Electronic Supplementary Information (ESI) for CrystEngComm

A unique 3-D (3,18)-connected coordination framework based on a new type of $\{Zn_{18}\}$ double-stranded metallacrown

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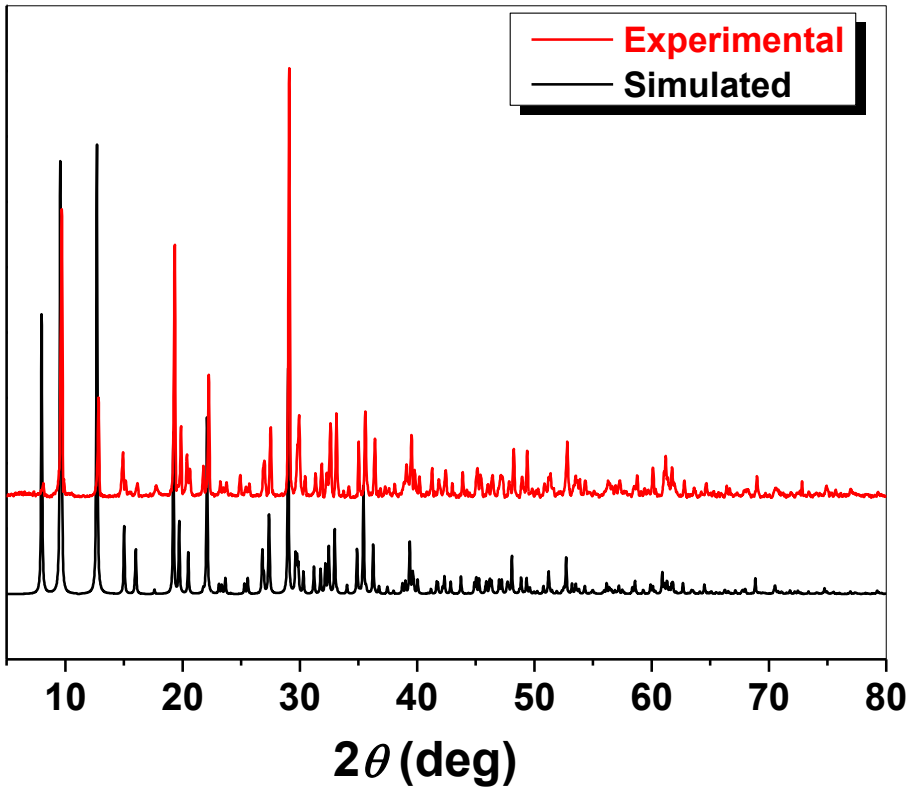
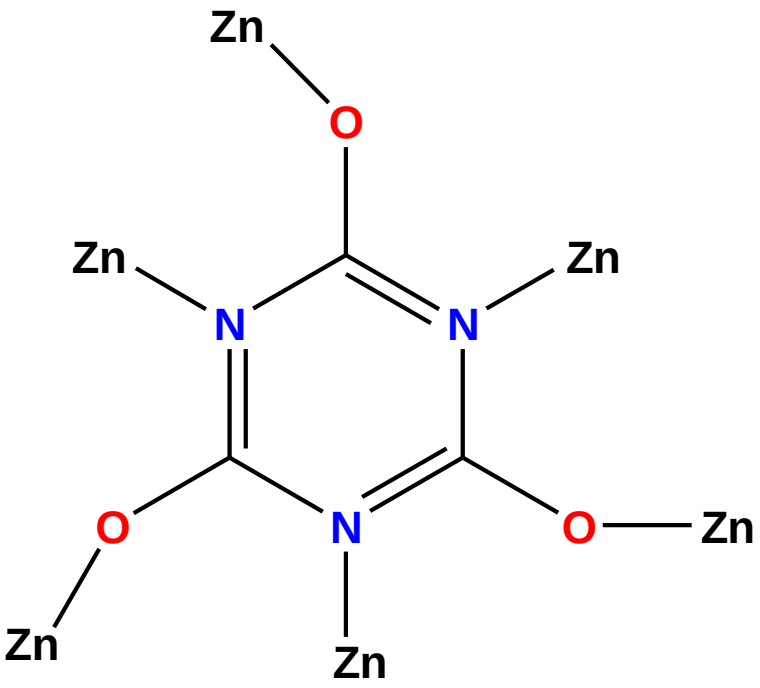


Fig. S1 Experimental and simulated X-ray powder diffraction (XRPD) patterns of **1**.



Scheme S1 Hexadentate coordination mode of **CA** ligand in **1**.

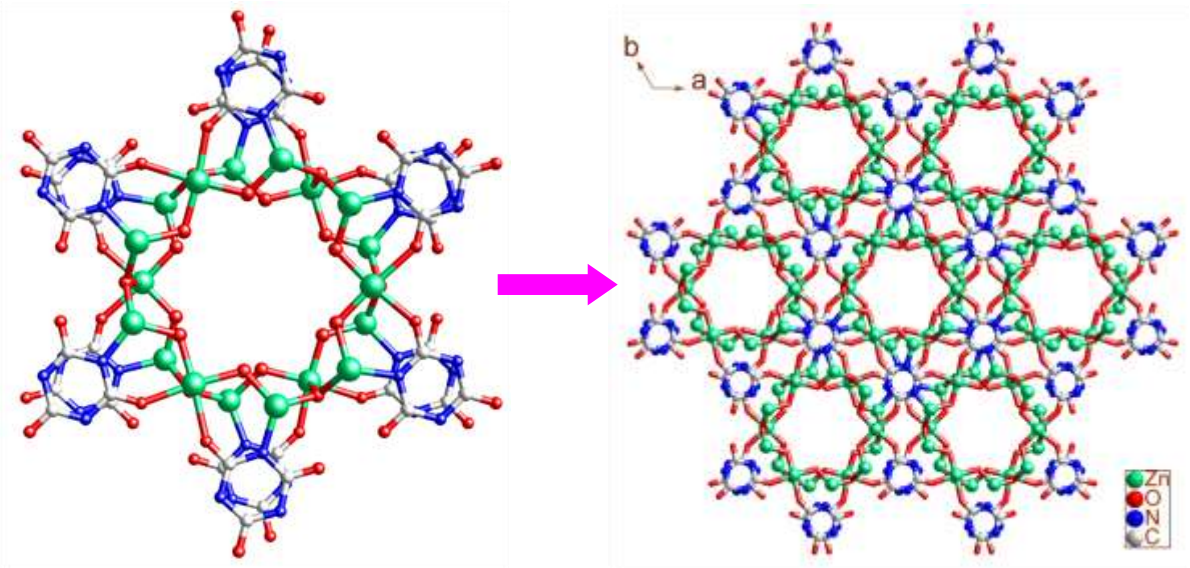


Fig. S2 View of (left) one $\{Zn_{18}\}$ cluster and (right) the 2-D motif extended by **CA** ligands.

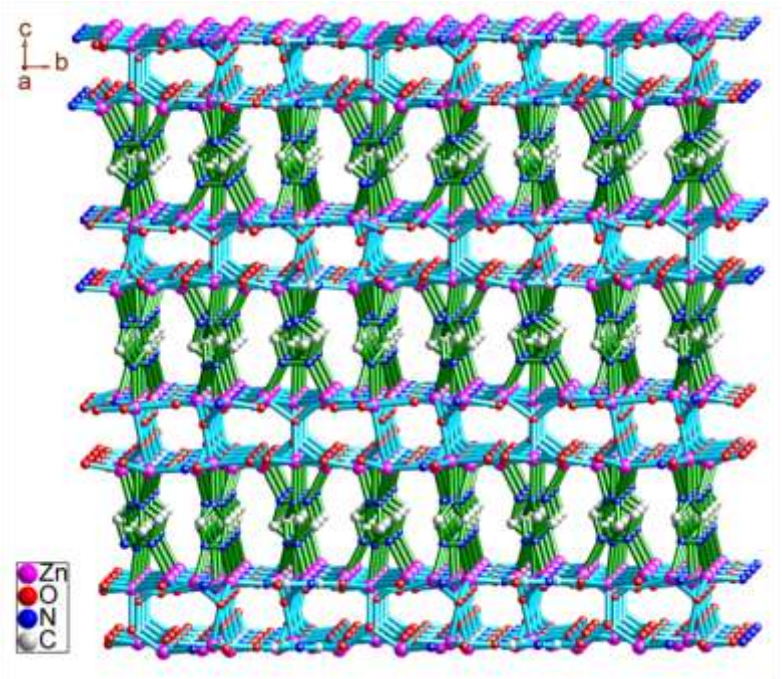


Fig. S3 Ball-and-stick representation of the 3-D pillared-layer framework of **1** with **tz** ligands (green part) as pillars, viewed along the [100] axis.

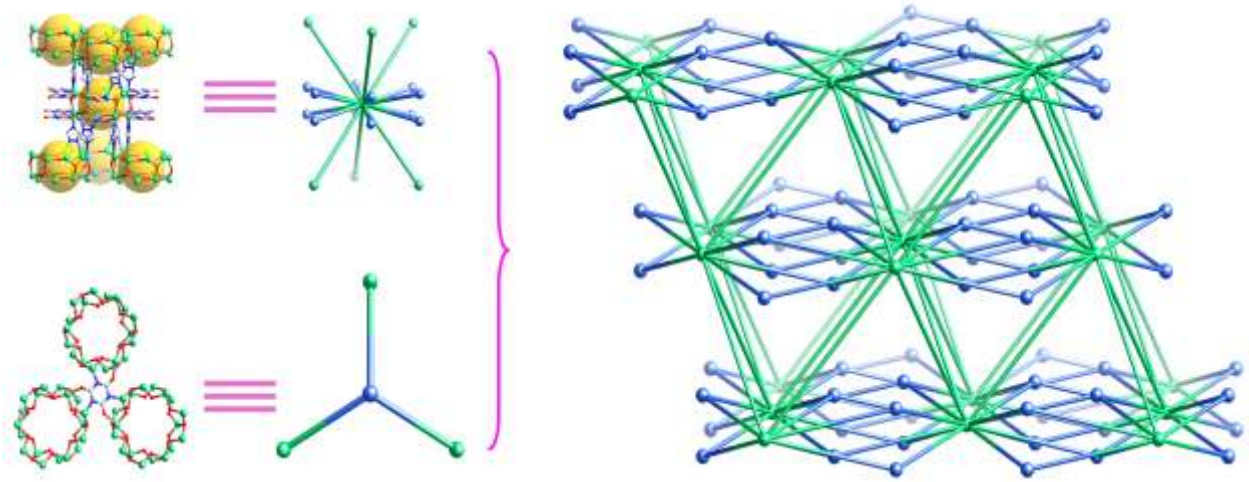


Fig. S4 Schematic view of the (3,18)-connected topological network of **1**.

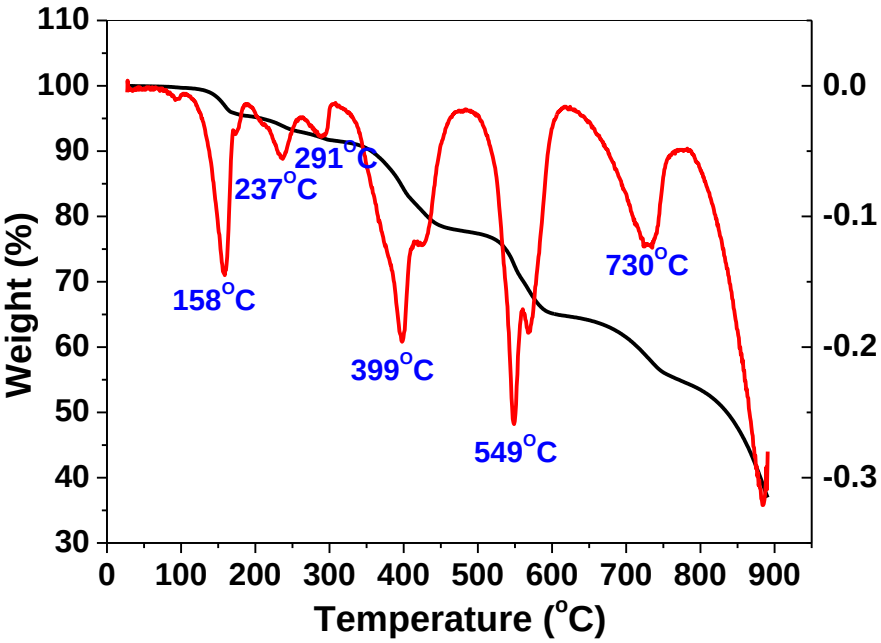
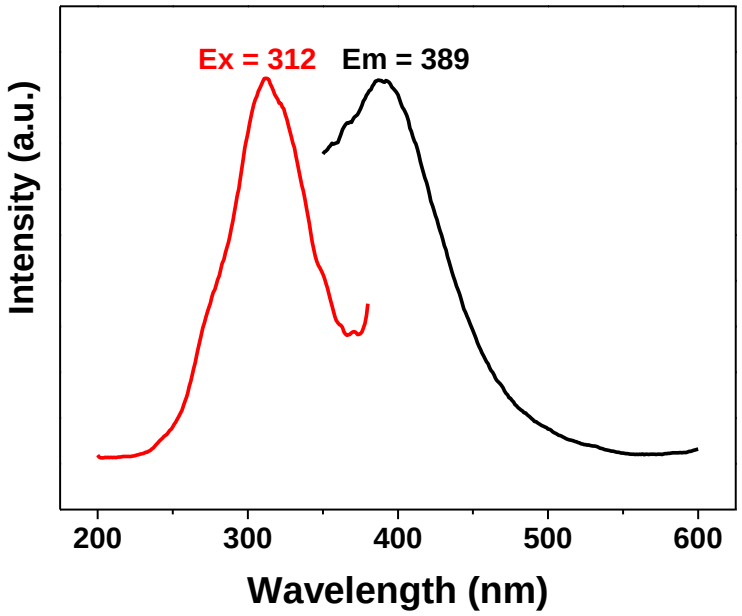
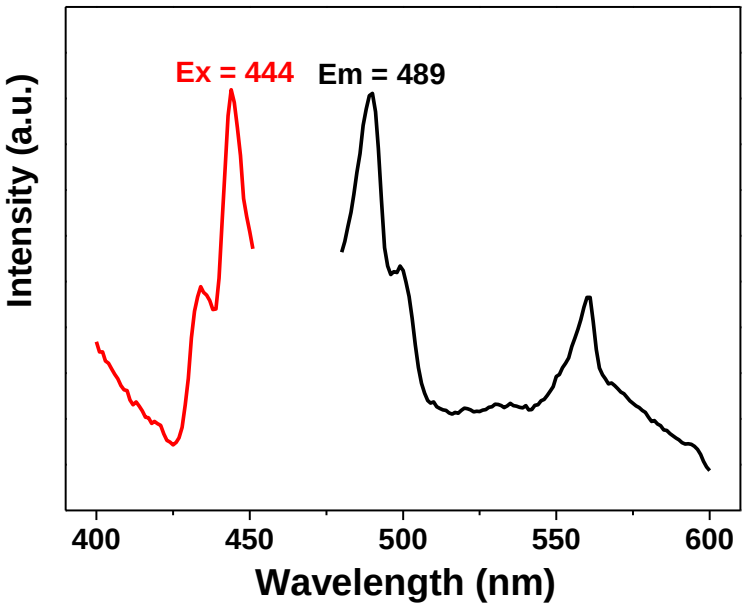


Fig. S5 Thermogravimetric analysis (TGA) curve of **1**.



(a)



(b)

Fig. S6 Solid-state excitation and emission spectra of (a) the free H_3**CA** ligand and (b) **1**.

Table S1 Crystallographic data and structure refinement parameters for **1**

	1
Empirical formula	$C_{12}H_{15}N_{15}O_{15}Zn_9$
Formula weight	1197.72
Crystal system	Trigonal
Space group	$P\bar{3}$
Unit cell dimensions (Å, °)	
a	13.9309(4)
b	13.9309(4)
c	27.6863(12)
α	90
β	90
γ	120
Volume (Å^3)	4653.2(3)
Z	6
D_{calcd} (g/cm^3)	2.564
μ (mm^{-1})	6.920
Crystal size (mm)	0.22 × 0.20 × 0.20
F (000)	3492
Range of *h*, *k*, *l*	–13/16, –16/10, –32/32
Reflections collected/unique	12471/5474
Data/restraints/parameters	5474/205/461
R(int)	0.0332
T(K)	293(2)
Goodness-of-fit on F^2	1.052
R_1[a] & wR_2[b] [$I > 2\sigma(I)$]	0.0557 & 0.1875
R_1[a] & wR_2[b] (all data)	0.0879 & 0.2221

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, where F_o = observed and F_c = calculated structure factors, respectively.

Table S2 Selected bond distances (Å) and bond angles (º) for **1**[a]

Zn(1)–O(10)$^{\#1}$	2.037(9)	Zn(5)–O(12)	1.935(10)
Zn(1)–O(11)$^{\#2}$	2.050(8)	Zn(5)–N(12)	1.950(9)
Zn(1)–O(7)	2.080(7)	Zn(5)–O(8)	2.029(7)
Zn(1)–N(1)	2.105(9)	Zn(5)–N(2)$^{\#3}$	2.050(10)
Zn(1)–O(1)	2.179(9)	Zn(6)–O(13)	1.920(9)
Zn(1)–O(2)	2.326(7)	Zn(6)–N(13)	1.960(10)
Zn(2)–O(10)	1.891(10)	Zn(6)–O(8)	1.997(7)
Zn(2)–N(11)$^{\#3}$	1.958(10)	Zn(6)–N(3)$^{\#3}$	2.033(9)
Zn(2)–N(5)	2.013(11)	Zn(7)–O(15)$^{\#6}$	2.011(9)
Zn(2)–O(7)	2.046(8)	Zn(7)–O(14)	2.042(9)
Zn(3)–O(11)	1.909(9)	Zn(7)–N(7)	2.103(9)
Zn(3)–N(10)$^{\#3}$	1.919(9)	Zn(7)–O(8)	2.128(7)
Zn(3)–O(7)	2.027(8)	Zn(7)–O(5)	2.203(8)
Zn(3)–N(6)	2.039(11)	Zn(7)–O(6)$^{\#7}$	2.296(9)
Zn(4)–O(13)$^{\#4}$	2.029(8)	Zn(8)–O(14)	1.949(9)
Zn(4)–O(12)	2.055(9)	Zn(8)–N(14)	1.977(11)
Zn(4)–N(4)	2.121(9)	Zn(8)–O(9)	1.994(8)
Zn(4)–O(9)	2.154(7)	Zn(8)–N(9)$^{\#8}$	2.014(11)
Zn(4)–O(4)$^{\#5}$	2.186(8)	Zn(9)–O(15)	1.932(8)
Zn(4)–O(3)	2.317(9)	Zn(9)–N(15)	1.971(11)
Zn(9)–O(9)	1.993(8)	Zn(9)–N(8)$^{\#8}$	2.054(10)
O(10)$^{\#1}$–Zn(1)–O(11)$^{\#2}$	91.8(4)	O(7)–Zn(1)–O(2)	84.3(3)
O(10)$^{\#1}$–Zn(1)–O(7)	95.0(4)	N(1)–Zn(1)–O(2)	85.5(4)
O(11)$^{\#2}$–Zn(1)–O(7)	97.8(3)	O(1)–Zn(1)–O(2)	82.6(3)
O(10)$^{\#1}$–Zn(1)–N(1)	92.2(4)	O(10)–Zn(2)–N(11)$^{\#3}$	117.5(4)
O(11)$^{\#2}$–Zn(1)–N(1)	91.8(4)	O(10)–Zn(2)–N(5)	109.1(4)
O(7)–Zn(1)–N(1)	167.8(4)	N(11)$^{\#3}$–Zn(2)–N(5)	111.3(4)
O(10)$^{\#1}$–Zn(1)–O(1)	175.1(4)	O(10)–Zn(2)–O(7)	107.1(4)
O(11)$^{\#2}$–Zn(1)–O(1)	93.1(3)	N(11)$^{\#3}$–Zn(2)–O(7)	111.0(4)
O(7)–Zn(1)–O(1)	85.0(3)	N(5)–Zn(2)–O(7)	99.3(4)
N(1)–Zn(1)–O(1)	87.0(4)	O(11)–Zn(3)–N(10)$^{\#3}$	112.9(4)
O(10)$^{\#1}$–Zn(1)–O(2)	92.5(4)	O(11)–Zn(3)–O(7)	105.7(3)

O(11)$^{\#2}$–Zn(1)–O(2)	175.0(3)	N(10)$^{\#3}$–Zn(3)–O(7)	118.4(4)
O(11)–Zn(3)–N(6)	106.9(4)	N(13)–Zn(6)–N(3)$^{\#3}$	113.5(4)
N(10)$^{\#3}$–Zn(3)–N(6)	112.7(4)	O(8)–Zn(6)–N(3)$^{\#3}$	98.2(3)
O(7)–Zn(3)–N(6)	98.8(4)	O(15)$^{\#6}$–Zn(7)–O(14)	91.5(3)
O(13)$^{\#4}$–Zn(4)–O(12)	91.5(4)	O(15)$^{\#6}$–Zn(7)–N(7)	96.6(4)
O(13)$^{\#4}$–Zn(4)–N(4)	98.1(4)	O(14)–Zn(7)–N(7)	97.4(4)
O(12)–Zn(4)–N(4)	92.0(4)	O(15)$^{\#6}$–Zn(7)–O(8)	92.7(3)
O(13)$^{\#4}$–Zn(4)–O(9)	95.8(4)	O(14)–Zn(7)–O(8)	95.4(3)
O(12)–Zn(4)–O(9)	92.6(3)	N(7)–Zn(7)–O(8)	163.9(4)
N(4)–Zn(4)–O(9)	165.2(4)	O(15)$^{\#6}$–Zn(7)–O(5)	174.3(3)
O(13)$^{\#4}$–Zn(4)–O(4)$^{\#5}$	94.0(4)	O(14)–Zn(7)–O(5)	93.4(4)
O(12)–Zn(4)–O(4)$^{\#5}$	173.9(4)	N(7)–Zn(7)–O(5)	85.6(4)
N(4)–Zn(4)–O(4)$^{\#5}$	90.0(4)	O(8)–Zn(7)–O(5)	83.9(3)
O(9)–Zn(4)–O(4)$^{\#5}$	84.1(3)	O(15)$^{\#6}$–Zn(7)–O(6)$^{\#7}$	92.6(3)
O(13)$^{\#4}$–Zn(4)–O(3)	176.3(3)	O(14)–Zn(7)–O(6)$^{\#7}$	175.6(4)
O(12)–Zn(4)–O(3)	92.2(3)	N(7)–Zn(7)–O(6)$^{\#7}$	83.9(4)
N(4)–Zn(4)–O(3)	81.7(4)	O(8)–Zn(7)–O(6)$^{\#7}$	82.6(4)
O(9)–Zn(4)–O(3)	84.1(3)	O(5)–Zn(7)–O(6)$^{\#7}$	82.4(3)
O(4)$^{\#5}$–Zn(4)–O(3)	82.3(3)	O(14)–Zn(8)–N(14)	112.2(4)
O(12)–Zn(5)–N(12)	117.9(4)	O(14)–Zn(8)–O(9)	104.4(3)
O(12)–Zn(5)–O(8)	105.8(3)	N(14)–Zn(8)–O(9)	118.5(4)
N(12)–Zn(5)–O(8)	110.2(4)	O(14)–Zn(8)–N(9)$^{\#8}$	110.3(4)
O(12)–Zn(5)–N(2)$^{\#3}$	110.6(4)	N(14)–Zn(8)–N(9)$^{\#8}$	113.1(4)
N(12)–Zn(5)–N(2)$^{\#3}$	112.4(4)	O(9)–Zn(8)–N(9)$^{\#8}$	97.3(4)
O(8)–Zn(5)–N(2)$^{\#3}$	97.9(3)	O(15)–Zn(9)–N(15)	116.0(4)
O(13)–Zn(6)–N(13)	111.3(4)	O(15)–Zn(9)–O(9)	106.3(3)
O(13)–Zn(6)–O(8)	105.0(4)	N(15)–Zn(9)–O(9)	110.3(4)
N(13)–Zn(6)–O(8)	118.3(4)	O(15)–Zn(9)–N(8)$^{\#8}$	111.5(4)
O(13)–Zn(6)–N(3)$^{\#3}$	109.4(4)	N(15)–Zn(9)–N(8)$^{\#8}$	112.5(4)
O(9)–Zn(9)–N(8)$^{\#8}$	98.6(4)		

[a] Symmetry codes for 1: #1 = $x – y + 1, x + 1, –z + 2$; #2 = $y – 1, – x + y, –z + 2$; #3 = $–x + 1, –y + 2, –z + 2$; #4 = $–x + y, –x + 2, z$; #5 = $–y + 1, x – y + 1, z$; #6 = $–y + 2, x – y + 2, z$; #7 = $–x + y, –x + 1, z$; #8 = $–x + 1, –y + 2, –z + 1$.