

## Supporting Materials

Crystallized Water: Internal and External Ice Fragments in Polycyclic Hosts

Sung Ok Kang, Douglas Powell, Victor W. Day and Kristin Bowman-James\*

*Department of Chemistry, University of Kansas, Lawrence, Kansas 66045*

E-mail: kbjames@ku.edu

### X-ray studies

**L1·(H<sub>2</sub>O)<sub>6</sub>·H<sub>2</sub>O:** Colorless rectangular parallelepiped shaped crystals of [C<sub>33</sub>H<sub>39</sub>N<sub>11</sub>O<sub>6</sub>]·(H<sub>2</sub>O)<sub>6</sub>·H<sub>2</sub>O are, at 100(2) K, triclinic, space group P1 - C<sub>1</sub><sup>1</sup> (No. 1) (1) with  $a = 10.3691(5)$  Å,  $b = 10.4155(5)$  Å,  $c = 11.0993(5)$  Å,  $\alpha = 64.144(1)^\circ$ ,  $\beta = 71.293(1)^\circ$ ,  $\gamma = 63.249(1)^\circ$ ,  $V = 951.7(1)$  Å<sup>3</sup> and  $Z = 1$  [C<sub>33</sub>H<sub>39</sub>N<sub>11</sub>O<sub>6</sub>]·(H<sub>2</sub>O)<sub>6</sub>·H<sub>2</sub>O formula unit ( $d_{\text{calcd}} = 1.417$  g/cm<sup>3</sup>;  $\mu_a(\text{Mo K}\alpha) = 0.110$  mm<sup>-1</sup>). A full hemisphere of diffracted intensities (1850 10-second frames with an  $\omega$  scan width of 0.30°) was measured for a single-domain specimen using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Bruker SMART APEX CCD Single Crystal Diffraction System (2). X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 35mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 6611 reflections. A total of 11641 integrated reflection intensities having  $2\theta(\text{MoK}\alpha) < 61.01^\circ$  were produced using the Bruker program SAINT(3); 10046 of these were unique and gave  $R_{\text{int}} = 0.014$  with a coverage which was 98.2% complete. The Bruker software package SHELXTL Version 6.10 was used to solve the structure using “direct methods” techniques. All stages of weighted full-matrix least-squares refinement were conducted using  $F_o^2$  data with the SHELXTL software package (4). All hydrogen atoms were located from difference Fourier syntheses and included in the structural model as individual isotropic atoms whose parameters were allowed to vary in least-squares refinement cycles.

The final structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. A total of 726 parameters were refined using 3 restraints, 10046 data and weights of  $w = 1/[\sigma^2(F^2) + (0.084 P)^2 + 0.0562 P]$ , where  $P = [F_o^2 + 2F_c^2] / 3$ . Final agreement factors at

convergence are:  $R_1$ (unweighted, based on  $F$ ) = 0.043 for 9697 independent “observed” reflections having  $2\theta(\text{Mo K}\alpha) < 61.01^\circ$  and  $I > 2\sigma(I)$ ;  $R_1$ (unweighted, based on  $F$ ) = 0.045 and  $wR_2$ (weighted, based on  $F^2$ ) = 0.114 for all 10046 independent reflections having  $2\theta(\text{Mo K}\alpha) < 61.01^\circ$ . The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.52 and -0.46  $\text{e}^-/\text{\AA}^3$ , respectively.

**L2·(H<sub>2</sub>O)<sub>6</sub>·2H<sub>2</sub>O:** Colorless block shaped crystals of  $[\text{C}_{48}\text{H}_{60}\text{N}_{16}\text{O}_8] \cdot (\text{H}_2\text{O})_6 \cdot 2\text{H}_2\text{O}$  are, at 100(2) K, triclinic, space group  $P\bar{1} - C_1^1$  (No. 2) (1) with  $a = 10.649(1) \text{ \AA}$ ,  $b = 11.789(1) \text{ \AA}$ ,  $c = 11.946(1) \text{ \AA}$ ,  $\alpha = 88.667(3)^\circ$ ,  $\beta = 81.501(3)^\circ$ ,  $\gamma = 64.577(3)^\circ$ ,  $V = 1338.3(2) \text{ \AA}^3$  and  $Z = 1$  [ $\text{C}_{48}\text{H}_{60}\text{N}_{16}\text{O}_8$ ]·(H<sub>2</sub>O)<sub>6</sub>·2H<sub>2</sub>O formula unit ( $d_{\text{calcd}} = 1.400 \text{ g/cm}^3$ ;  $\mu_a(\text{Mo K}\alpha) = 0.106 \text{ mm}^{-1}$ ). A full hemisphere of diffracted intensities (1850 10-second frames with an  $\omega$  scan width of  $0.30^\circ$ ) was measured for a single-domain specimen using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Bruker SMART APEX CCD Single Crystal Diffraction System (2). X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 35mA. Lattice constants were determined with the Bruker SAINT software package using peak centers for 5505 reflections. A total of 13613 integrated reflection intensities having  $2\theta(\text{Mo K}\alpha) < 60.00^\circ$  were produced using the Bruker program SAINT(3); 7602 of these were unique and gave  $R_{\text{int}} = 0.020$  with a coverage which was 97.6% complete. The intensity data were corrected empirically (5) for variable absorption effects; the relative transmission factors ranged from 0.777 to 1.000. The Bruker software package SHELXTL Version 6.10 was used to solve the structure using “direct methods” techniques. All stages of weighted full-matrix least-squares refinement were conducted using  $F_o^2$  data with the SHELXTL software package (4).

All amide and water hydrogen atoms except those on the fifth (partial-occupancy) water molecule were located from difference Fourier syntheses and included in the structural model as individual isotropic atoms whose parameters were allowed to vary in least-squares refinement cycles. The fourth crystallographically-independent water molecule is disordered over two contiguous sites (corresponding to oxygen atoms O4W and O5W) in the unit cell. The occupancy factor of O4W and its hydrogen atoms refined to 0.675(5). The occupancy factor of O5W refined to 0.196(4); the hydrogen atoms for

this partial-occupancy water molecule could not be located with difference Fouriers. The remaining hydrogen atoms were included in the structural model as idealized atoms (assuming  $sp^2$ - or  $sp^3$ -hybridization of the carbon atoms and C-H bond lengths of 0.95 or 0.99 Å). The isotropic thermal parameters of all idealized hydrogen atoms were fixed at values 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded.

The final structural model incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all included hydrogen atoms. A total of 420 parameters were refined using no restraints, 7602 data and weights of  $w = 1/[\sigma^2(F^2) + (0.0841 P)^2 + 0.2238 P]$ , where  $P = [F_o^2 + 2F_c^2] / 3$ . Final agreement factors at convergence are:  $R_1$ (unweighted, based on  $F$ ) = 0.048 for 6472 independent absorption-corrected “observed” reflections having  $2\theta(\text{MoK}\alpha) < 60.00^\circ$  and  $I > 2\sigma(I)$ ;  $R_1$ (unweighted, based on  $F$ ) = 0.056 and  $wR_2$ (weighted, based on  $F^2$ ) = 0.137 for all 7602 independent absorption-corrected reflections having  $2\theta(\text{Mo K}\alpha) < 60.00^\circ$ . The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.84 and -0.57  $e^-/\text{\AA}^3$ , respectively.

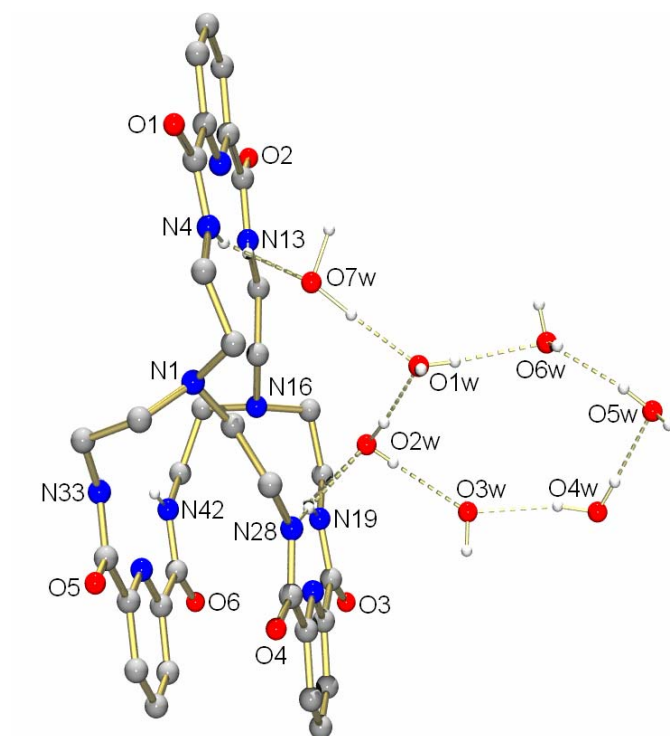
## References

- (1) International Tables for Crystallography, Vol A, 4<sup>th</sup> ed., Kluwer: Boston (1996).
- (2) Data Collection: SMART Software Reference Manual (1998). Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.
- (3) Data Reduction: SAINT Software Reference Manual (1998). Bruker-AXS, 6300 Enterprise Dr., Madison, WI 53719-1173, USA.
- (4) G. M. Sheldrick (2000). SHELXTL Version 6.10 Reference Manual. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.
- (5) G. M. Sheldrick (2002). SADABS. Program for Empirical Absorption Correction of Area Detector Data. University of Göttingen, Germany.

**Table S1.** Crystallographic Data for **L1**·(H<sub>2</sub>O)<sub>6</sub>·H<sub>2</sub>O and **L2**·(H<sub>2</sub>O)<sub>6</sub>·2H<sub>2</sub>O.

	<b>L1</b> ·(H <sub>2</sub> O) <sub>6</sub> ·H <sub>2</sub> O	<b>L2</b> ·(H <sub>2</sub> O) <sub>6</sub> ·2H <sub>2</sub> O
Empirical Formula	C <sub>33</sub> H <sub>53</sub> N <sub>11</sub> O <sub>13</sub>	C <sub>48</sub> H <sub>76</sub> N <sub>16</sub> O <sub>16</sub>
Formula Weight	811.86	1133.25
Crystal System	Triclinic	Triclinic
Space Group	<i>P</i> 1	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.369(5)	10.649(1)
<i>b</i> (Å)	10.416(5)	11.789(1)
<i>c</i> (Å)	11.099(5)	11.946(1)
$\alpha$ (deg)	64.144(1)	88.667(3)
$\beta$ (deg)	71.293(1)	81.501(3)
$\gamma$ (deg)	63.249(1)	64.577(3)
<i>V</i> (Å <sup>3</sup> )	951.7(1)	1338.3(2)
<i>Z</i>	1 C <sub>33</sub> H <sub>53</sub> N <sub>11</sub> O <sub>13</sub> formula unit	1 C <sub>48</sub> H <sub>76</sub> N <sub>16</sub> O <sub>16</sub> formula unit
Diffractometer	Bruker APEX	Bruker APEX
<i>d</i> <sub>calcd</sub> (g/cm <sup>3</sup> )	1.417	1.400
$\lambda$ (Å)	0.71073	0.71073
<i>T</i> (K)	100(2)	100(2)
<i>F</i> (000)	432	601
abs coeff(mm <sup>-1</sup> )	0.110	0.106
$\theta$ range (deg)	2.48-30.51	2.14-30.00
Reflns collected	11641	13613
Indep. Reflections	10046	7602
Data/restr/param	10046/ 3/ 726	7602/ 0/ 420
<i>R</i> <sub>1</sub> ; <i>wR</i> <sub>2</sub> <sup>a</sup>	0.043; 0.114	0.048; 0.137
GOF ( <i>F</i> <sup>2</sup> )	1.046	1.061

$$^a R_1(\text{obsd data}) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|. \quad wR_2(\text{all data}) = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$$

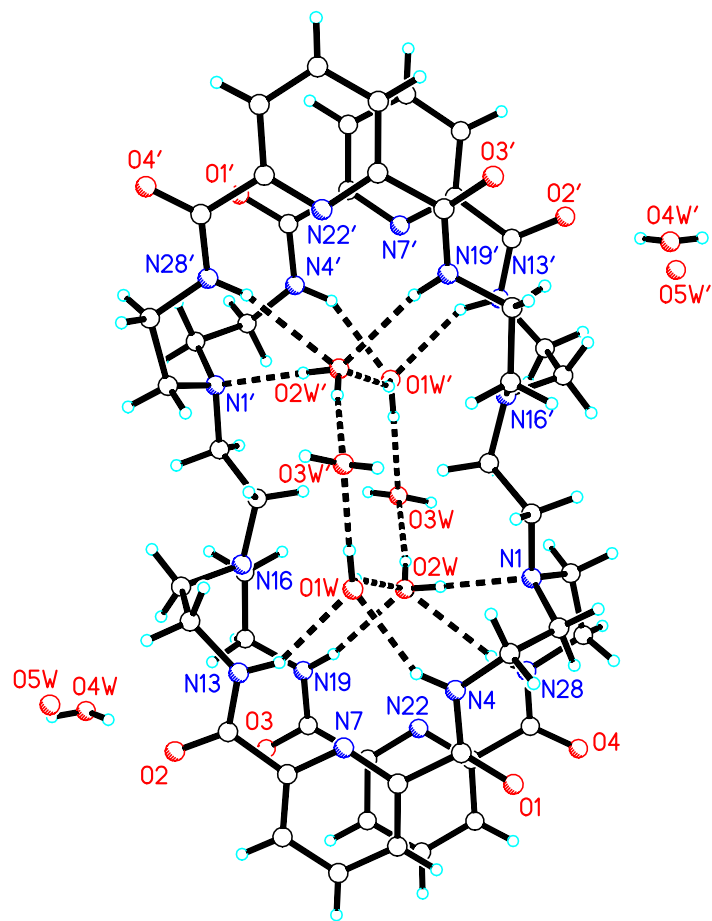


**Figure S1.** Perspective view of  $\text{L1} \cdot (\text{H}_2\text{O})_6 \cdot \text{H}_2\text{O}$ .

**Table S2.** Selected hydrogen bonds for **L1**·(H<sub>2</sub>O)<sub>6</sub>·H<sub>2</sub>O [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4N)...O(7W)	0.87(3)	2.26(3)	3.008(2)	144(2)
N(4)-H(4N)...O(5W)#1	0.87(3)	2.76(3)	3.253(2)	118(3)
N(13)-H(13N)...O(7W)	0.86(3)	2.35(2)	3.088(2)	145(2)
N(13)-H(13N)...O(5W)#1	0.86(3)	2.82(3)	3.375(2)	124(3)
N(19)-H(19N)...O(2W)	0.89(3)	2.58(3)	3.261(2)	134(2)
N(28)-H(28N)...O(2W)	0.92(2)	2.12(2)	2.979(2)	156(2)
N(33)-H(33N)...O(4W)#1	0.73(3)	2.29(3)	2.973(2)	158(3)
N(42)-H(42N)...O(4W)#1	0.73(2)	2.31(2)	3.001(2)	161(2)
O(1W)-H(1W1)...O(6W)	0.80(3)	2.03(3)	2.829(2)	172(3)
O(1W)-H(1W2)...O(6)#2	0.79(4)	2.00(4)	2.759(2)	164(3)
O(2W)-H(2W1)...O(1W)	0.89(3)	1.93(3)	2.816(2)	175(2)
O(2W)-H(2W2)...O(3W)	0.74(3)	2.11(3)	2.851(2)	180(3)
O(3W)-H(3W1)...O(1)#3	0.90(4)	1.78(4)	2.670(2)	173(3)
O(3W)-H(3W2)...O(2)#4	0.84(3)	1.90(3)	2.740(2)	176(3)
O(4W)-H(4W1)...O(3W)	0.89(3)	2.00(3)	2.862(2)	166(3)
O(4W)-H(4W2)...O(5W)	0.81(3)	1.94(3)	2.744(2)	173(3)
O(5W)-H(5W1)...O(6W)	0.81(3)	2.02(3)	2.825(2)	172(2)
O(5W)-H(5W2)...N(1)#5	0.75(3)	2.13(3)	2.870(2)	168(3)
O(6W)-H(6W1)...O(3)#2	0.83(3)	1.85(3)	2.665(2)	168(3)
O(6W)-H(6W2)...O(4)#6	0.82(3)	1.95(3)	2.723(2)	156(3)
O(7W)-H(7W2)...O(1W)	1.06(3)	1.83(3)	2.859(2)	163(3)
O(6w)...O(1w)...O(2w)				108.4(1)
O(3w)...O(4w)...O(5w)				115.3(1)
O(4w)...O(5w)...O(6w)				102.0(1)
O(2w)...O(3w)...O(4w)				138.8(1)
O(5w)...O(6w)...O(1w)				140.8(1)

Symmetry transformations used to generate equivalent atoms: #1: x,y,z+1; #2: x-1,y,z; #3: x+1,y,z-1; #4: x,y+1,z-1; #5: x,y,z-1; #6: x,y-1,z.



**Figure S2.** Perspective view of the asymmetric unit for  $\text{L2} \cdot (\text{H}_2\text{O})_6 \cdot 2\text{H}_2\text{O}$ .

**Table S3.** Selected hydrogen bonds for **L2**·(H<sub>2</sub>O)<sub>6</sub>·2H<sub>2</sub>O [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4N)...O(1W)	0.86(2)	2.13(2)	2.903(1)	150(2)
N(13)-H(13N)...O(1W)	0.88(2)	2.13(2)	2.922(1)	150(2)
N(19)-H(19N)...O(2W)	0.88(2)	2.29(2)	3.148(1)	167(2)
N(28)-H(28N)...O(2W)	0.86(2)	2.44(2)	3.272(1)	165(2)
O(1W)-H(1W1)...O(2W)	0.81(2)	2.19(2)	2.913(1)	148(2)
O(1W)-H(1W2)...O(3W)#1	0.90(2)	1.94(2)	2.839(1)	178(2)
O(2W)-H(2W1)...N(1)	0.87(2)	2.10(2)	2.963(1)	175(2)
O(2W)-H(2W2)...O(3W)	0.83(2)	2.05(2)	2.878(1)	174(2)
O(3W)-H(3W1)...O(3)#3	0.89(2)	1.91(2)	2.796(1)	169(2)
O(3W)-H(3W2)...O(4)#4	0.87(2)	1.90(2)	2.745(1)	166(2)
O(4W)-H(4W1)...O(1)#5	0.75(4)	2.14(4)	2.888(2)	179(3)
O(4W)-H(4W2)...O(2)	0.83(3)	1.88(3)	2.689(2)	164(3)
O(1W)...O(2W)...O(3W)				129.52(4)
O(2W)...O(3W)...O(1W)#1				105.52(4)
O(2W)...O(1W)...O(3W)#1				119.15(4)

Symmetry transformations used to generate equivalent atoms: #1: -x+1,-y,-z+1; #2: -x+1,-y-1,-z; #3: -x,-y,-z+1; #4: -x,-y+1,-z+1; #5: x,y-1,z.