Interaction with DNA of a Heteronuclear [Na_2Cu_4] Coordination Cluster obtained from the Assembly of Two Hydroxo-Bridged [Cu^{II}_2] Units by a Dimeric Sodium Nitrate Template¶

Debashree Mandal,[a] Mala Chauhan,[b] Farukh Arjmand,[b] Guillem Aromí[c] and Debashis Ray*,[a]

[a]*Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India,*
[b]*Department of Chemistry, Aligarh Muslim University, Aligarh-202002, India,*
[c]*Department de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Diagonal 647, 08028-Barcelona, Spain.*

Supplementary Information

Crystallographic data: Crystal data for complex **1**·5H_2O: Molecular formula $C_{26}H_{50}Na_2Cu_4N_6O_{23}$, Molecular weight = 1114.70, Monoclinic, C2/c, a = 28.09(3) Å, b = 9.13(2) Å, c = 18.26(3) Å, β = 115.98(5)º, V = 4210(12) Å^3, Z = 4, D_C = 1.727 g cm^{-3}, μ(Mo Kα) = 2.103 mm^{-1}, F(000) = 2200, final R_1 and wR_2 {$I > 2\sigma(I)$} were 0.0593 and 0.1524, respectively. GOF = 1.069, largest difference peak and hole: 1.072 and −0.935 eÅ^{-3}. Precise unit cell dimensions were determined from the least squares refinement of 25 well centered reflections having 2θ values 1.61 to 24.97º. The data are collected in the 0≤h≤33, 0≤k≤10, -21≤l≤19 range.

Crystal Structure Determinations

The crystal data of compound (**1**·5H_2O) were collected at room temperature using a Bruker-Nonius Mach3 CAD4 X-ray diffractometer using graphite-monochromated Mo Kα radiation (λ= 0.71073 Å) using a single crystal with dimensions 0.36 × 0.34 × 0.23 mm^3 by ω-scan method. The intensities of three reference reflections of each complex were monitored every one-hour. The data collection shows no sign of crystal deterioration. All calculations were performed using SHELXL-97[1] implemented in WINGX[2] system of programs. Direct phase determination yielded Cu, Na and most of the

C, N, O atoms. Anisotropic thermal parameters are used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms.

The crystal data are given in Table S1. Selected bond distance and angles are given in Table S2. Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 654549. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or on application to CCDC, Union Road, Cambridge, CB2 1EZ, UK [fax: (+44)1223-336033, e-mail: deposit@ccdc.cam.ac.uk]

Table S1. Crystallographic data of **1**·5H_2O

Compound	**1**·5H_2O
Formula	$C_{26}H_{50}Na_2Cu_4N_6O_{23}$
M	1114.70
Space group	*C2/c*
Crystal system	Monoclinic
a/Å	28.09(3)
b/Å	9.13(2)
c/Å	18.26(3)
β/°	115.98(5)
U/Å^3	4210(12)
Z	4
T/K	293(2)
D_c/g cm^{-3}	1.727
F(000)	2200
μ(Mo-Kα)/cm^{-1}	2.103
Measured Reflections	3783
Unique Reflections	3710
R_{int}	0.0867
Obs. Refl.ns [I≥2σ(I)]	2617
θ_{min}- θ_{max}/°	1.61–24.97
hkl ranges	0,33;0,10;-21,19
$R(F^2)$	0.0593
$wR(F^2)$ {I > 2σ(I)}	0.1524
No. Variables	276
Goodness of fit	1.069
$\Delta\rho_{max}$; $\Delta\rho_{min}$ /e Å^{-3}	1.072; -0.935

$R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

$w = 0.75/(\sigma^2(F_o) + 0.0010F_o^2)$.

Table S2. Selected bond Distances (Å) and Bond Angles (Degrees) of **(1**·5H_2O**)**.

Na(1)-O(8)	2.370(6)	N(3)-O(5)	1.258(8)
Na(1)-O(9)	2.409(7)	O(9)-Na(1*)	2.419(6)
Na(1)-O(9*)	2.419(6)	Cu(1)-O(2)	1.891(5)
Na(1)-O(6)	2.434(7)	Cu(1)-N(2)	1.917(6)
Na(1)-O(4)	2.560(6)	Cu(1)-O(4)	1.929(5)
Na(1)-O(5)	2.573(7)	Cu(1)-O(3)	1.943(5)
Na(1)-N(3)	2.902(7)	Cu(1)-Cu(2)	2.943(4)
Na(1)-Na(1*)	3.340(6)	Cu(2)-O(1)	1.895(5)
Na(1)-Cu(1)	3.600(6)	Cu(2)-O(4)	1.926(4)
O(6)-N(3)	1.248(8)	Cu(2)-N(1)	1.928(6)
O(7)-N(3)	1.231(8)	Cu(2)-O(3)	1.950(5)

O(8)-Na(1)-O(9)	89.8(2)	O(9*)-Na(1)-O(4)	93.1(2)
O(8)-Na(1)-O(9*)	85.2(2)	O(6)-Na(1)-O(4)	82.5(2)
O(9)-Na(1)-O(9*)	92.48(1)	O(8)-Na(1)-O(5)	117.8(2)
O(8)-Na(1)-O(6)	103.1(2)	O(9)-Na(1)-O(5)	146.4(2)
O(9)-Na(1)-O(6)	107.2(2)	O(9*)-Na(1)-O(5)	107.7(2)
O(9*)-Na(1)-O(6)	158.5(2)	O(6)-Na(1)-O(5)	50.8(2)
O(8)-Na(1)-O(4)	168.6(2)	O(4)-Na(1)-O(5)	73.5(2)
O(9)-Na(1)-O(4)	79.0(2)	O(8)-Na(1)-N(3)	111.8(2)
O(9)-Na(1)-N(3)	128.8(2)	O(5)-Na(1)-Na(1*)	145.24(1)
O(9*)-Na(1)-N(3)	133.4(2)	N(3)-Na(1)-Na(1*)	161.78(1)
O(6)-Na(1)-N(3)	25.15(1)	O(8)-Na(1)-Cu(1)	145.23(1)
O(4)-Na(1)-N(3)	77.49(1)	O(9)-Na(1)-Cu(1)	69.47(1)
O(5)-Na(1)-N(3)	25.68(1)	O(9*)-Na(1)-Cu(1)	122.04(1)
O(8)-Na(1)-Na(1*)	86.38(1)	O(6)-Na(1)-Cu(1)	60.13(1)
O(9)-Na(1)-Na(1*)	46.36(1)	O(4)-Na(1)-Cu(1)	31.04(1)
O(9*)-Na(1)-Na(1*)	46.12(1)	O(5)-Na(1)-Cu(1)	77.02(1)
O(6)-Na(1)-Na(1*)	152.5(2)	N(3)-Na(1)-Cu(1)	66.99(1)
O(4)-Na(1)-Na(1*)	84.31(1)	Na(1*)-Na(1)-Cu(1)	97.54(16)
N(3)-O(6)-Na(1)	98.9(5)	O(7)-N(3)-O(5)	120.4(6)
O(7)-N(3)-O(6)	121.3(7)	O(6)-N(3)-O(5)	118.3(6)
O(6)-N(3)-O(5)	118.3(6)	Cu(2)-Cu(1)-Na(1)	68.66(1)
O(7)-N(3)-Na(1)	177.2(5)	O(1)-Cu(2)-O(4)	101.8(2)
O(6)-N(3)-Na(1)	56.0(4)	O(1)-Cu(2)-N(1)	87.6(2)
O(5)-N(3)-Na(1)	62.4(4)	O(4)-Cu(2)-N(1)	170.6(2)
N(3)-O(5)-Na(1)	91.9(4)	O(1)-Cu(2)-O(3)	171.0(2)
Na(1)-O(9)-Na(1*)	87.52(1)	O(4)-Cu(2)-O(3)	80.5(2)
O(2)-Cu(1)-N(2)	87.5(2)	N(1)-Cu(2)-O(3)	90.2(2)
O(2)-Cu(1)-O(4)	100.8(2)	O(1)-Cu(2)-Cu(1)	139.54(1)
N(2)-Cu(1)-O(4)	171.0(2)	O(4)-Cu(2)-Cu(1)	40.27(1)
O(2)-Cu(1)-O(3)	174.4(2)	N(1)-Cu(2)-Cu(1)	130.59(1)
N(2)-Cu(1)-O(3)	91.5(2)	O(3)-Cu(2)-Cu(1)	40.78(1)
O(4)-Cu(1)-O(3)	80.6(2)	Cu(1)-O(3)-Cu(2)	98.2(2)
O(2)-Cu(1)-Cu(2)	139.33(16)	Cu(2)-O(4)-Cu(1)	99.5(2)
N(2)-Cu(1)-Cu(2)	132.31(18)	Cu(2)-O(4)-Na(1)	111.7(2)
O(4)-Cu(1)-Cu(2)	40.19(1)	Cu(1)-O(4)-Na(1)	105.8(2)
O(3)-Cu(1)-Cu(2)	40.97(1)	O(4)-Cu(1)-Na(1)	43.19(1)
O(2)-Cu(1)-Na(1)	89.8(2)	O(3)-Cu(1)-Na(1)	94.89(1)
N(2)-Cu(1)-Na(1)	134.50(1)		

(*): -x,-y,-z

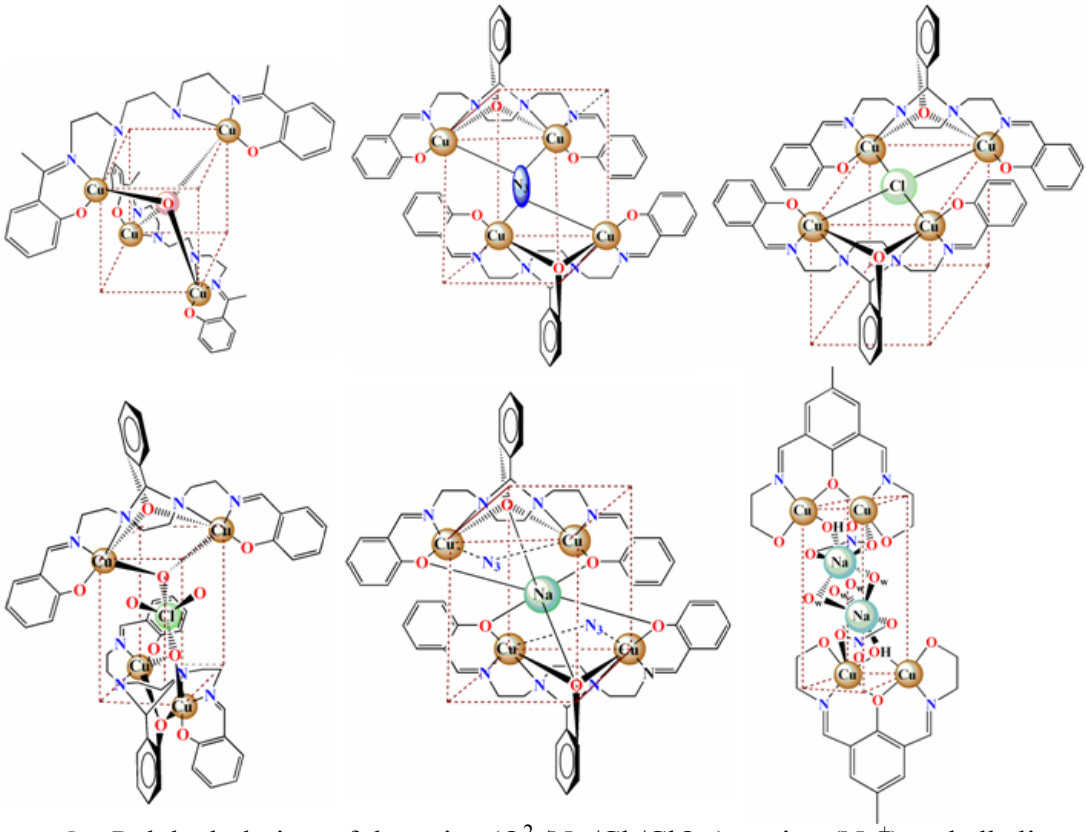


Figure S1. Polyhedral view of the anion (O^{2-}/N_3^-/Cl^-/ClO_4^-), cation (Na^+) and alkali metal salt templated Cu_4 complexes.

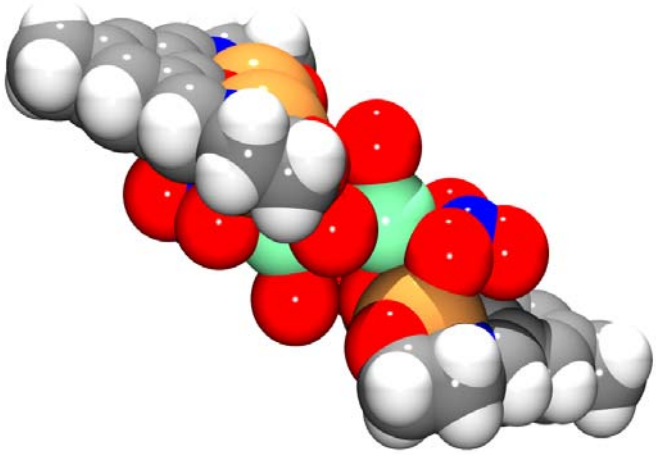


Figure S2. Space-filling model of complex **1**·$5H_2O$ showing that the fragment $\{Na(NO_3)(\mu\text{-}OH_2)(OH_2)\}_2$ acts here as a structural bridge between the two copper dimeric units.

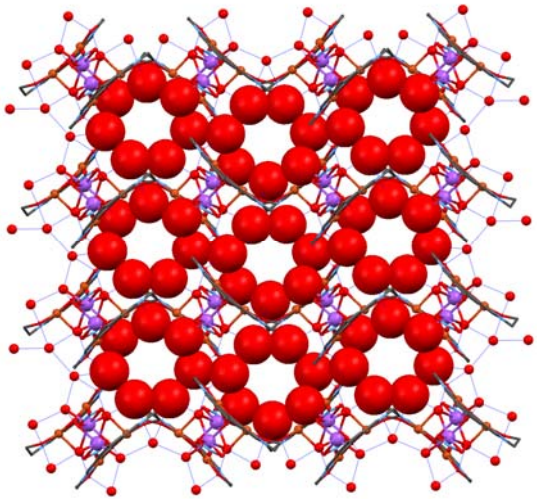
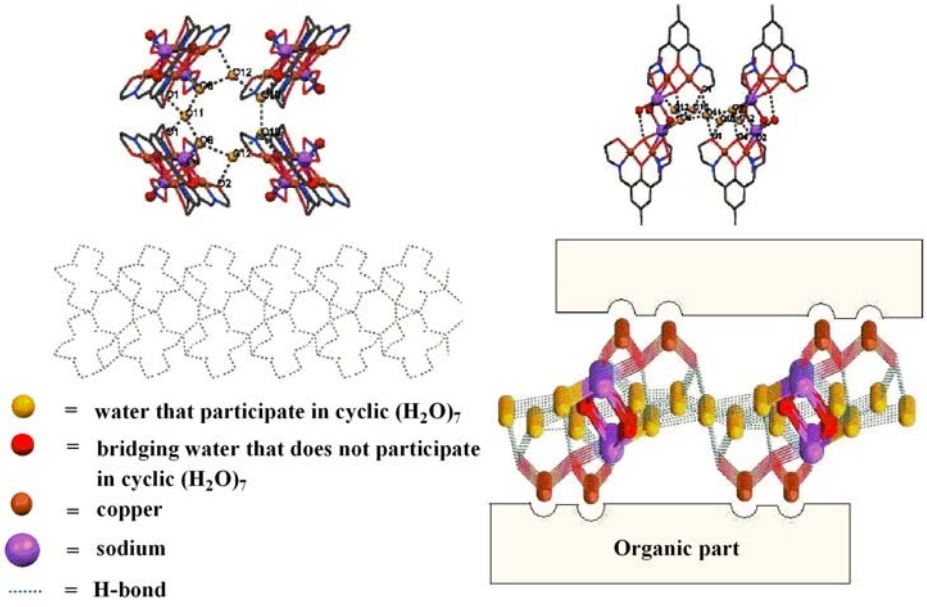


Figure S3. Ball stick view of complex **1**·5H_2O showing the water cycles within the crystal structure of the complex.



(a) (b)

Figure S4. (a) Representation of the structure of **1**·5H_2O along the crystallographic *a* axis, emphasizing the H-bonding networks involving the cyclic water heptamer. (b) The corrugated water layer within the organic ligands and metal ions shown along the crystallographic *b* axis.

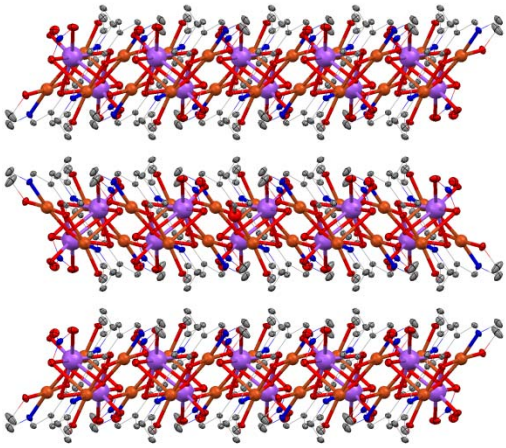


Figure S5. Packing diagram of **1**·5H_2O along the crystallographic '*b*' axis.

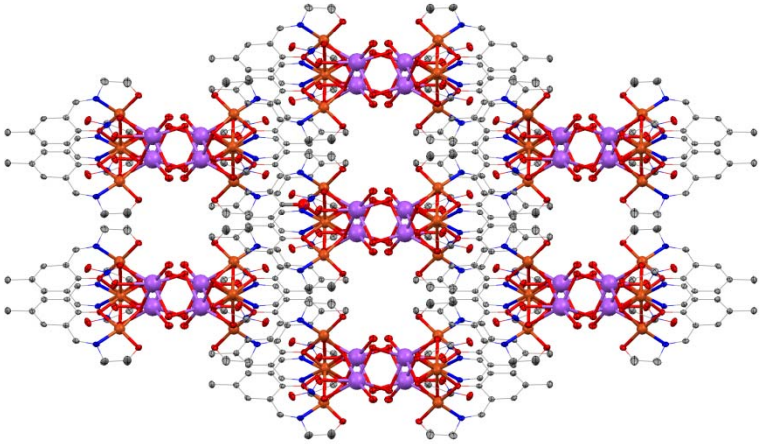


Figure S6. Packing diagram of **1**·5H_2O along the crystallographic *c*-axis. The Na groups are in space-filling style and the rest is in the stick style emphasizing the formation of a metal organic framework (MOF).

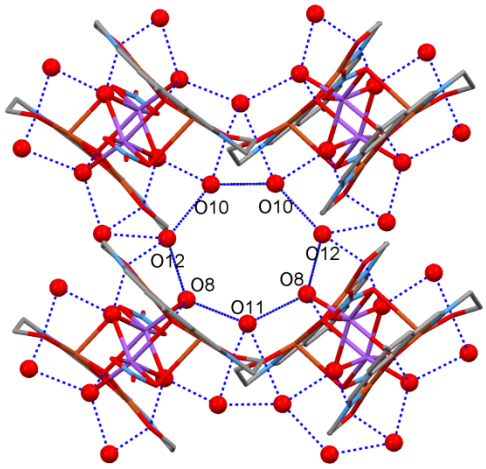


Figure S7. Hydrogen bonding of **1**·5H_2O shows the positions of the water molecules.

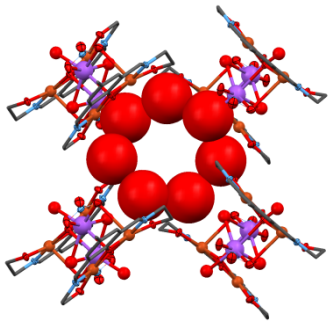


Figure S8. Space-filling diagram of the heptameric water cycle within the structure of **1**·**5H$_2$O**, as surrounded by four [Na_2Cu_4] complexes.

References

(1) G. M. Sheldrick, SHELX-97, *Program for Crystal Structure Refinement*, University of Gottingen, Germany, **1997**.

(2) (a) L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, *32*, 837; (b) M. N. Burnett, C. K. Johnson, ORTEP III, Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, 1996.