Supplementary material for manuscript:

Experimental and theoretical studies on the coordination chemistry of the N^1-hexyl substituted pyrimidines (uracil, 5-fluorouracil and cytosine).

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Crystal packing of the water molecules net in $[Hg(N^1\text{-hexyl-5-fluorouracilate})_2]_4 \cdot 6H_2O$ (1):

The water molecules present in the crystal structure are related between them in a row by means of hydrogen bond interactions [distances: O(2W)-O(3W), 2.578(8) Å; O(3W)-O(1W), 2.647(8) Å; O(1W)-O(2W), 2.712(5) Å; O(3W)-O(2W), 2.578(8) Å] forming a hydrogen bond interactions line through all the crystal. The hydrogen bonds lines are sited parallels in a plane and the planes subsequently turned 90º and piled. In Figure S1 it is shown the net formed by the water molecules. The tetrameric units are disposed at free spaces, linked to the water lines thanks to more hydrogen bonds [distances (where #1: *x,y-1/2,z+1/2*; #2: *-x+1/4,y+1/4,z+1/4*; #3: *x+1/4,-y+1/4,z+1/4*): O(3W)-F(45)#1, 2.989(6) Å; O(1W)-O(4)#2, 2.754(3) Å; O(1W)-C(66), 3.207(5) Å and 167.2(2)º; O(2W)-C(46), 3.235(4) Å and 171.5(2)º; O(2W)#3-O(24), 2.797(3) Å].

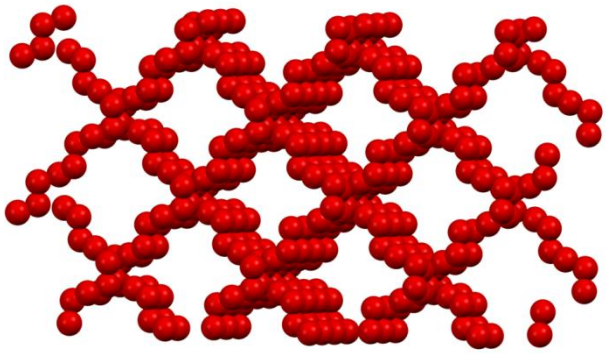

Figure S1. Water molecules net interacting through hydrogen bonds in structure **1**.

Crystal packing of $[Ag(NO_3)(N^1\text{-hexyluracil-}\kappa O^4)_4]$ (3)

As has been indicated at the beginning of the description, the molecules are packed forming a 2D layer of uracil rings with the silver nitrate at one side and the aliphatic chains at the other. The aliphatic parts of two consecutive layers are mixed thanks to hydrophobic interactions, resembling a lipid bi-layer. The separation between the two parallel layers (mean planes) is of 9.497 Å (it was 9.968 Å in the structure of the N^1-hexyluracil ligand). Then the bi-layers are piled, by interaction between hydrophilic planes, which appear at a separation between mean planes of 2.894 Å (a value of 2.945 Å in the ligand indicates that the silver-mediated uracil quartet has a more compact packing).

In order to form each hydrophilic layer, the uracil bases that form the quartets are related by a hydrogen bonds network. Within the layer, each quartet (i.e. Ag(1)) is surrounded by 4 quartets of the other type (i.e. Ag(2)) and the layer is formed by lines of each type of silver quartets. They form two superimposed square networks in which one of them is occupying the centres of the squares of the other one. The network is maintained by two types of intermolecular non-standard hydrogen bonds (each uracil moiety forms just one hydrogen bond). The two bonds are of the C_{arom}-H···O kind, like the third hydrogen bond presents in the adenine-thymine Watson-Crick base pairing:[i] C(66)···O(2), 3.246 Å and 158.76º; C(46)···O(22), 3.194 Å and 159.44º.

Finally, each two bi-layers lay together due to the presence of stacking interactions and hydrogen bonds. The silver atoms present on top of both hydrophilic layers are in the same plane sited at half distance between the two mean planes and present the nitrato group immersed in the opposite layer. Each nitrate is linked to the opposite layer with a tandem of C_{arom}-H···O hydrogen bonds: C(6)···O(103), 3.171 Å and 153.82º; C(26)···O(206), 3.165 Å and 157.30º. The main stacking interactions, although not the only ones, present in the crystal are: i) the uracil rings corresponding to N(1)-C(6) of different layers partially stack with angles between mean planes of 0º and a distance between those planes of 3.307 Å (mainly the region C(4)-C(5)-C(6)); ii) the uracil moieties labelled N(61)-C(66) of different layers interact between them at 3.186 Å and angle of 0º between mean planes (the interaction is mainly via carbonyl O(62)-N(63) and *vice versa*); iii) an interaction between carbonyls, mainly O(42) interacts with C(24) at 3.186 Å with an angle of 3.67º.

i G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology, IUCr Monographs on Crystallography 9*, International Union of Crystallography and Oxford Science Publications, Oxford, 1999, p. 399.