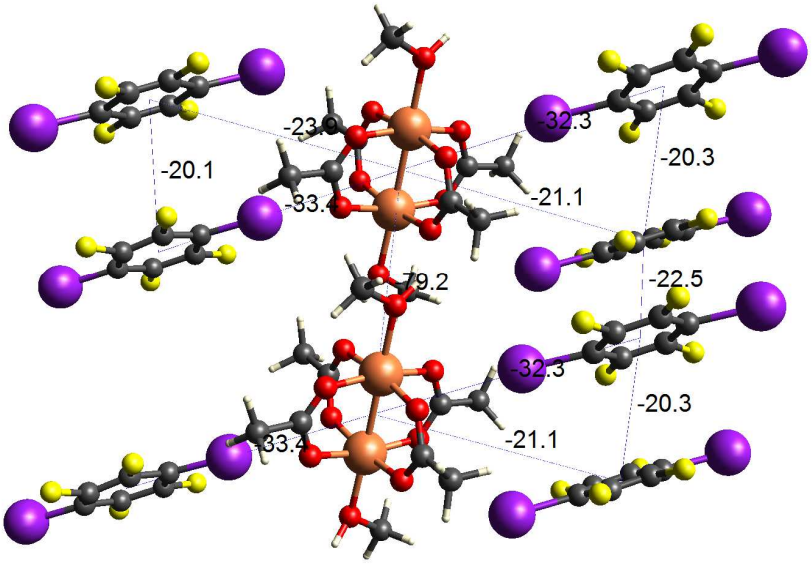
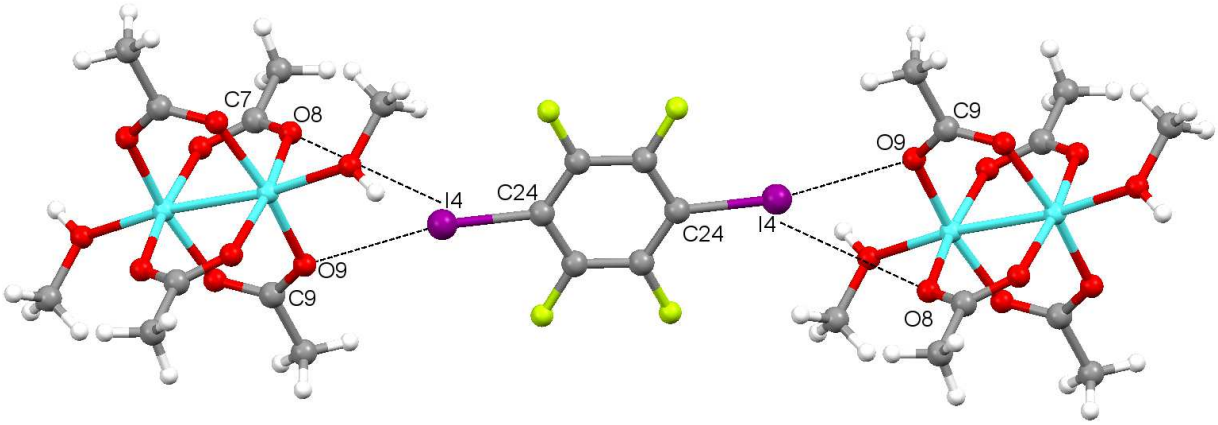
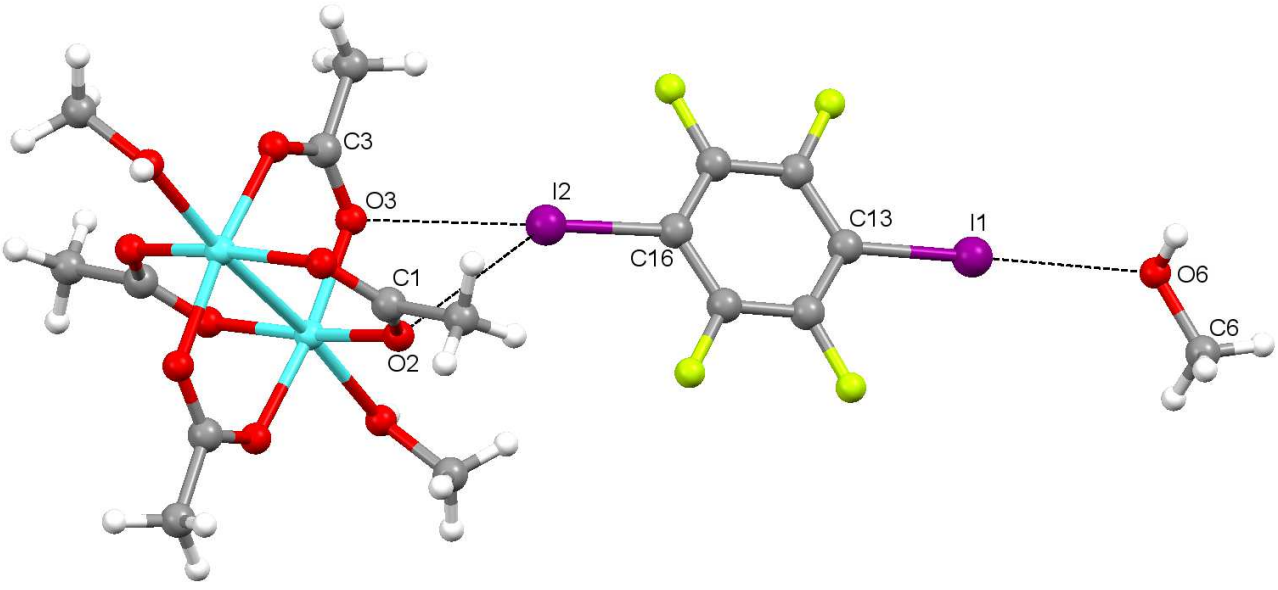


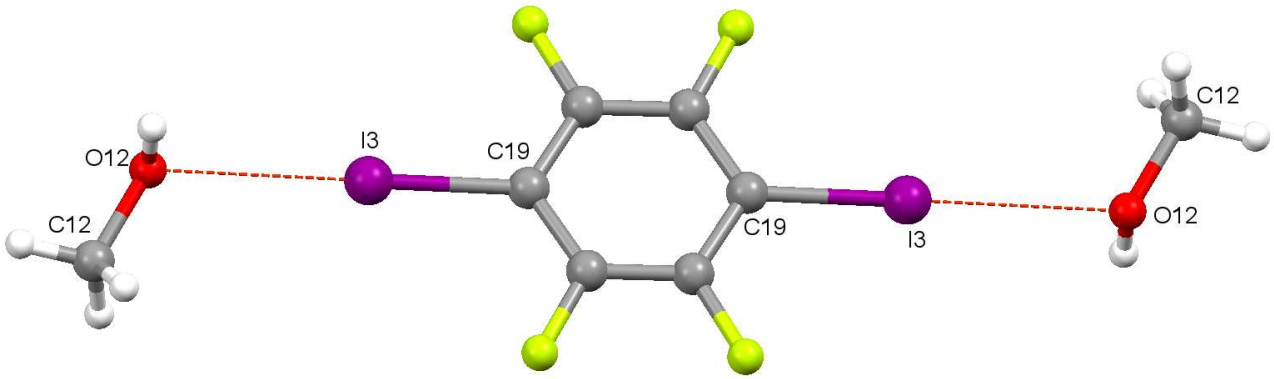

**Figure S2.** Showing the intermolecular interaction eneegies (in kJ/mol) in the fragment of cocrystal **2** packing,




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

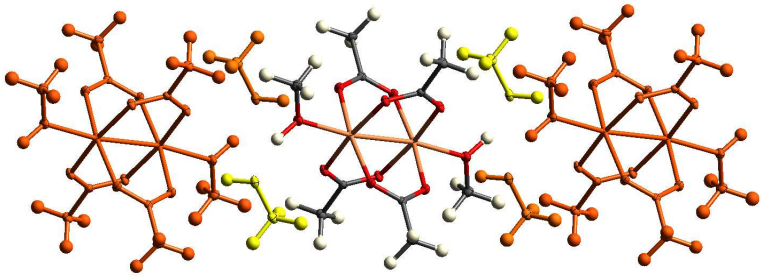



**(b)** Selected intermolecular distances (Å): O(3)-I2 3.032(3), I(2) O(2) 3.748(3), I(1) O(6) 2.917(3)




**(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 solavates.



| | E_ele | E_pol | E_dis | E_rep | E_tot |
|---|---|---|---|---|---|
| | -22.0 | -3.5 | -19.6 | 11.7 | -35.6 |
| | -37.1 | -9.0 | -21.6 | 44.3 | -37.3 |
| | -58.0 | -13.4 | -16.0 | 67.4 | -43.5 |

**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).

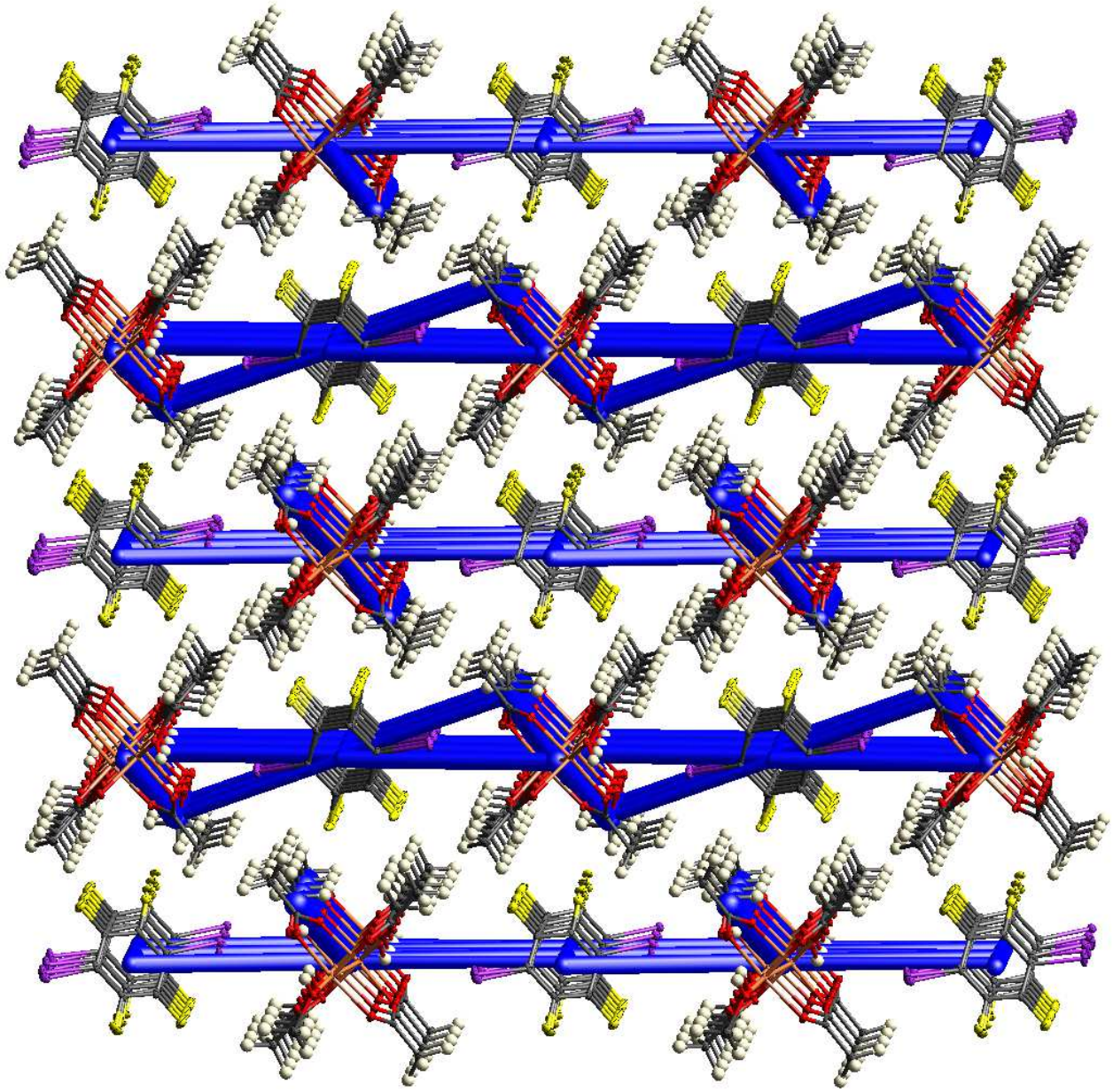


**Figure S5.** Showing the energy framework of **2** along the *c*-axis (cutoff 20 kJ/mol). Notice the absence of planar homomolecular energy frameworks.

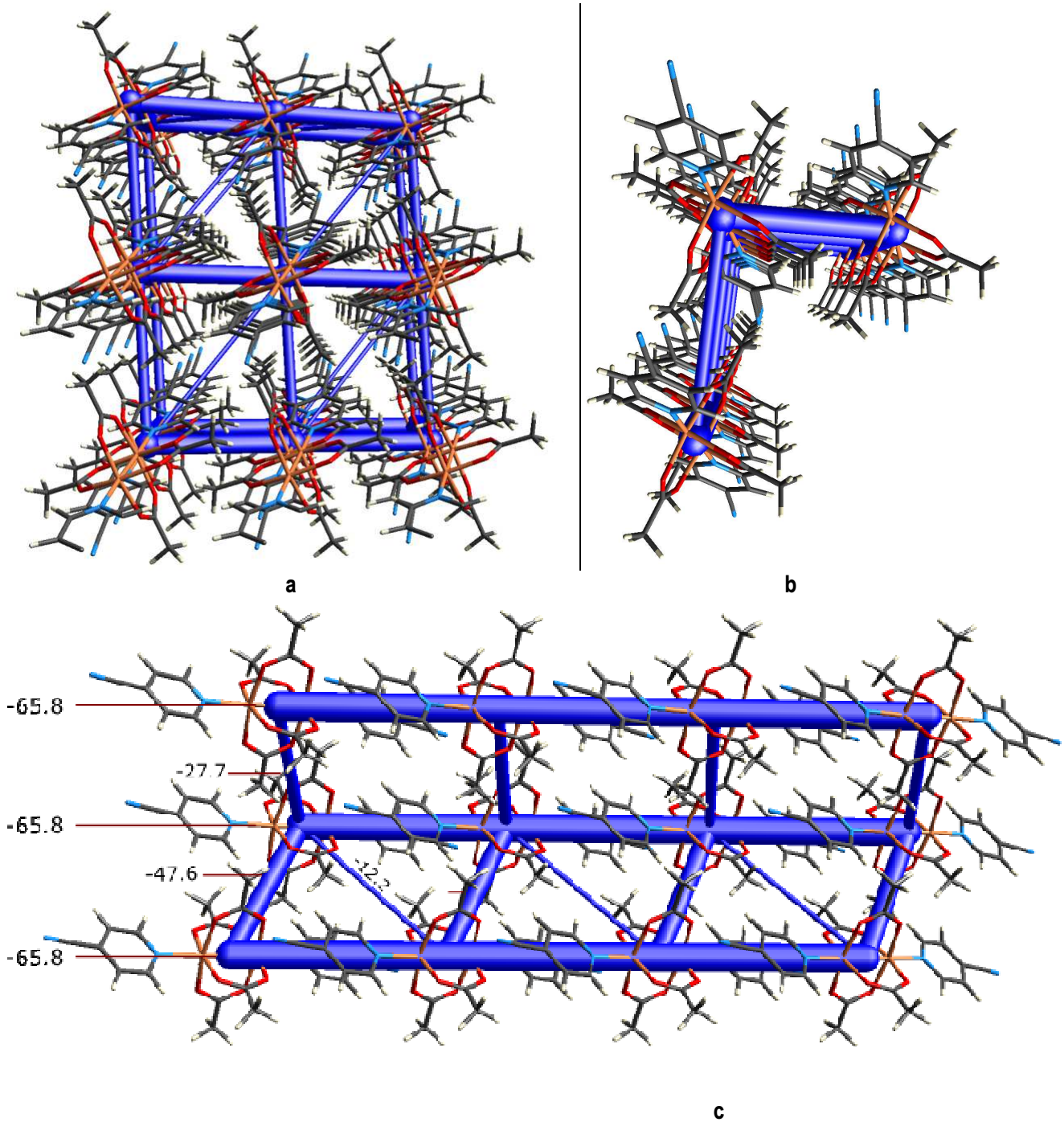



**Figure S6.** Showing (**a**) the energy framework of the native $[Cu(OAc)_2(4CNpy)]_2$ crystal (notice the intersection of three planes) and its side projections (**b**) and (**c**). Cutoff 5 kJ/mol. Intermolecular interactions are given in kJ/mol.

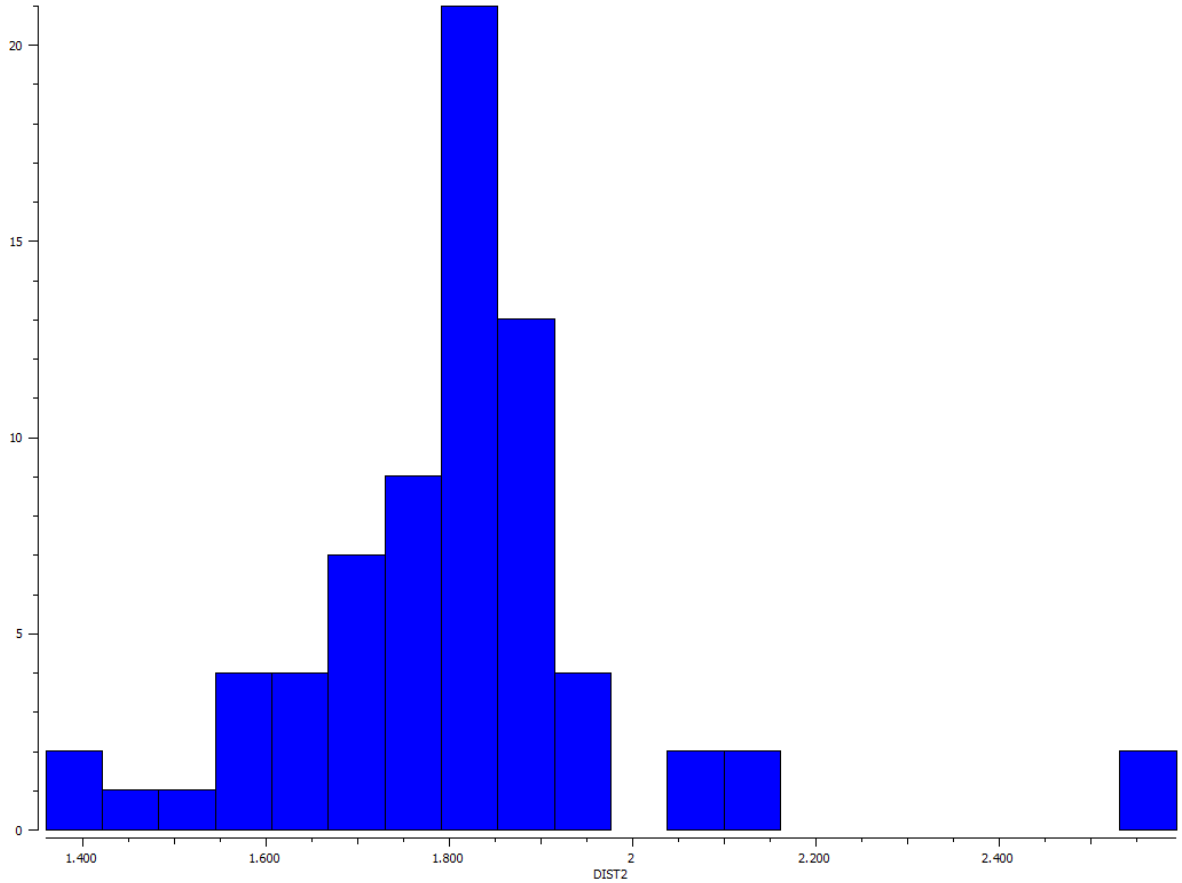
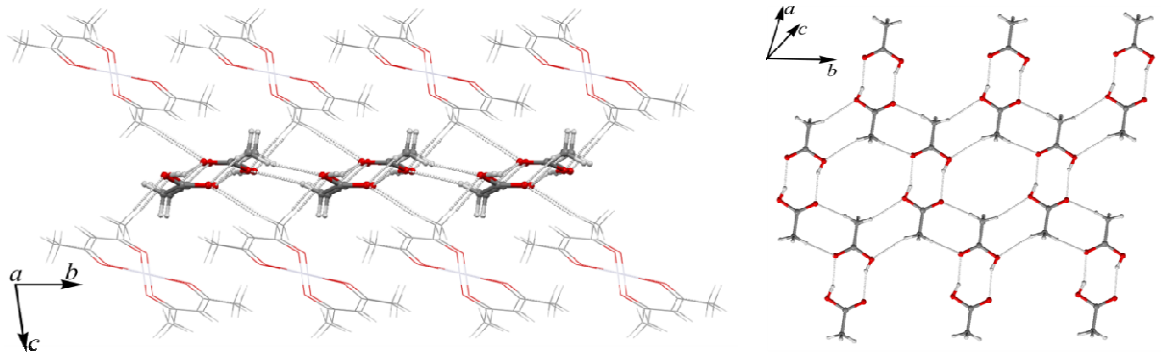



**Figure S7.** Distribution of O-H---O=C distance in AcOH dimers in the structures, deposited in CCDC CSD (Release 2020.0) [1].




**a**

**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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