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Self-assembly of Dialkyltin(IV) moieties and a thiosemicarbone to a trinuclear macrocycle and the unpresedented formation of two *pseudo*-polymorfs with different cavities.

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ESI

X – ray data collection

X-ray data for **1** and **2** were collected at low temperature using an Oxford Cryosystem device on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). Crystals were positioned at 65 mm from the CCD camera. 612 frames were measured at 0.75^{o} intervals with a counting time of 10-20 sec. Accurate cell parameters were determined and refined by least-squares fit of 11200 and 12000 the strongest reflections for **1** and **2**, respectively. The data were corrected for Lorentz and polarization effects. Analytical absorption correction was applied for both crystals. Data reduction and analysis were carried out with the Oxford Diffraction (Poland) Sp. z o.o programs. Crystal structures were solved by direct methods (program SHELXS97 [1]) and refined by the full-matrix least-squares method on all F^2 data using the SHELXL97 [2] programs. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were included from geometry of molecules and Δρ maps. During the refinement process they treated as riding atoms. Crystal data are given in Table 1, together with refinement details.

[1] G. M. Sheldrick, *Acta Crystallogr*., **A46**, 1990, 467-473.
[2] G. M. Sheldrick, SHELXL97, program for crystal structure refinement, University of Göttingen, 1997.

Table 1. Crystal data, data collection and structure refinement for **1** and **2**

Empirical formula	C_{30} H_{57} N_9 O_9 S_3 Sn_3	C_{24} H_{45} N_9 $O_{7.5}$ S_3 Sn_3
Formula weight	1140.19	1031.94
Temperature /K	100(2)	100(2)
Wavelength /A	0.71073	0.71073
Crystal system	Hexagonal	Cubic
Space group	P6(3)/m (No.176)	I23 (No.197)
a /A	18.2141(5)	20.1191(5)
b /A	18.2141(5)	20.1191(5)
c /A	7.6303(3)	20.1191(5)
alpha /o	90	90
beta /o	90	90
gamma /o	120	90
Volume /A^3	2192.24(12)	8143.8(4)
Z	2	**8**
Dc /Mg.m^-3	1.727	1.683
Absorption coefficient /mm^-1	1.895	2.029
F(000)	1140	4080
Crystal size /mm	0.16 x 0.14 x 0.12	0.18 x 0.16 x 0.12
Diffractometer	Kuma KM4CCD	Kuma KM4CCD
Theta range for data collection /o	3.42 - 36.60	3.20 - 36.61
Ranges of h,k,l	-29=>29, -30=>30, -9=>12	-33=>22, -33=>33, -33=>33
Reflections collected	37222	66056
Independent reflections (Rint)	3772 (0.0390)	6610 (0.0600)
Absorption coefficients min./max	0.7513/0.8045	0.7116/0.7028
Data/parameters	3772/126	6610/144
Goodness-of-fit (F^2)	1.094	0.946
Final R1/wR2 indices (I>2sI)	0.0259/0.0529	0.0292/0.0602
Largest diff. peak/hole /e.A^-3	2.445/-0.675	1.142/-0.869

Table 2. Bond lengths (Å) and valency angles (°) in **1**

Sn(1)-C(5)	2.1133(14)
Sn(1)-C(5)#1	2.1133(14)
Sn(1)-N(1)	2.3130(14)
Sn(1)-O(1)	2.3209(13)
Sn(1)-O(2)#2	2.4077(12)
Sn(1)-S(1)	2.5516(5)
S(1)-C(4)	1.7405(19)
O(1)-C(1)	1.276(2)
O(2)-C(1)	1.261(2)
O(2)-Sn(1)#3	2.4077(12)
N(1)-C(2)	1.297(2)
N(1)-N(2)	1.367(2)
N(2)-C(4)	1.325(2)
N(3)-C(4)	1.343(3)
N(3)-H(3D)	0.80(3)
N(3)-H(3E)	0.87(3)
C(1)-C(2)	1.498(2)
C(2)-C(3)	1.484(2)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
O(1T)-C(1T1)	1.39(2)
O(1T)-C(1T1)#1	1.39(2)
O(1T)-C(1T2)	1.48(2)
O(1T)-C(1T2)#1	1.48(2)
C(1T1)-C(2T1)	1.51(2)
C(1T1)-H(1T1)	0.9900
C(1T1)-H(1T2)	0.9900
C(2T1)-C(2T1)#1	1.181(11)
C(2T1)-H(2T1)	0.9900
C(2T1)-H(2T2)	0.9900
C(1T2)-C(2T2)	1.48(2)
C(1T2)-H(1T3)	0.9900
C(1T2)-H(1T4)	0.9900
C(2T2)-C(2T2)#1	1.395(11)
C(2T2)-H(2T3)	0.9900
C(2T2)-H(2T4)	0.9900

C(5)-Sn(1)-C(5)#1	157.43(7)
C(5)-Sn(1)-N(1)	97.85(4)
C(5)#1-Sn(1)-N(1)	97.85(4)
C(5)-Sn(1)-O(1)	85.19(4)
C(5)#1-Sn(1)-O(1)	85.19(4)
N(1)-Sn(1)-O(1)	69.62(5)
C(5)-Sn(1)-O(2)#2	86.10(4)
C(5)#1-Sn(1)-O(2)#2	86.10(4)
N(1)-Sn(1)-O(2)#2	156.11(5)
O(1)-Sn(1)-O(2)#2	134.27(4)
C(5)-Sn(1)-S(1)	99.81(4)
C(5)#1-Sn(1)-S(1)	99.81(4)
N(1)-Sn(1)-S(1)	75.20(4)

O(1)-Sn(1)-S(1)	144.82(3)
O(2)#2-Sn(1)-S(1)	80.91(3)
C(4)-S(1)-Sn(1)	98.14(6)
C(1)-O(1)-Sn(1)	117.86(11)
C(1)-O(2)-Sn(1)#3	101.17(11)
C(2)-N(1)-N(2)	116.64(15)
C(2)-N(1)-Sn(1)	119.55(11)
N(2)-N(1)-Sn(1)	123.81(11)
C(4)-N(2)-N(1)	114.65(15)
C(4)-N(3)-H(3D)	112(2)
C(4)-N(3)-H(3E)	122(2)
H(3D)-N(3)-H(3E)	126(3)
O(2)-C(1)-O(1)	122.42(16)
O(2)-C(1)-C(2)	119.12(16)
O(1)-C(1)-C(2)	118.46(15)
N(1)-C(2)-C(3)	124.99(16)
N(1)-C(2)-C(1)	114.51(15)
C(3)-C(2)-C(1)	120.50(15)
C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
N(2)-C(4)-N(3)	115.56(17)
N(2)-C(4)-S(1)	128.20(14)
N(3)-C(4)-S(1)	116.24(15)
Sn(1)-C(5)-H(5A)	109.5
Sn(1)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
Sn(1)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(1T1)-O(1T)-C(1T1)#1	106.5(18)
C(1T1)-O(1T)-C(1T2)	10.8(11)
C(1T1)#1-O(1T)-C(1T2)	109.2(2)
C(1T1)-O(1T)-C(1T2)#1	109.2(2)
C(1T1)#1-O(1T)-C(1T2)#1	10.8(11)
C(1T2)-O(1T)-C(1T2)#1	109.9(19)
O(1T)-C(1T1)-C(2T1)	106.3(15)
O(1T)-C(1T1)-H(1T1)	110.5
C(2T1)-C(1T1)-H(1T1)	110.5
O(1T)-C(1T1)-H(1T2)	110.5
C(2T1)-C(1T1)-H(1T2)	110.5
H(1T1)-C(1T1)-H(1T2)	108.7
C(2T1)#1-C(2T1)-C(1T1)	110.5(10)
C(2T1)#1-C(2T1)-H(2T1)	109.6
C(1T1)-C(2T1)-H(2T1)	109.6
C(2T1)#1-C(2T1)-H(2T2)	109.6
C(1T1)-C(2T1)-H(2T2)	109.6
H(2T1)-C(2T1)-H(2T2)	108.1
C(2T2)-C(1T2)-O(1T)	104.8(16)
C(2T2)-C(1T2)-H(1T3)	110.8
O(1T)-C(1T2)-H(1T3)	110.8
C(2T2)-C(1T2)-H(1T4)	110.8

O(1T)-C(1T2)-H(1T4)	110.8
H(1T3)-C(1T2)-H(1T4)	108.9
C(2T2)#1-C(2T2)-C(1T2)	110.3(10)
C(2T2)#1-C(2T2)-H(2T3)	109.6
C(1T2)-C(2T2)-H(2T3)	109.6
C(2T2)#1-C(2T2)-H(2T4)	109.6
C(1T2)-C(2T2)-H(2T4)	109.6
H(2T3)-C(2T2)-H(2T4)	108.1

Symmetry transformations used to generate equivalent atoms:
#1 x,y,-z+3/2 #2 -y,x-y+1,z #3 -x+y-1,-x,z

Table 3. Bond lengths (Å) and valency angles (°) in **2**

Sn(1)-C(5)	2.105(2)
Sn(1)-C(6)	2.107(3)
Sn(1)-N(1)	2.308(2)
Sn(1)-O(1)	2.3154(16)
Sn(1)-O(2)#1	2.4502(17)
Sn(1)-S(1)	2.5441(7)
S(1)-C(4)	1.735(2)
O(1)-C(1)	1.271(3)
O(2)-C(1)	1.256(3)
N(1)-C(2)	1.297(3)
N(1)-N(2)	1.359(3)
N(2)-C(4)	1.334(3)
N(3)-C(4)	1.339(3)
C(1)-C(2)	1.503(3)
C(2)-C(3)	1.486(3)
O(1T)-C(1T)	1.537(7)
C(1T)-C(2T)	1.684(12)
C(2T)-C(2T)#3	1.87(2)
C(5)-Sn(1)-C(6)	158.00(11)
C(5)-Sn(1)-N(1)	97.55(8)
C(6)-Sn(1)-N(1)	97.97(9)
C(5)-Sn(1)-O(1)	86.03(8)
C(6)-Sn(1)-O(1)	84.73(9)
N(1)-Sn(1)-O(1)	70.01(6)
C(5)-Sn(1)-O(2)#1	85.60(8)
C(6)-Sn(1)-O(2)#1	86.52(8)
N(1)-Sn(1)-O(2)#1	156.07(6)
O(1)-Sn(1)-O(2)#1	133.92(6)
C(5)-Sn(1)-S(1)	96.95(7)
C(6)-Sn(1)-S(1)	101.98(8)
N(1)-Sn(1)-S(1)	75.47(5)
O(1)-Sn(1)-S(1)	145.43(5)
O(2)#1-Sn(1)-S(1)	80.60(4)
C(4)-S(1)-Sn(1)	97.97(8)
C(1)-O(1)-Sn(1)	117.51(14)
C(1)-O(2)-Sn(1)#2	101.74(14)
C(2)-N(1)-N(2)	117.2(2)
C(2)-N(1)-Sn(1)	119.21(15)
N(2)-N(1)-Sn(1)	123.61(15)
C(4)-N(2)-N(1)	114.7(2)
O(2)-C(1)-O(1)	122.2(2)
O(2)-C(1)-C(2)	119.1(2)
O(1)-C(1)-C(2)	118.7(2)
N(1)-C(2)-C(3)	125.0(2)
N(1)-C(2)-C(1)	114.5(2)
C(3)-C(2)-C(1)	120.5(2)
N(2)-C(4)-N(3)	115.2(2)
N(2)-C(4)-S(1)	128.12(19)
N(3)-C(4)-S(1)	116.70(18)
C(1T)#3-O(1T)-C(1T)	129.4(8)
O(1T)-C(1T)-C(2T)	99.6(7)
C(1T)-C(2T)-C(2T)#3	105.6(4)

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,-z+1,x #2 z,-x+1,-y+1 #3 x,-y+2,-z

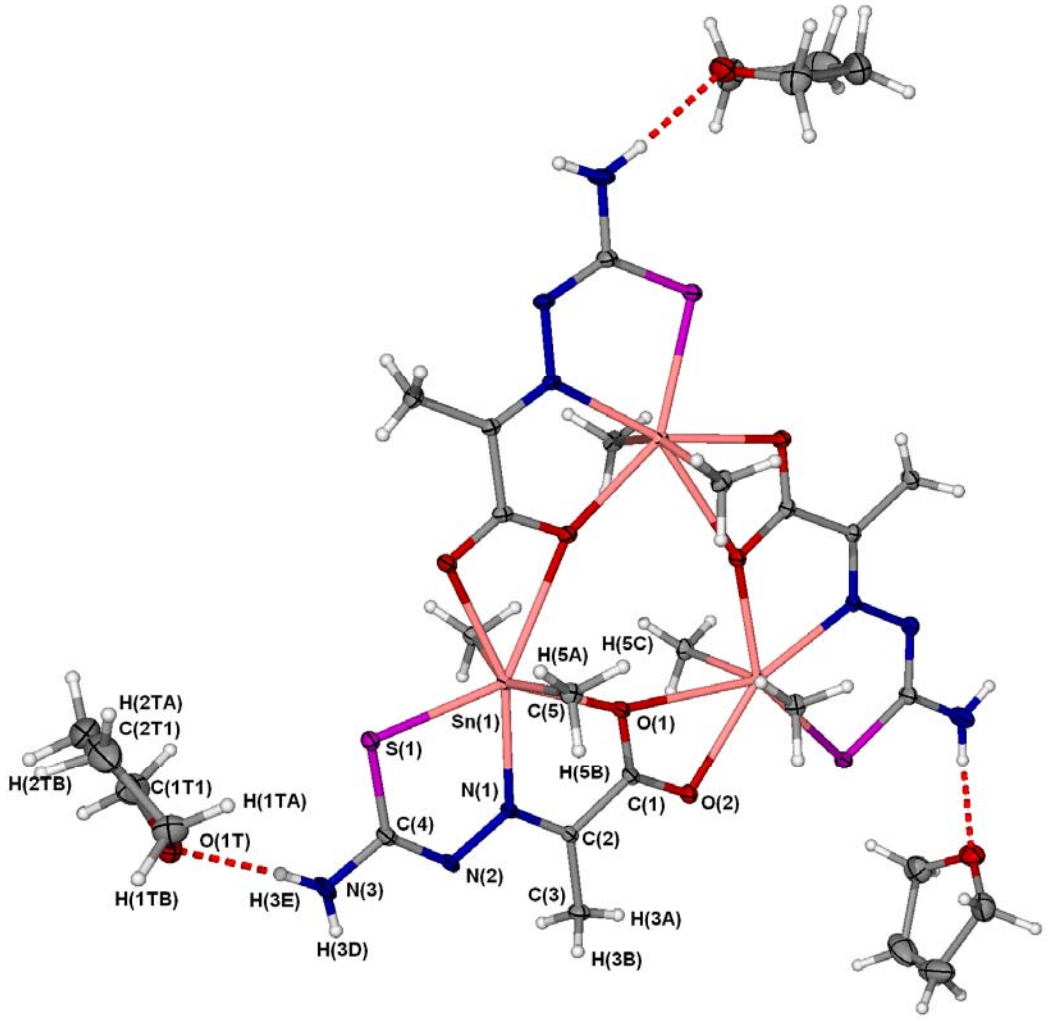
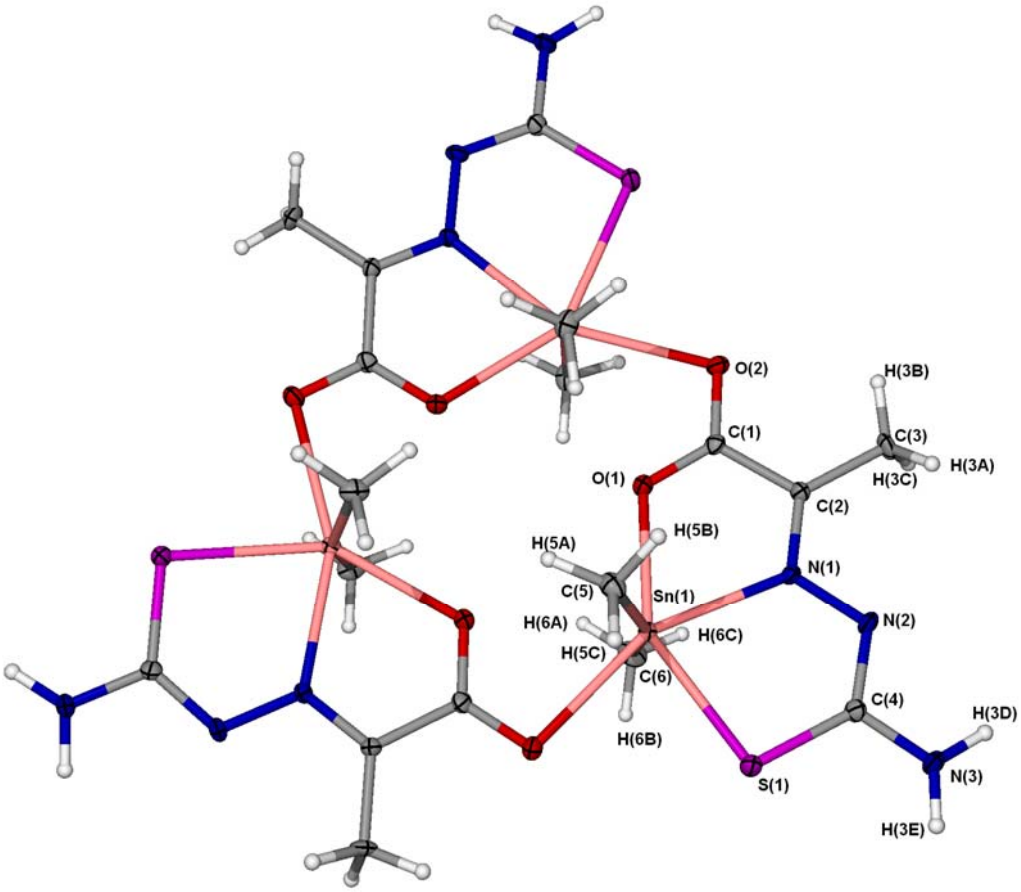
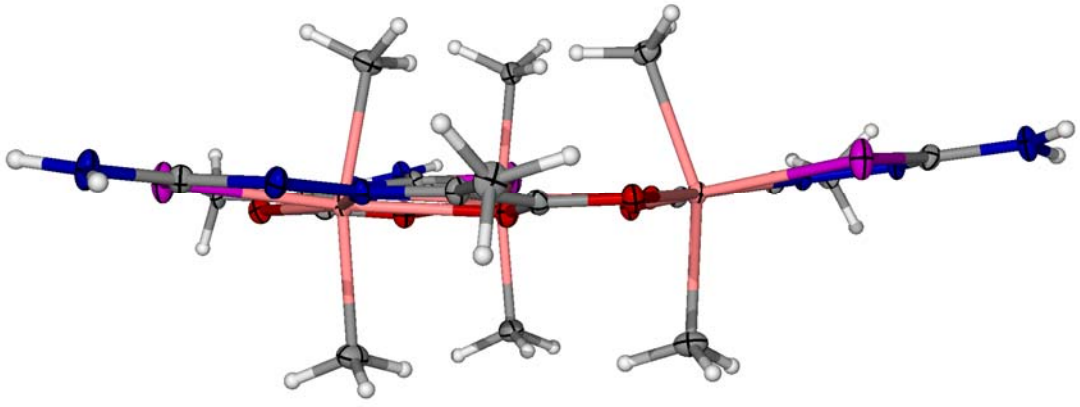


Fig. S1. A thermal ellipsoid plot (50%), including the complete labelling scheme, of the molecular structure of $[(CH_3)_2Sn(pt)]_3.3THF$ (**1**). The second atom set of the disordered THF solvate has been omitted for clarity.



a



b

Fig. S2. Two thermal ellipsoid plots (50%) of the trinuclear unit in $[(CH_3)_2Sn(pt)]_3.1.5THF$ (**2**); a) showing the labeling scheme, b) showing the curved arrangement.

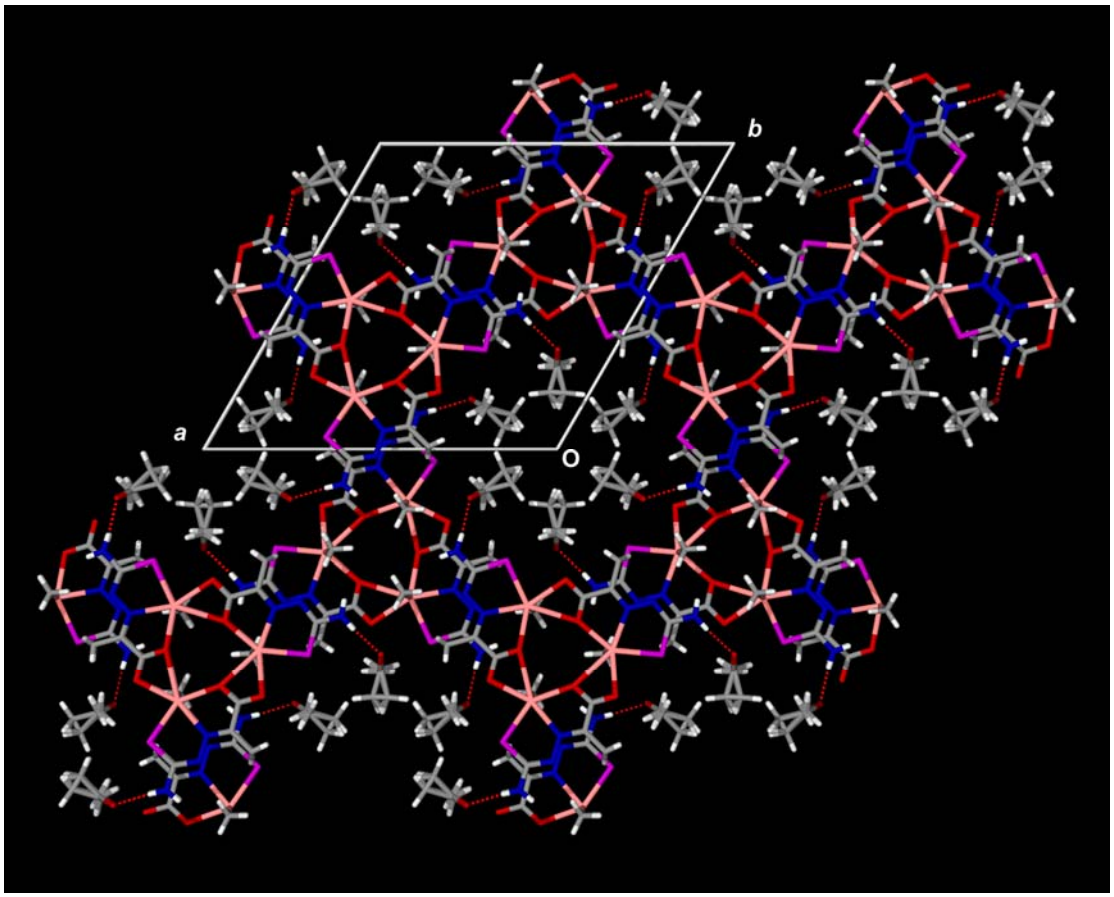


Fig. S3. A packing diagram of **1**, down to *c*, showing the lattice THF molecules that fill the hexagonal tubes of the structure.

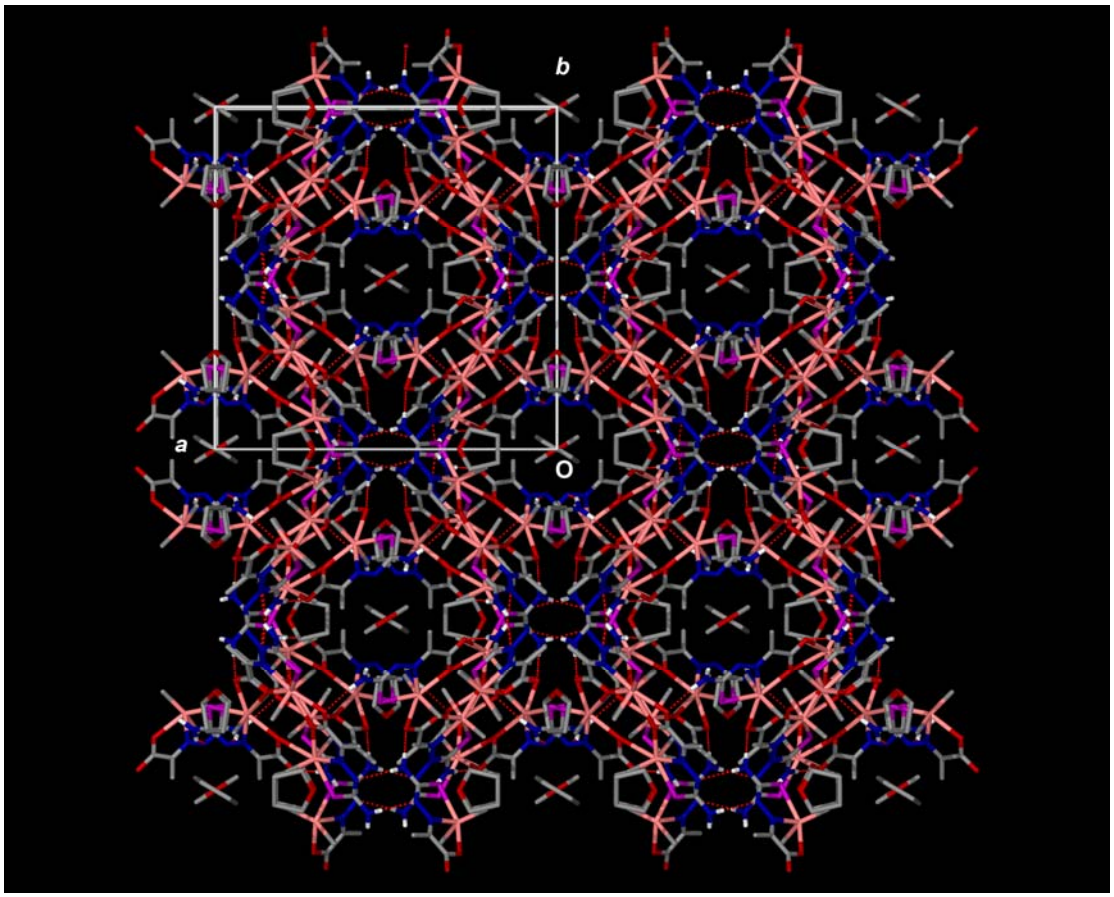


Fig. S4. A packing diagram of **2**, down to *c*, showing the lattice THF molecules that fill the truncated tetrahedral cavities of the structure.