Supplementary material (ESI) for Journal of Materials Chemistry

Electronic Supplementary Information for

Enhanced H_2 adsorption enthalpy in the low-surface area, partially fluorinated coordination polymer $Zn_5(triazolate)_6(tetrafluoroterephthalate)_2(H_2O)_2 \bullet 4H_2O$

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Contents:

Synthesis methods	2
Structure determinations	2-3
Crystal data and refinement parameters	4-13
Thermogravimetric analysis	14
Variable temperature X-ray powder diffraction	15

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Synthesis methods

All reagents were used as received from Aldrich. Syntheses were carried out in Parr Teflon-lined stainless steel autoclaves under autogenous pressure. Compound **1** was typically synthesized using an aqueous mixture (3 mL) of $Zn(NO_3)_2 \bullet 6H_2O$ (0.4 mmol), 1,2,4-triazole (0.4 mmol), and tetrafluoroterephthalic acid (0.2 mmol) at 125 °C. The addition of KOH was necessary for product formation, occurring approximately between pH 4 and 7, with the optimum conditions for single crystal formation at around 4.5. Colorless block-shaped crystals were collected by filtration, washed with water and acetone, and dried in air. Elemental analysis (C, H, N) was carried out by the Marine Sciences Institute Analytical Laboratory at UCSB. Calcd (wt.%): C, 25.5; H, 1.83; N, 19.2. Found (wt%): C, 24.8; H, 1.83; N 20.8. The synthesis was attempted with other transition metals but was not successful, probably due to the inability of the other first-row transition metals to adopt the three different coordination modes that zinc displays in **1**.

Structure determinations

A suitable colorless block was selected under a polarizing microscope and glued to a glass fiber. Crystal structure determination by XRD was performed on a Siemens SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation, λ = 0.71073 Å) operating at 45 kV and 35 mA. A hemisphere of intensity data was collected at room temperature. Absorption corrections were made using SADABS[1]. The structure was solved by direct methods and difference Fourier

[1] Sheldrick, G. M. *SADABS User Guide*; University of Göttingen: Göttingen, 1995.

synthesis and were refined against $|F|^2$ using the SHELXTL software package.[2] The relevant details of structure determination are shown in Table 1. The extinction coefficient refined to within three esd's of zero and was therefore removed from the refinement. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically, with thermal parameters equal to 1.2 times those of the respective mother atoms. The hydrogen atoms on two of the three unique triazolate ligands and those on the coordinated water molecule (O11) were found in the Fourier difference map and restrained to chemically reasonable positions. Two riding hydrogen atoms were assigned to the third unique triazolate ligand. The hydrogen atoms on the two solvent water molecules could not be found in the Fourier map and were therefore not included in the refinement.

[2] Sheldrick, G. M. *SHELXTL-97, A program for crystal structure determination*, version 5.1; University of Göttingen: Göttingen, 1995.

Table 1. Crystal Data and Structure Refinement Parameters.

Empirical formula	$C_{28}H_{24}F_8N_{18}O_{14}Zn_5$
Formula weight	1315.50
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	*P*-1
a (Å)	10.137(5)
b (Å)	10.228(5)
c (Å)	12.747(7)
α (°)	74.562(8)
β (°)	83.796(9)
γ (°)	60.952(7)
Volume (Å^3)	1113.3(10)
Z	1
ρ_{calcd} (g cm^{-3})	1.950
Abs. coeff. (mm^{-1})	2.771
F_{000}	644
Crystal size (mm)	0.4 × 0.3 × 0.3
θ range	2.30-26.02°
Index ranges	$-11 \le h \le 12$, $-12 \le k \le 12$, $-15 \le l \le 15$
Reflections collected	9014
Independent reflections	4219 (R_{int} = 0.0593)
Completeness to θ = 26.02°	96.2%
Absorption correction	SADABS
Refinement method	Full-matrix least-squares on $\|F\|^2$
Data/restraints/parameters	4219 / 8 / 351
GOF on $\|F\|^2$	1.025
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0634, wR_2 = 0.1515
R indices (all data)	R_1 = 0.1102, wR_2 = 0.1822
Largest diff. peak and hole (e Å^{-3})	1.584 and -0.610

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn(1)	5000	5000	0	21(1)
Zn(2)	4921(1)	4046(1)	2851(1)	22(1)
Zn(3)	1549(1)	1138(1)	1538(1)	25(1)
C(1)	8383(8)	2257(8)	2528(6)	25(2)
C(2)	8324(8)	2914(9)	801(6)	26(2)
C(3)	3023(8)	2699(9)	2336(6)	26(2)
C(4)	3133(8)	3114(9)	646(6)	29(2)
C(5)	3235(8)	7623(8)	2434(6)	25(2)
C(6)	3303(8)	8226(8)	730(5)	27(2)
C(7)	4846(8)	2818(9)	5079(6)	28(2)
C(8)	3940(8)	2609(9)	6072(6)	25(2)
C(9)	3027(9)	3844(9)	6545(6)	28(2)
C(10)	3925(8)	1242(9)	6555(6)	30(2)
C(11)	2160(10)	3697(9)	7448(6)	34(2)
C(12)	3055(10)	1119(9)	7445(6)	36(2)
C(13)	2148(9)	2339(9)	7881(6)	28(2)
C(14)	1152(9)	2205(8)	8806(5)	26(2)
F(1)	3016(6)	5201(6)	6119(4)	51(1)
F(2)	4706(6)	35(6)	6104(4)	56(2)
F(3)	1296(7)	4918(6)	7863(4)	58(2)
F(4)	3061(7)	-259(6)	7863(4)	62(2)
N(1)	6945(6)	3160(7)	2211(4)	21(1)
N(2)	6902(6)	3571(7)	1094(5)	23(1)
N(3)	9302(6)	2088(7)	1660(5)	24(1)
N(4)	3782(7)	3449(7)	2043(5)	28(2)
N(5)	3839(7)	3735(7)	918(5)	29(2)
N(6)	2589(7)	2412(7)	1490(5)	23(1)
N(7)	4001(6)	6318(7)	2135(5)	25(1)
N(8)	4049(7)	6712(7)	1013(5)	28(2)

N(9)	2769(7)	8877(7)	1589(5)	26(1)
O(1)	4055(6)	3880(6)	4275(4)	36(1)
O(2)	6198(6)	1940(7)	5077(4)	44(2)
O(3)	-238(7)	2698(9)	8522(5)	64(2)
O(4)	1643(6)	1669(6)	9769(4)	28(1)
O(11)	1631(6)	581(7)	3437(4)	38(1)
O(12)	877(8)	5914(9)	3702(6)	70(2)
O(13)	672(10)	2995(10)	4471(7)	91(3)

Table 3. Bond lengths [Å] and angles [°] for **1**.

Zn(1)-N(2)#1	2.135(6)
Zn(1)-N(2)	2.135(6)
Zn(1)-N(5)	2.191(6)
Zn(1)-N(5)#1	2.191(6)
Zn(1)-N(8)	2.226(6)
Zn(1)-N(8)#1	2.226(6)
Zn(2)-O(1)	1.932(5)
Zn(2)-N(1)	1.981(6)
Zn(2)-N(4)	2.010(6)
Zn(2)-N(7)	2.014(6)
Zn(3)-N(3)#2	2.003(6)
Zn(3)-N(9)#3	2.010(6)
Zn(3)-N(6)	2.022(6)
Zn(3)-O(4)#4	2.178(5)
Zn(3)-O(11)	2.335(6)
C(1)-N(1)	1.328(9)
C(1)-N(3)	1.357(9)
C(2)-N(2)	1.322(8)
C(2)-N(3)	1.351(9)
C(3)-N(4)	1.296(9)
C(3)-N(6)	1.355(9)
C(4)-N(5)	1.284(9)
C(4)-N(6)	1.351(9)
C(5)-N(7)	1.315(9)
C(5)-N(9)	1.347(9)
C(6)-N(8)	1.313(9)
C(6)-N(9)	1.359(9)
C(7)-O(2)	1.220(9)
C(7)-O(1)	1.269(9)
C(7)-C(8)	1.511(10)
C(8)-C(10)	1.377(10)
C(8)-C(9)	1.401(10)
C(9)-F(1)	1.344(9)

C(9)-C(11)	1.392(10)
C(10)-F(2)	1.346(8)
C(10)-C(12)	1.376(10)
C(11)-F(3)	1.340(9)
C(11)-C(13)	1.358(10)
C(12)-C(13)	1.363(11)
C(12)-F(4)	1.365(9)
C(13)-C(14)	1.489(10)
C(14)-O(4)	1.250(8)
C(14)-O(3)	1.302(10)
N(1)-N(2)	1.372(8)
N(3)-Zn(3)#5	2.003(6)
N(4)-N(5)	1.386(8)
N(7)-N(8)	1.381(8)
N(9)-Zn(3)#6	2.010(6)
O(4)-Zn(3)#7	2.178(5)
N(2)#1-Zn(1)-N(2)	180.0
N(2)#1-Zn(1)-N(5)	90.1(2)
N(2)-Zn(1)-N(5)	89.9(2)
N(2)#1-Zn(1)-N(5)#1	89.9(2)
N(2)-Zn(1)-N(5)#1	90.1(2)
N(5)-Zn(1)-N(5)#1	180.0
N(2)#1-Zn(1)-N(8)	89.7(2)
N(2)-Zn(1)-N(8)	90.3(2)
N(5)-Zn(1)-N(8)	92.4(2)
N(5)#1-Zn(1)-N(8)	87.6(2)
N(2)#1-Zn(1)-N(8)#1	90.3(2)
N(2)-Zn(1)-N(8)#1	89.7(2)
N(5)-Zn(1)-N(8)#1	87.6(2)
N(5)#1-Zn(1)-N(8)#1	92.4(2)
N(8)-Zn(1)-N(8)#1	180.0
O(1)-Zn(2)-N(1)	137.8(2)
O(1)-Zn(2)-N(4)	101.5(2)
N(1)-Zn(2)-N(4)	101.9(2)
O(1)-Zn(2)-N(7)	106.1(2)

N(1)-Zn(2)-N(7)	103.8(2)
N(4)-Zn(2)-N(7)	99.9(2)
N(3)#2-Zn(3)-N(9)#3	119.6(3)
N(3)#2-Zn(3)-N(6)	119.9(2)
N(9)#3-Zn(3)-N(6)	120.4(3)
N(3)#2-Zn(3)-O(4)#4	97.9(2)
N(9)#3-Zn(3)-O(4)#4	89.6(2)
N(6)-Zn(3)-O(4)#4	86.9(2)
N(3)#2-Zn(3)-O(11)	86.2(2)
N(9)#3-Zn(3)-O(11)	90.4(2)
N(6)-Zn(3)-O(11)	89.0(2)
O(4)#4-Zn(3)-O(11)	175.3(2)
N(1)-C(1)-N(3)	111.2(6)
N(2)-C(2)-N(3)	112.8(6)
N(4)-C(3)-N(6)	113.5(6)
N(5)-C(4)-N(6)	114.5(7)
N(7)-C(5)-N(9)	113.2(6)
N(8)-C(6)-N(9)	113.6(6)
O(2)-C(7)-O(1)	125.8(7)
O(2)-C(7)-C(8)	120.1(7)
O(1)-C(7)-C(8)	113.9(6)
C(10)-C(8)-C(9)	115.8(7)
C(10)-C(8)-C(7)	123.5(7)
C(9)-C(8)-C(7)	120.7(7)
F(1)-C(9)-C(11)	119.4(7)
F(1)-C(9)-C(8)	118.5(6)
C(11)-C(9)-C(8)	122.1(7)
F(2)-C(10)-C(12)	119.7(7)
F(2)-C(10)-C(8)	118.9(7)
C(12)-C(10)-C(8)	121.3(7)
F(3)-C(11)-C(13)	120.2(7)
F(3)-C(11)-C(9)	119.7(7)
C(13)-C(11)-C(9)	120.1(7)
C(13)-C(12)-F(4)	119.6(7)
C(13)-C(12)-C(10)	122.2(7)

F(4)-C(12)-C(10)	118.2(7)
C(11)-C(13)-C(12)	118.4(7)
C(11)-C(13)-C(14)	120.2(7)
C(12)-C(13)-C(14)	121.4(7)
O(4)-C(14)-O(3)	124.2(7)
O(4)-C(14)-C(13)	121.3(7)
O(3)-C(14)-C(13)	114.5(6)
C(1)-N(1)-N(2)	107.3(5)
C(1)-N(1)-Zn(2)	139.6(5)
N(2)-N(1)-Zn(2)	113.2(4)
C(2)-N(2)-N(1)	105.6(5)
C(2)-N(2)-Zn(1)	125.1(5)
N(1)-N(2)-Zn(1)	129.3(4)
C(2)-N(3)-C(1)	103.2(6)
C(2)-N(3)-Zn(3)#5	123.9(5)
C(1)-N(3)-Zn(3)#5	132.5(5)
C(3)-N(4)-N(5)	105.9(6)
C(3)-N(4)-Zn(2)	134.3(5)
N(5)-N(4)-Zn(2)	119.6(5)
C(4)-N(5)-N(4)	105.5(6)
C(4)-N(5)-Zn(1)	133.7(5)
N(4)-N(5)-Zn(1)	120.8(5)
C(4)-N(6)-C(3)	100.7(6)
C(4)-N(6)-Zn(3)	130.9(5)
C(3)-N(6)-Zn(3)	128.3(5)
C(5)-N(7)-N(8)	106.3(6)
C(5)-N(7)-Zn(2)	137.3(5)
N(8)-N(7)-Zn(2)	116.1(4)
C(6)-N(8)-N(7)	105.3(6)
C(6)-N(8)-Zn(1)	130.6(5)
N(7)-N(8)-Zn(1)	123.7(4)
C(5)-N(9)-C(6)	101.6(6)
C(5)-N(9)-Zn(3)#6	131.2(5)
C(6)-N(9)-Zn(3)#6	127.2(5)
C(7)-O(1)-Zn(2)	120.0(5)

C(14)-O(4)-Zn(3)#7 157.4(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z; #2 x-1,y,z; #3 x,y-1,z; #4 x,y,z-1; #5 x+1,y,z; #6 x,y+1,z; #7 x,y,z+1

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn(1)	21(1)	21(1)	19(1)	-4(1)	2(1)	-9(1)
Zn(2)	22(1)	21(1)	20(1)	-5(1)	4(1)	-9(1)
Zn(3)	20(1)	20(1)	33(1)	-8(1)	4(1)	-9(1)
C(1)	24(4)	23(4)	26(4)	-9(3)	8(3)	-9(3)
C(2)	14(4)	32(4)	23(4)	-7(3)	2(3)	-5(3)
C(3)	29(4)	37(5)	19(4)	-7(3)	4(3)	-22(4)
C(4)	36(5)	36(5)	24(4)	-9(3)	5(3)	-25(4)
C(5)	31(4)	24(4)	19(4)	-9(3)	1(3)	-12(3)
C(6)	35(4)	20(4)	15(4)	-4(3)	1(3)	-4(3)
C(7)	24(4)	32(4)	30(4)	-12(4)	6(3)	-13(4)
C(8)	27(4)	29(4)	21(4)	-6(3)	3(3)	-15(3)
C(9)	36(4)	31(4)	25(4)	-5(3)	5(3)	-24(4)
C(10)	30(4)	22(4)	32(4)	-13(3)	10(3)	-6(3)
C(11)	51(5)	28(4)	32(4)	-18(4)	18(4)	-24(4)
C(12)	53(5)	30(5)	20(4)	0(3)	8(4)	-21(4)
C(13)	31(4)	36(5)	22(4)	-7(3)	9(3)	-21(4)
C(14)	47(5)	16(4)	14(4)	0(3)	-8(3)	-14(3)
F(1)	83(4)	45(3)	46(3)	-21(2)	29(3)	-46(3)
F(2)	73(4)	31(3)	53(3)	-17(2)	29(3)	-18(3)
F(3)	90(4)	41(3)	51(3)	-29(3)	40(3)	-37(3)
F(4)	95(4)	31(3)	56(3)	-14(3)	37(3)	-33(3)
N(1)	19(3)	22(3)	19(3)	-7(2)	5(2)	-7(3)
N(2)	18(3)	30(3)	23(3)	-8(3)	4(2)	-12(3)
N(3)	21(3)	27(3)	22(3)	-6(3)	2(3)	-11(3)
N(4)	34(4)	33(4)	22(3)	-11(3)	8(3)	-19(3)
N(5)	30(4)	36(4)	24(3)	-7(3)	5(3)	-19(3)
N(6)	29(3)	24(3)	25(3)	-7(3)	7(3)	-20(3)
N(7)	26(3)	21(3)	21(3)	-8(3)	0(3)	-6(3)
N(8)	39(4)	22(3)	22(3)	-6(3)	5(3)	-15(3)
N(9)	25(3)	22(3)	26(3)	-8(3)	4(3)	-8(3)

O(1)	25(3)	46(4)	22(3)	-1(3)	9(2)	-10(3)
O(2)	32(3)	46(4)	32(3)	2(3)	8(3)	-9(3)
O(3)	46(4)	112(6)	31(3)	-11(4)	10(3)	-41(4)
O(4)	29(3)	32(3)	24(3)	-10(2)	10(2)	-14(2)
O(11)	36(4)	39(4)	29(3)	-8(3)	1(3)	-11(3)
O(12)	47(4)	97(6)	51(4)	-8(4)	6(3)	-28(4)
O(13)	110(7)	83(6)	77(6)	-39(5)	33(5)	-41(5)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **1**.

	x	y	z	U(eq)
H(1)	8680(70)	1820(80)	3260(20)	26(8)
H(2)	8710(70)	2920(80)	100(30)	26(8)
H(3)	2810(80)	2460(80)	3050(20)	26(8)
H(4)	3007	3145	-74	26(8)
H(5)	3090(80)	7720(80)	3150(30)	26(8)
H(6)	3155	8798	10	26(8)
H(11A)	1020(80)	1270(50)	3720(20)	50(20)
H(11B)	2080(80)	-160(50)	3940(40)	50(20)

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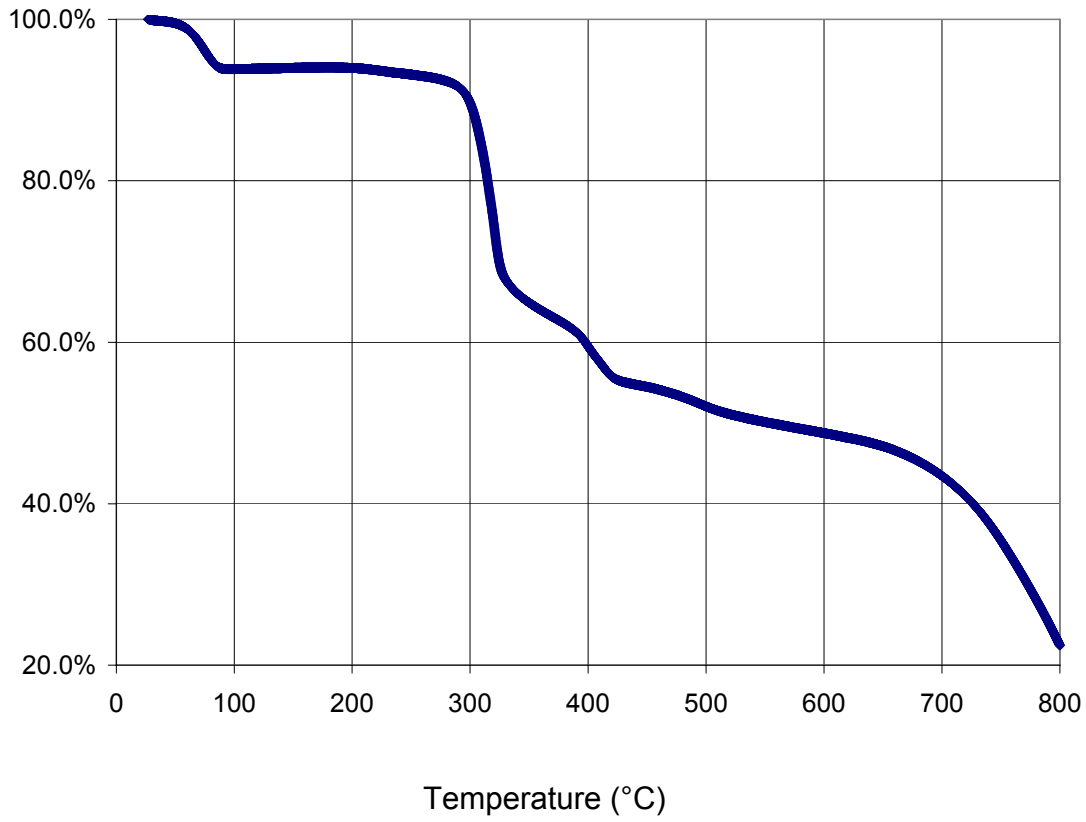
Thermal stability of 1

TGA of **1**



Thermogravimetric analysis was carried out at a heating rate of 2 °C min^{-1} from room temperature to 800 °C on a Mettler 851eTG/sDTA coupled to a Blazers ThermoStar 300 AMU mass spectrometer. The first mass loss between 50 and 90 °C corresponds to the loss of the two solvent water molecules (calculated 5.5%, found 6.0%). It appears that the coordinated water is also removed slowly between 220 and 290 °C (weight loss to 290 °C = 8.4%, calculated for solvent and coordinated water = 8.2%). After the removal of the coordinated water the structure gradually decomposes.

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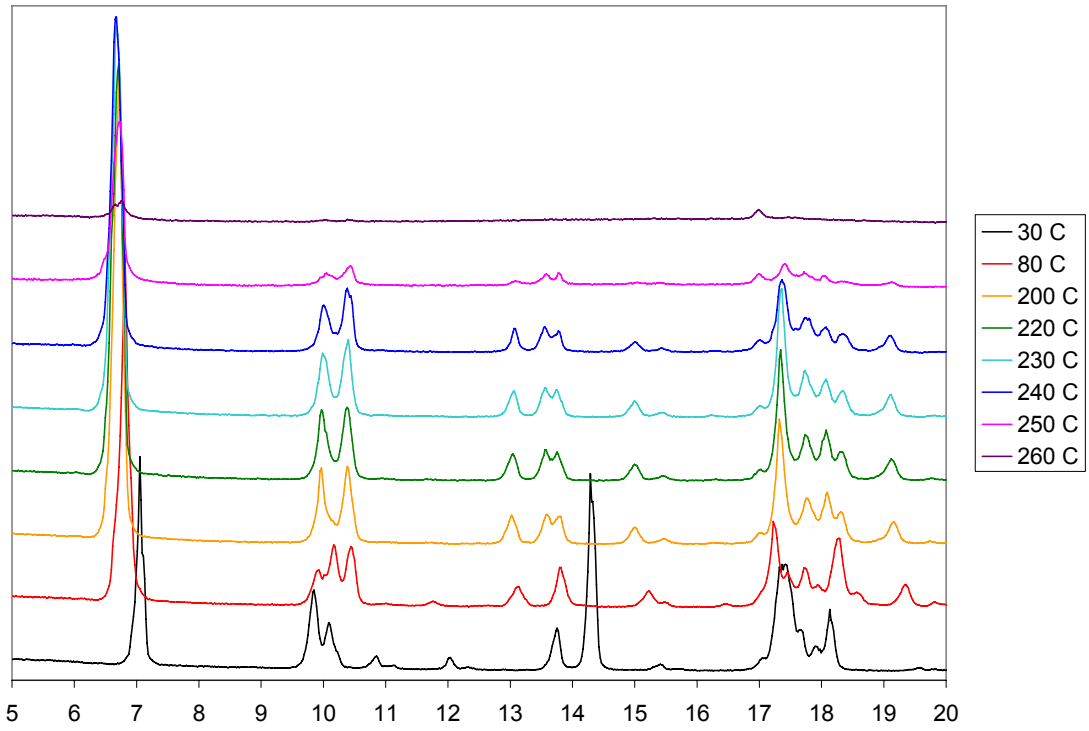
Variable temperature X-ray powder diffraction patterns for **1**



X-ray thermodiffractometry (Cu Kα radiation, λ = 1.5418 Å) was performed under static air on a Bruker D8 Advance diffractometer outfitted with a Bruker Lynxeye Position Sensitive Detector and an Anton Paar HTK 16 high-temperature stage. Patterns were scanned at every 20 °C from room temperature to 220 °C, and then every 10 °C to 320 °C. In correlation with the TGA data, **1** shows a slight structure change with the first dehydration step between 50 and 90 °C to give the 200 °C (orange) pattern. Patterns measured between 100 and 200 °C are not shown because they are identical. The 80 °C pattern seems to show an intermediate structure during the removal of the two solvent water molecules. Crystallinity starts to degrade with the 240 °C pattern (dark blue) and is gone by the 260 °C pattern (purple), indicating that as the coordinated water molecule is removed the structure collapses.