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Title: Simultaneous co-ordination of three cytosine ligands displaying different binding sites around the copper centres

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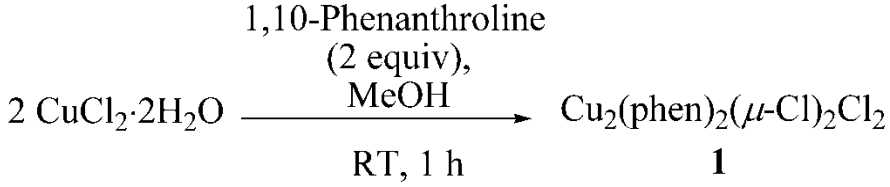
Supplementary Materials:

Materials and Methods:

Synthesis of precursor complex $Cu_2(phen)_2(\mu\text{-}Cl)_2Cl_2$ (1):

The precursor complex **1** was prepared with different procedure than reported earlier[1]. To the methanolic solution of cupric chloride (500 mg, 2.93 mmol); 1,10 phenanthroline (581.3 mg, 2.932 mmol) in methanol (5 ml) was added and the reaction mixture was stirred for about 1 hour. The green colored precipitate thus formed was filtered, washed with methanol and kept under vacuum drying over fused calcium chloride.(yield 1.7129 g, 93.4%) [**Scheme 1.1]**



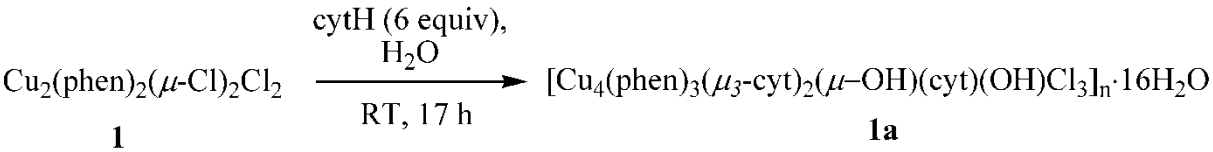
Scheme 1.1

1. Yu, J.-H. *et al.* Syntheses, characterization and optical properties of some copper(i) halides with 1,10-phenanthroline ligand. *New J. Chem.* **28**, 940-945, doi:10.1039/b314974a (2004).

Synthesis of complex $[Cu_4(phen)_3(\mu_3\text{-}cyt)_2(\mu\text{-}OH)(cyt)(OH)Cl_3]_n \cdot 16H_2O$ (1a):

Complex **1a** was prepared by mixing aqueous solution of **1** (50 mg, 0.08 mmol) with 5ml aqueous solution of cytosine (26.5 mg, 0.24 mmol) and stirring the mixture for 17 hours. A blue color solution was obtained which was kept for crystallization by slow evaporation to get a pure product. Complex **1a** was obtained as sky blue colored plate like crystals along with some green crystals of the **1** and the cocrystal $[Cu_2(phen)_2(OH)_2(H_2O)_2][Cu_2(phen)_2(OH)_2Cl_2]Cl_2 \cdot 6H_2O$ (intermediate **II** and **III** in figure 4) . These crystals were separated manually under a microscope and used for the single crystal X-ray diffraction studies. (yield =1.5 mg, 11.5%) [**Scheme 1.2**]. The reaction was reproducible with the same results. Selected IR data (cm^{-1}): 3546 sh,w = ν(O-

H) , 3354br, 3199 ms = ν(O-H) and ν(NH2), 1645ms = ν(C=O) and ν(NH), 1585s = ν(C=O) and ν(NH), 423s = ν(Cu-N) (s, strong; w, weak; br, broad; ms, medium strong; sh, shoulder).



Scheme 1.2

IR spectral analysis

The IR spectrum of 1a is complex and unambiguous assignment of the bands is not possible owing to the presence of three cytosine ligands with different coordination. So tentative assignments of the selected bands is done by comparing them with the earlier reports.[10, 26] The band near 3199cm^{-1} to 3546cm^{-1} corresponds to water (free and hydrogen bonded) and to the NH_2 group. There is a band near 1645cm^{-1}, assigned to carbonyl and NH vibrations, which occurs at same place in cytosine. This may be due to the third dangling cytosine ligand which is coordinated through the N3 nitrogen atom. Similarly a band near 1589cm^{-1} also corresponds to carbonyl and NH vibrations which is due to the other two cytosine showing a tridentate coordination. The decrease in the stretching frequency is due to longer carbonyl bond lengths for these cytosine ligands. (supplementary table S2)

10. G. De Munno, M. Medaglia, D. Armentano, J. Anastassopoulou and T. Theophanides, *J. Chem. Soc., Dalton Trans.*, 2000, 1625-1629.

26. B. García, J. Garcia-Tojal, R. Ruiz, R. Gil-García, S. Ibeas, B. Donnadieu and J. M. Leal, *J. Inorg. Biochem.*, 2008, **102**, 1892-1900.

Variable Temperature Experiment:

The variable temperature diffraction data on single crystals of 1a was recorded on Bruker SMART Apex CCD diffractometer. The nitrogen flow was maintained with the help of oxford cryojet tube. Heating of the crystals was done at the rate of 40K per hour. The diffraction data above room temperature was poor with low angle diffraction and hence could not be modeled to obtain the crystal structure. However the reflections were enough to index the crystal with the available indexing methods (Table S5).

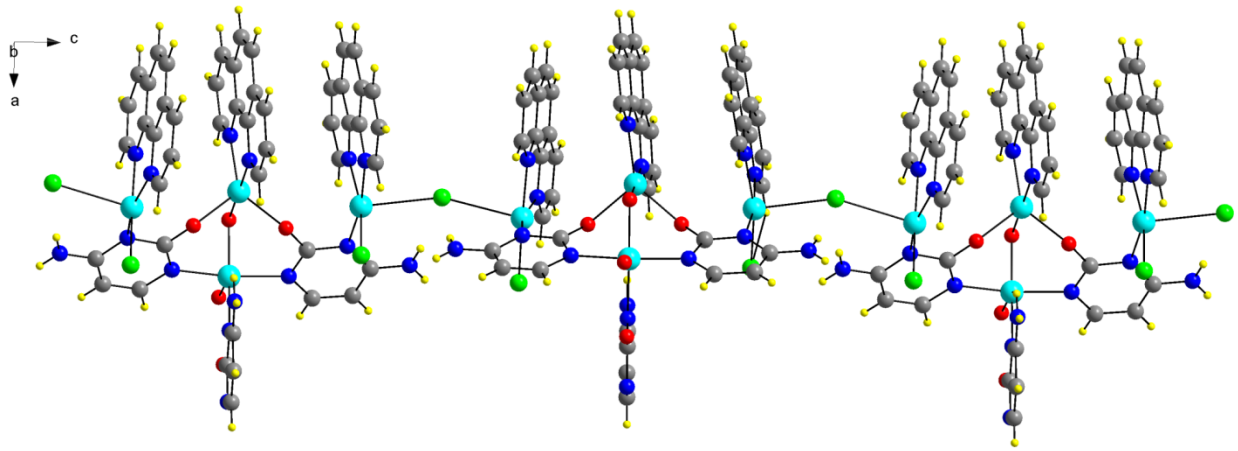


Fig. S1. Polymeric nature of the complex **1a**.

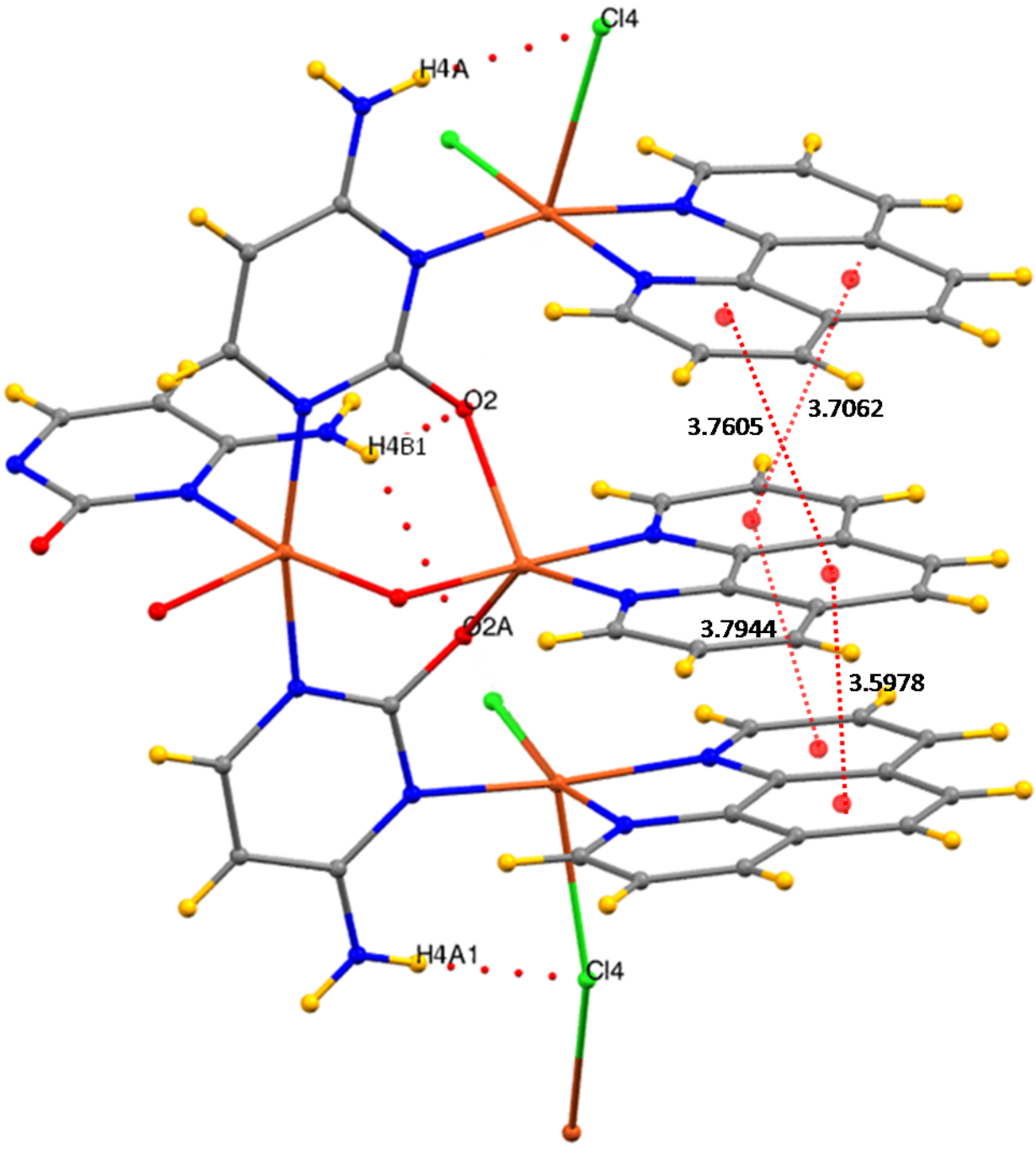


Figure S2 Intramolecular non covalent interactions in the monomeric unit of **1a** [Distances mentioned are in Å unit]

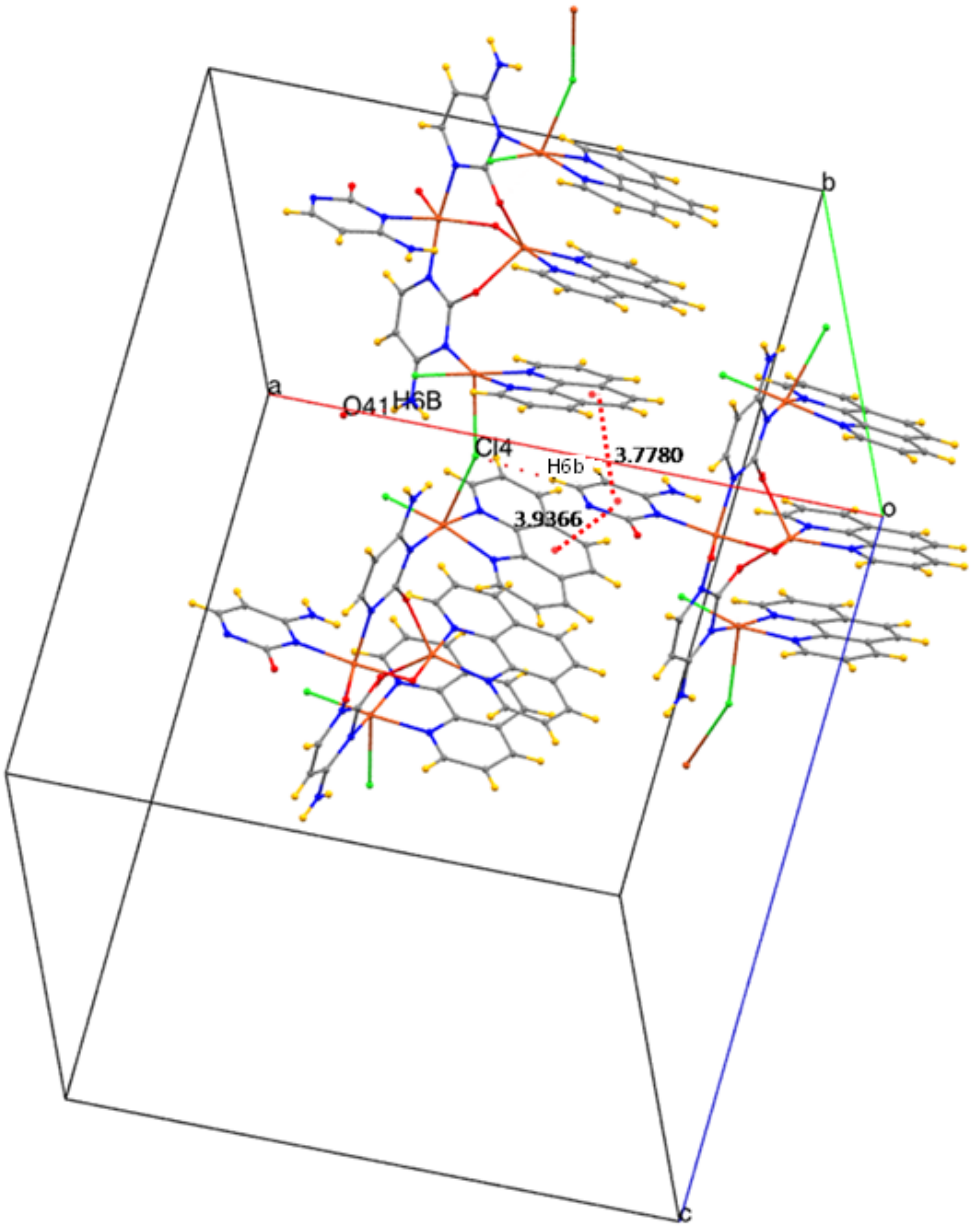


Fig. S3. Intermolecular non covalent interactions between the polymeric chains of **1a** [Distances mentioned are in Å unit].

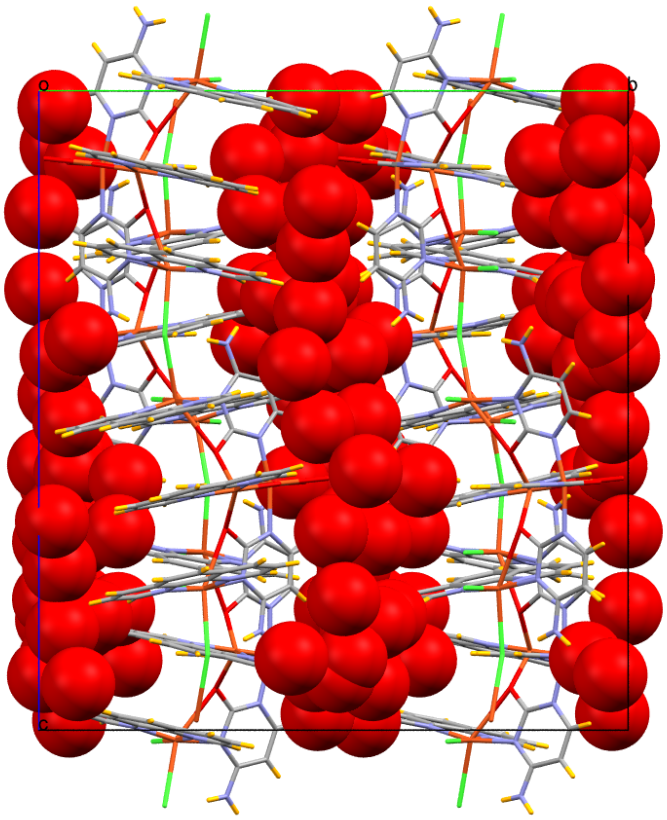


Figure S4 Packing of water molecules in between the polymeric chains shown down *a* axis.

Table S1 Selected interatomic distances (Å) and angles (°) of **1a**

	1a		**1a**
Cu(1)-N(3)	1.990(7)	**N(3)-Cu(1)-Cl(1)**	90.8(2)
Cu(1)-N(7)	2.019(7)	**N(7)-Cu(1)-N(8)**	81.5(3)
Cu(1)-N(8)	2.021(8)	**N(8)-Cu(1)-Cl(1)**	94.2(2)
Cu(1)-Cl(1)1	2.249(2)	**O(1D)-Cu(2)-O(2A)**	92.9(2)
Cu(2)-O(1D)	1.920(5)	**O(1D)-Cu(2)-O(2)**	91.7(2)
Cu(2)-N(10)	1.991(7)		
Cu(2)-N(9)	2.030(7)		
Cu(2)-O(2A)	2.052(5)	**O(2A)-Cu(2)-O(2)**	96.2(2)
Cu(2)-O(2)	2.155(5)		
Cu(3)-N(3A)	1.998(7)	**N(3A)-Cu(3)-Cl(3)**	90.8(2)
Cu(3)-Cl(4)	2.733(2)	**N(3A)-Cu(3)-Cl(4)**	102.48(19)
Cu(3)-N(12)	2.015(7)		
Cu(3)-N(11)	2.052(7)		
Cu(3)-Cl(3)	2.257(2)	**Cl(3)-Cu(3)-Cl(4)**	98.84(9)
Cu(4)-O(1D)	1.974(5)	**O(1D)-Cu(4)-N(1)**	88.0(3)
		O(1D)-Cu(4)-O(1)	89.4(4)
Cu(4)-N(1)	1.983(7)	**N(1)-Cu(4)-N(3B)**	89.2(3)
Cu(4)-N(1A)	1.990(7)	**N(1A)-Cu(4)-N(3B)**	90.8(3)
Cu(4)-O(1)	2.391(11)	**N(1A)-Cu(4)-O(1)**	96.2(3)
Cu(4)-N(3B)	2.048(8)	**N(3B)-Cu(4)-O(1)**	101.3(4)

Table S2 Interatomic distances (Å) and angles (°) for the three cytosine rings compared with cytosine tautomer I and III.

	A	B	C	Anhydrous cytosine Tautomer I[a]	Tautomer III[b]
C6-N1-C2	118.1(7)	117.8(7)	118.4(15)	121.9(2)	118.0
N1-C2-N3	123.3(7)	122.9(7)	118.1(15)	118.2(2)	115.9
N1-C2-O2	120.8(7)	119.7(7)	118.4(14)	119.5(2)	
N3-C2-O2	115.9(7)	117.4(7)	123.4(12)	122.2(2)	118.3
C2-N3-C4	117.0(7)	119.0(7)	120.3(11)	119.4(2)	125.4
N3-C4-C5	120.3(8)	120.4(8)	122.2(14)	122.7(2)	117.4
C5-C4-N4	121.8(9)	120.1(9)	117.5(14)	120.2(2)	125.5
N3-C4-N4	117.9(9)	119.5(9)	120.2(11)	117.1(2)	
C4-C5-C6	119.1(9)	117.6(8)	114.0(15)	117.0(2)	116.4
C5-C6-N1	122.1(9)	122.3(8)	127.0(15)	120.8(2)	126.9
C(2)-N(1)	1.330(10)	1.353(10)	1.387(17)	1.381(3)	1.386
C(2)-O(2)	1.276(9)	1.284(9)	1.255(17)	1.241(3)	1.225
C(2)-N(3)	1.368(10)	1.351(10)	1.381(15)	1.364(3)	1.424
C(4)-N(3)	1.381(11)	1.340(10)	1.353(14)	1.336(3)	1.358
C(4)-N(4)	1.311(11)	1.317(11)	1.278(15)	1.342(3)	1.381
C(4)-C(5)	1.383(13)	1.416(13)	1.431(16)	1.410(3)	1.377
C(6)-C(5)	1.325(13)	1.355(12)	1.31(2)	1.340(3)	1.412
C(6)-N(1)	1.368(11)	1.356(10)	1.36(2)	1.353(3)	1.318

The three cytosine rings in 1a labeled as A, B and C, where A= N1, C2, O2, N3, C4, N4, C5, C6; B= N1A, C2A, O2A, N3A, C4A, N4A, C5A, C6A and C= N1B, C2B, O2B, N3B, C4B, N4B, C5B, C6B.

a) R. J. McClure and B. M. Craven, *Acta Crystallogr. Sect. B* 1973, **29**, 1234-1238.
b) C. Colominas, F. J. Luque and M. Orozco, *J. Am. Chem. Soc*. 1996, **118**, 6811-6821.

Table S3 Least square basal plane and deviation of metal from the plane (Å) of **1a**

Plane number	Atom	Deviation	Plane number	Atom	Deviation
1	N7	0.122(7)	**2**	N9	0.000(7)
	N8	-0.173(8)		O2	0.000(6)
	N3	-0.099(7)		O2A	0.000(5)
	Cl1	0.025(3)		Cu2*	0.146(1)
	Cu1	0.104(1)			
3	N3A	-0.037(6)	**4**	O1D	0.015(6)
	N11	0.050(7)		N1	-0.023(7)
	N12	-0.054(7)		N3B	0.047(10)
	Cl3	0.007(3)		N1A	-0.022(7)
	Cu3*	-0.195(1)		Cu4*	0.219(1)

Plane 1:
Through the basal plane of Cu1 [N7, N8, N3, Cl1]; $(d/s)^2$ = 1027.36. Equation of the plane: (-0.1097)X+ (0.0999)Y+ (-0.988)Z= 0.6352

Plane 2:
Through the basal plane of Cu2 [N9, O2, O2a]; $(d/s)^2$ = 0.000. Starred atoms are not included in plane calculation. Equation of the plane: (0.3424)X+ (-0.9320)Y+ (-0.1183)Z= -3.5881

Plane 3:
Through the basal plane of Cu3 [N3a, N11, N12, Cl3]; $(d/s)^2$ = 149.225. Starred atoms are not included in plane calculation. Equation of the plane: (-0.0007)X+ (0.1329)Y+ (-0.9911)Z= -6.3148

Plane 4:
Through the basal plane of Cu4 [O1D, N1, N3B, N1A]; $(d/s)^2$ = 51.839. Starred atoms are not included in plane calculation. Equation of the plane: (0.2835)X+ (-0.9523)Y+ (-0.1126)Z= -1.7250

Table S4 Hydrogen bonds for complex **1a** (Å and °)

D-H···A	D-H	D···A	H···A	<D-H···A
C27-H27···O5W^{i}	0.93	3.45(2)	2.64	146
N4B-H4B1···O2^{i}	0.86	3.03(1)	2.28	145
N4B-H4B1···O2A^{i}	0.86	3.32(1)	2.65	137
N4B-H4B2···O2W^{i}	0.86	3.10(2)	2.25	169
N4A-H4A1···Cl4^{i}	0.86	3.11(1)	2.26	171
C6A-H6A···O6W^{ii}	0.93	3.47(2)	2.74	136
C6B-H6B···Cl4^{iii}	0.93	3.54(2)	2.62	173
C8-H8···O7W^{iv}	0.93	3.52(2)	2.72	145
N4-H4B···O41^{v}	0.86	3.26(3)	2.43	163
C7-H7···O12W^{vi}	0.93	3.39(2)	2.57	147
N4-H4A···Cl4^{vii}	0.86	3.26(1)	2.41	169
N4A-H4A2···O10W^{viii}	0.86	3.00(1)	2.17	162

Symmetry transformations used to generate equivalent atoms: (i) *x*, *y*, *z*; (ii) -*x* + ½, +*y* – ½, +*z*; (iii) *x* + ½, +*y*, -*z* + ½; (iv) -*x*, -*y* + 1, -*z*; (v) *x* – ½, -*y* + ½, -*z*; (vi) *x*, +*y*, +*z* - 1; (vii) *x*, -*y* + ½, +*z* – ½; (viii) -*x* + 1, +*y* - ½, -*z* + ½

Table S5 Geometrical parameters for π-π stacking for complex **1a**[a]

π-π stacking	**d_{C-C} (Å)**	**α(°)**	**β(°)**	**γ (°)**	**d⊥[Cg(J)- P(J)](Å)**	**d⊥[Cg(J)- P(I)] (Å)**
Intramolecular phen-phen						
Cg10 > Cg17[b]	3.760(1)	8.440	28.43	21.36	-3.5022	3.3069
Cg13 > Cg15[c]	3.794(1)	2.645	23.49	23.21	-3.4874	3.4800
Cg13 > Cg16[b]	3.706(1)	8.012	22.53	14.52	3.5878	-3.4234
Cg17 > Cg18[c]	3.597(2)	3.370	18.24	18.71	-3.4077	3.4170
Intermolecular phen-phen						
Cg9 > Cg16[d]	3.778(1)	10.650	26.97	22.67	-3.4860	-3.3671
Cg9 > Cg18[d]	3.936(2)	15.045	39.49	24.46	3.5834	3.0380

[a] d_{C-C}: centroids distance; α: dihedral angle between the rings; β, γ: slipping angles; d⊥[Cg(I)-P(J)] and d⊥[Cg(J)-P(I)]: centroid Cg(I) to plane J distance and the opposite.

[b] *x, y, z*

[c] *x,* ½ *- y,* ½ *+ z*

[d] ½ + *x,* ½ *- y, -z*

(Cg(9): N1b C2b N3b C4b C5b C6b, Cg(10): N7 C7 C8 C9 C10 C18,
Cg(13): N10 C25 C26 C27 C28 C29, Cg(14): N11 C31 C32 C33 C34 C42,
Cg(15): N12 C37 C38 C39 C40 C41, Cg(16): C10 C11 C12 C13 C17 C18
Cg(17): C22 C23 C24 C25 C29 C30, Cg(18): C34 C35 C36 C37 C41 C42).

Table S6 Possible Hydrogen bonds for complex **1a** (Å and °)

Possible D···A	Symmetry operation	Distance(Å)
C7···O12W	x,+y,+z-1	3.39(2)
O2B···O5W	-x+1/2,+y-1/2,+z	2.90(2)
O1···O8W	x,+y-1,+z	2.91(2)
O8W···O1	x,+y+1,+z	2.91(2)
O8W···O10W	x-1/2,-y+1/2+1,-z	2.90(2)
O8W···O13W	x,+y+1,+z	2.92(2)
O12W···O13W	x,+y,+z+1	2.77(2)
O12W···O7W	-x,-y+1,-z+1	2.65(2)
O14W···O9W	-x+1,+y-1/2,-z+1/2	2.87(2)
O14W···O7W	x,+y-1,+z	2.97(2)
O14W···O4W	-x+1/2,+y-1/2,+z	3.06(3)
O40_···O1W	-x+1/2+1,+y+1/2,+z	2.86(3)
O40A···O1W	-x+1/2+1,+y+1/2,+z	2.74(4)
O41_···O11W	x+1/2,-y+1/2,-z+1	2.80(3)
O11W···O41_	x-1/2,-y+1/2,-z+1	2.81(3)
O11W···O6W	x,-y+1/2,+z+1/2	2.62(3)
O13W···O8W	x,+y-1,+z	2.92(2)
O13W···O12W	x,+y,+z-1	2.77(2)
O13W···O7W	x,+y-1,+z	2.83(2)
O9W···O14W	-x+1,+y+1/2,-z+1/2	2.87(2)
O9W···O5W	x+1,+y,+z	2.70(4)
O7W···O12W	-x,-y+1,-z+1	2.65(2)
O7W···O14W	x,+y+1,+z	2.96(2)
O7W···O13W	x,+y+1,+z	2.83(2)
O5W···O2B	-x+1/2,+y+1/2,+z	2.90(2)
O5W···O9W	x-1,+y,+z	2.70(4)
O6W···O11W	x,-y+1/2,+z-1/2	2.62(3)

Table S7 Variable temperature experiment on the crystals of complex **1a**

Temperature	Unit cell dimensions					Crystal System	Remark
	a	b	c	Volume	Volume Change		
293K	20.63(1)	24.06(1)	26.13(1)	12987(5)	-	Orthorhombic	-
308K	20.35(5)	20.55(5)	26.43(6)	11439(21)	decrease	Orthorhombic	
318K	21.8(3)	21.8(3)	28.2(4)	13334(48)	decrease	Tetragonal	Phase transition
328K	28.8(3)	29.0(2)	26.6(2)	22216(46)	decrease	Orthorhombic C	Phase transition
338K	20.4(2)	20.4(2)	26.6(2)	11025(30)	decrease	Tetragonal	Phase transition
348K	20.7(2)	20.7(2)	27.3(2)	11674(30)	decrease	Tetragonal	Phase transition

Table S8: Fingerprint analysis of the interactions of the three cytosine rings

Interaction	Cu···N (%)	Cu···O (%)	C···C(%)	H···O(%)	O···O(%)	Others (%)
Cyt A	7.0	6.5	0.0	29.4	0.4	56.7
Cyt B	7.4	5.8	0.0	36.5	0.3	50.0
Cyt C	3.4	0.3	8.0	25.9	8.9	53.5