Peptide Bond Hydrolysis Catalyzed by the Wells-Dawson $Zr(\alpha_2\text{-}P_2W_{17}O_{61})_2$ Polyoxometalate

Gregory Absillis and Tatjana N. Parac-Vogt*

Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

Supporting Information

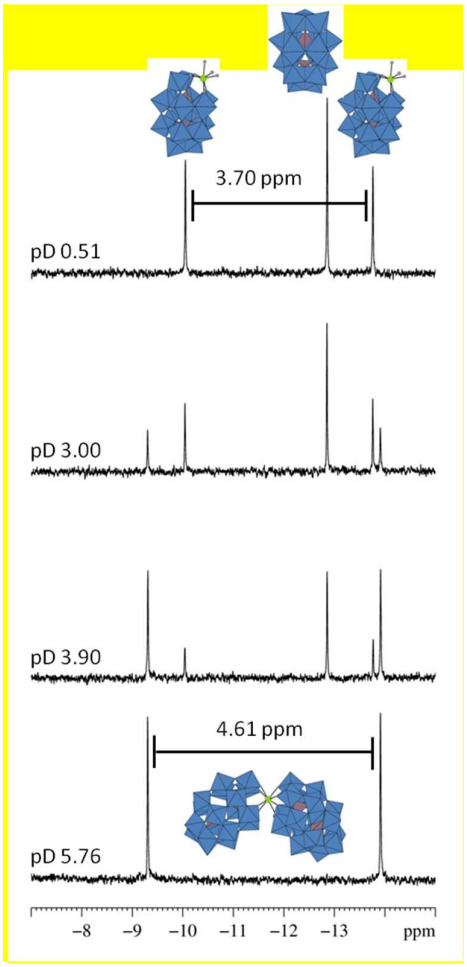

Figure S1. pD dependence of the ^{31}P NMR spectrum of 2.0 mM of **1**. The spectra were recorded immediately after mixing and pD adjustment. (242.94 MHz, D_2O, 293 K, n 128, d1 60 s, 25% H_3PO_4). The peaks at -9.34 ppm and -13.95 ppm (Δ = 4.61 ppm) are characteristic for the 1:2 species.[1] The 1:1 monomer can be found at -10.04 ppm and -13.76 ppm (Δ = 3.70 ppm).[2]

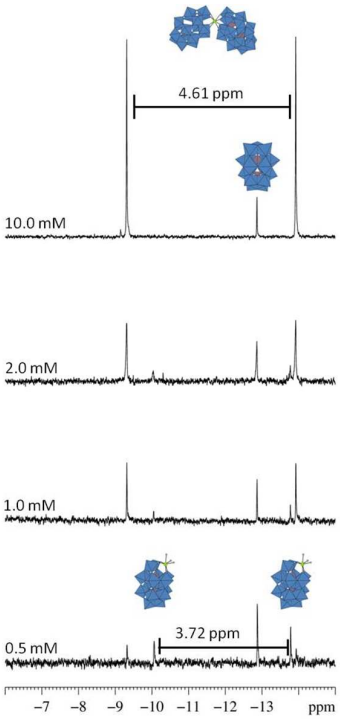

Figure S2. Concentration dependence of the ^{31}P NMR spectrum of **1** at pD 5.0. The spectra were recorded immediately after mixing. (242.94 MHz, D_2O, 293 K, n = 128, d1 = 60 s, 25% H_3PO_4) The peaks at -9.34 ppm and -13.95 ppm (Δ = 4.61 ppm) are characteristic for the 1:2 species.[1] The 1:1 monomer can be found at -10.04 ppm and -13.76 ppm (Δ = 3.70 ppm).[2]

Table S1: Concentration dependence of the species distribution of **1** at pD 5.0.

Concentration (mM)	% 1:2	% 1:1
10.0	100	0
2.0	80.92	19.08
1.0	73.18	26.82
0.5	16.88	83.12

Table S2. Time dependence of the species distribution of 2.0 mM and 10.0 mM of **1** at pD 5.0 and 60 °C.

Time	2.0 mM **1**		10.0 mM **1**	
	2:2[a]	1:2	2:2	1:2
1 day	39.54	60.46	16.77	83.23
2 days	48.26	51.74	21.65	78.35
1 week	46.79	53.21	22.52	77.48

a) The 2:2 dimer can be found at -9.87 and -12.82 ppm.[3]

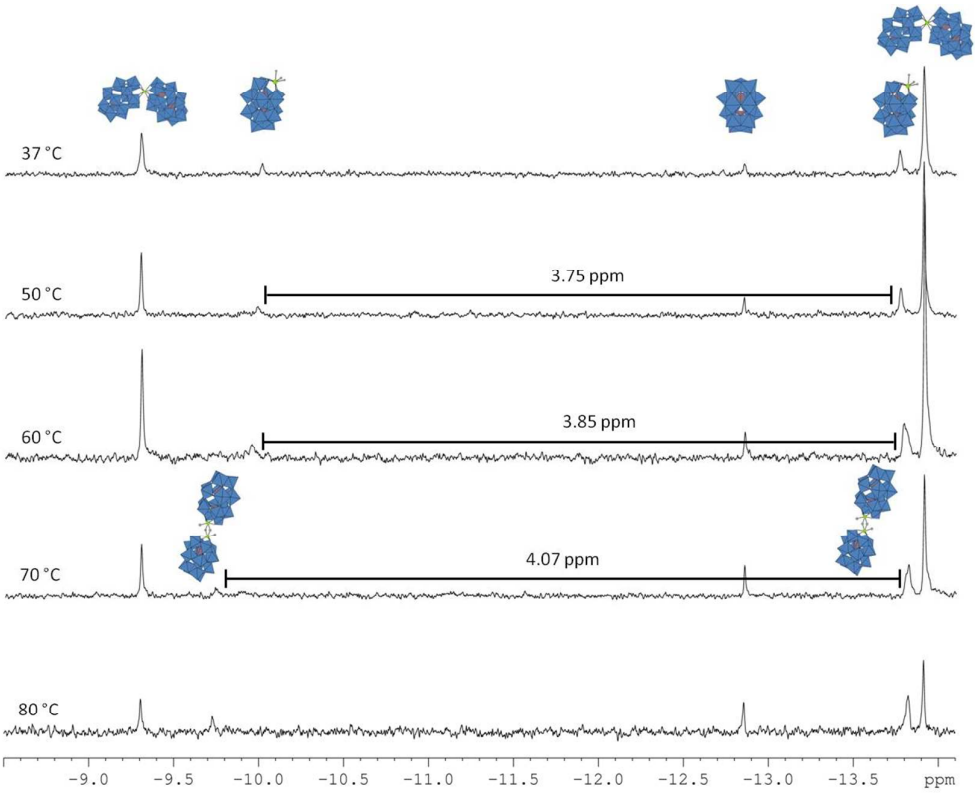

Figure S3: Temperature dependence of the ^{31}P NMR spectrum of 2.0 mM of **1** after 1 h at X °C and pD 5.0. (242.94 MHz, D_2O, 293 K, n = 512, d1 = 2 s, 25% H_3PO_4)

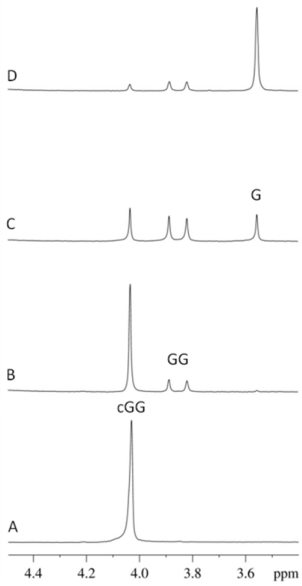

Figure S4. ^{1}H NMR spectra recorded at various reaction times during the hydrolysis of 2.0 mM of cGG in the presence of 2.0 mM of **1** at pD 5.0 and 60 °C. (400 MHz, D_2O, 293 K, n = 16, 0.5 mM TMSPA-d_4) (A) after mixing (B) after 1910 min (C) 10160 min (D) after 30455 min.

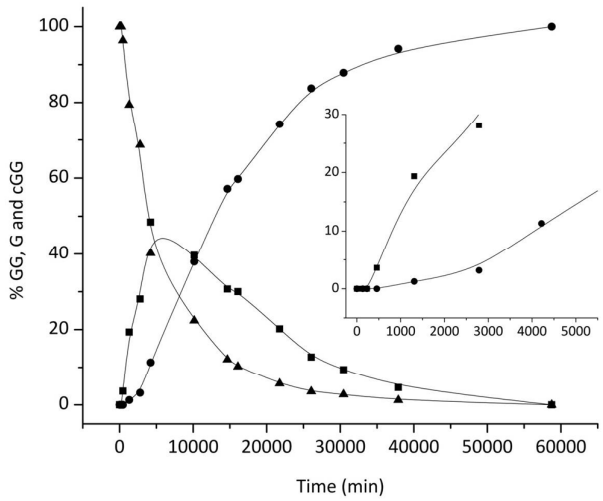

Figure S5. Hydrolysis of 2.0 mM of cGG in the presence of 2.0 mM of **1** at pD 5.0 and 60 °C. Percentage of GG (-■-), G (-●-), and cGG (-▲-) as a function of reaction time.

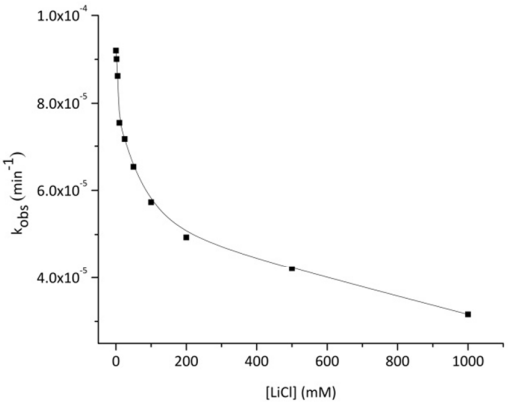

Figure S6. Effect of salt concentration on the rate constant for the hydrolysis of 2.0 mM of GG in the presence of 2.0 mM of **1** at pD 5.0 and 60 °C.

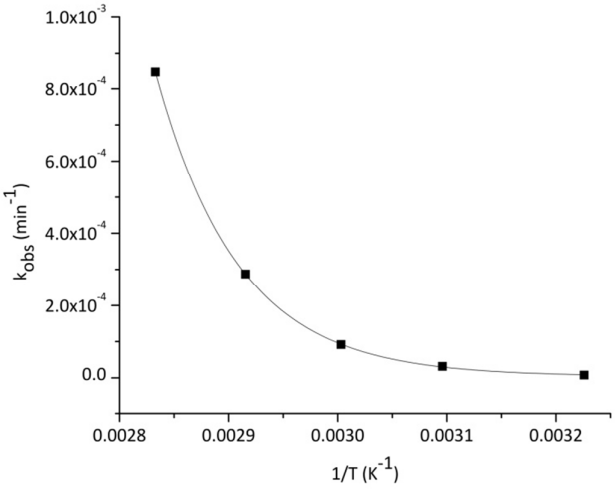

Figure S7. The reaction rate constant for the hydrolysis of GG as a function of the reciprocal temperature. (2.0 mM of GG - 2.0 mM of **1** at pD 5.0).

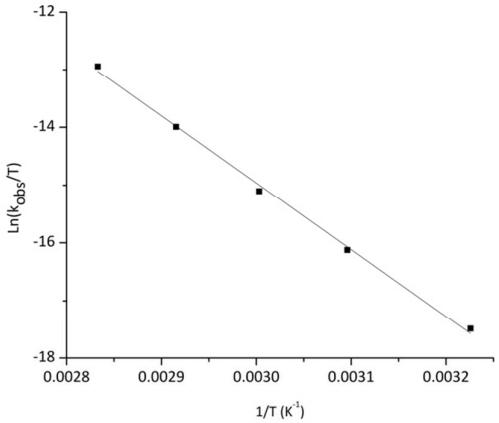

Figure S8. $\ln(k_{obs}/T)$ as a function of the reciprocal temperature (2.0 mM GG - 2.0 mM **1** at pD 5.0).

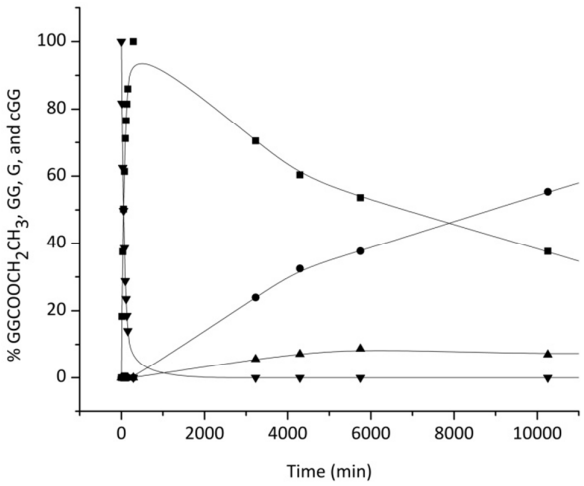

Figure S9. Hydrolysis of 2.0 mM of GGOEt in the presence of 2.0 mM of **1** at pD 5.0 and 60 °C. Percentage of GGOEt (-▼-), GG (-■-), G (-●-), and cGG (-▲-) as a function of reaction time.

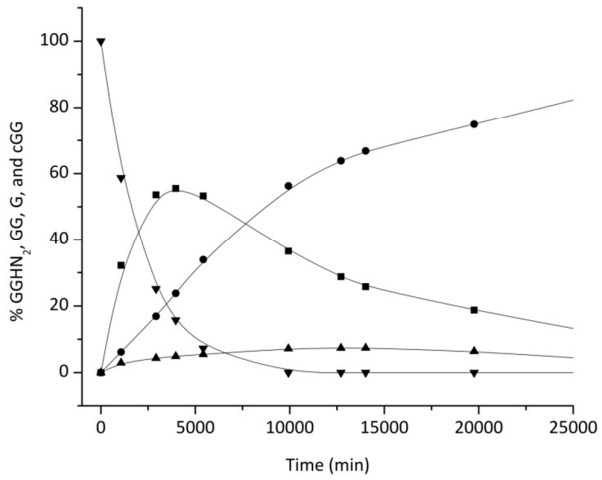

Figure S10. Hydrolysis of 2.0 mM of $GGNH_2$ in the presence of 2.0 mM of **1** at pD 5.0 and 60 °C. Percentage of $GGNH_2$ (-▼-), GG (-■-), G (-●-), and cGG (-▲-) as a function of reaction time.

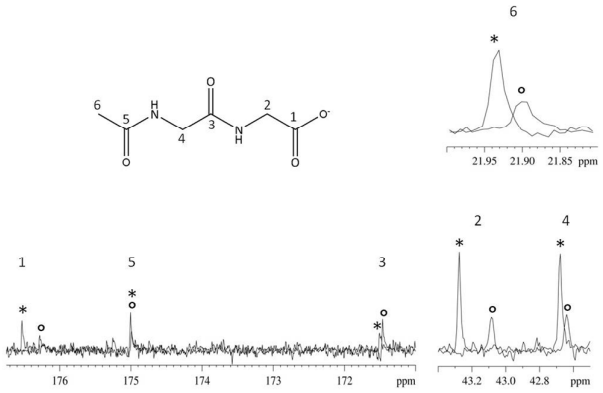

Figure S11. ^{13}C NMR spectrum of AcGG in the presence (*) and absence (°) of **1**.

Table S3. ^{13}C NMR chemical shift values (ppm) of AcGG in the presence and absence of **1**.

	30.0 mM AcGG	10 mM AcGG + 10 mM **1**	Δ (ppm)
C1(CO)	176.28	176.53	0.25
C3(CO)	171.51	171.46	-0.05
C5(CO)	174.99	175.01	0.02
C2(CH2)	43.08	43.28	0.20
C4(CH2)	42.64	42.67	0.03
C6(CH3)	21.90	21.93	0.03

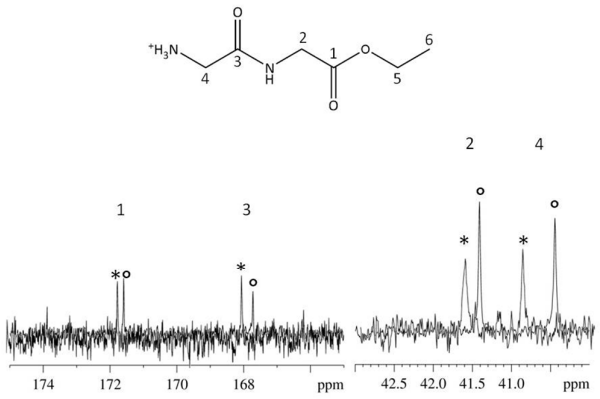

Figure S12. ^{13}C NMR spectrum of GGOEt in the presence (*) and absence (°) of **1**.

Table S4. ^{13}C NMR chemical shift values (ppm) of GGOEt in the presence and absence of **1**.

	30 mM GGOEt	10 mM GGOEt + 10 mM **1**	Δ (ppm)
C1(CO)	171.59	171.72	0.13
C3(CO)	167.72	168.03	0.31
C2(CH2)	41.41	41.70	0.29
C4(CH2)	40.44	40.98	0.54
C5(CH2)	62.75	62.75	0.00
C6(CH3)	13.33	13.40	0.07

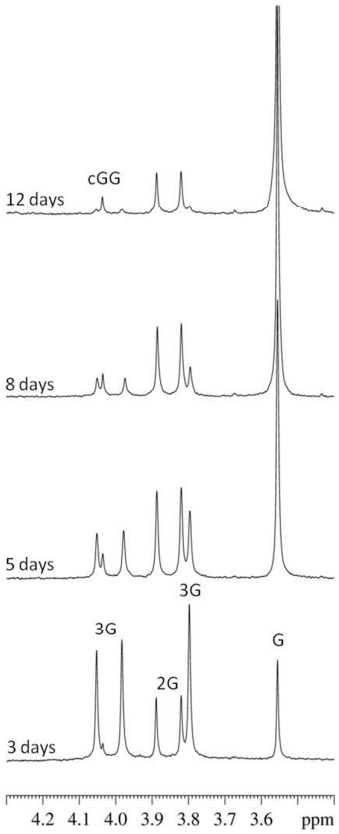

Figure S13. ^{1}H NMR spectra recorded at various reaction times during the hydrolysis of 2.0 mM of 3G in the presence of 2.0 mM of **1** at 60 °C and pD 5.0. (600 MHz, D_2O, 293 K, n = 16, 0.5 mM TMSPA-d_4)

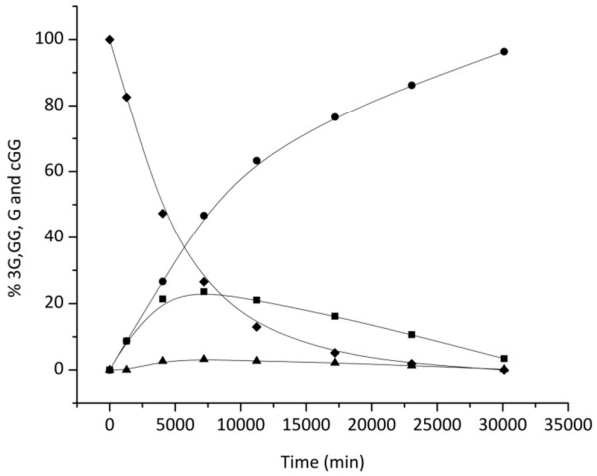

Figure S14. Hydrolysis of 2.0 mM of 3G in the presence of 2.0 mM of **1** at pD 5.0 and 60 °C. Percentage of 3G (-♦-), GG (-■-), G (-●-), and cGG (-▲-) as a function of reaction time.

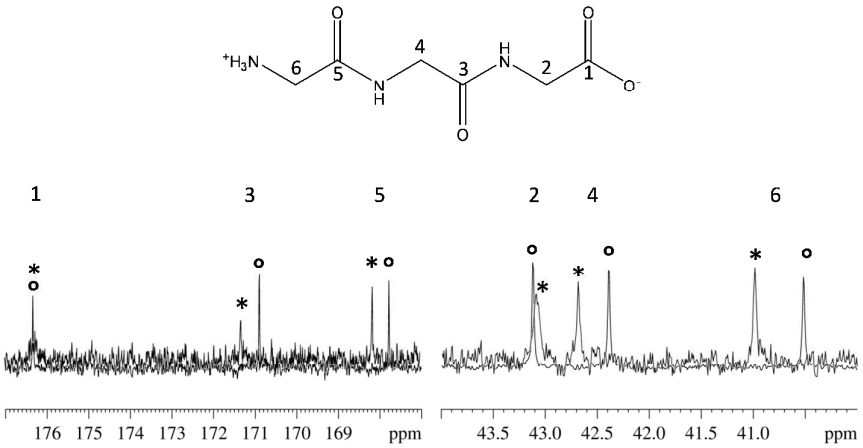

Figure S15. ^{13}C NMR spectrum of 3G in the presence (*) and absence (°) of **1**. (150.90 MHz, D_2O, 293 K, n = 20k, 1% TMS in $CDCl_3$)

Table S5. ^{13}C NMR chemical shift values (ppm) of 3G in the presence and absence of 1.

	30.0 mM 3G	10.0 mM 3G + 10.0 mM **1**	Δ (ppm)
C1(CO)	176.35	176.30	-0.05
C3(CO)	170.90	171.31	0.41
C5(CO)	167.79	168.15	0.36
C2(CH_2)	43.12	43.09	-0.03
C4(CH_2)	42.39	42.69	0.30
C6(CH_2)	40.52	40.99	0.47

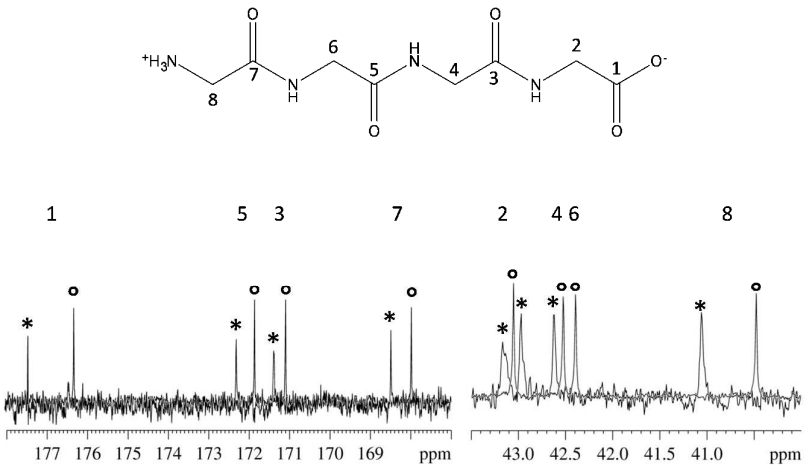

Figure S16. ^{13}C NMR spectrum of 4G in the presence (*) and absence (°) of **1**. (150.90 MHz, D_2O, 293 K, n = 20k, 1% TMS in $CDCl_3$)

Table S6. ^{13}C NMR chemical shift values (ppm) of 4G in the presence and absence of **1**.

	30.0 mM 4G	10.0 mM 4G + 10.0 mM 1	Δ (ppm)
C1(CO)	176.34	177.42	1.08
C3(CO)	171.10	171.34	0.24
C5(CO)	171.87	172.27	0.40
C7(CO)	167.99	168.44	0.45
C2(CH_2)	43.05	43.17	0.11
C4(CH_2)	42.52	42.97	0.45
C6(CH_2)	42.39	42.62	0.23
C8(CH_2)	40.48	41.06	0.58

(1) Kato, C. N.; Shinohara, A.; Hayashi, K.; Nomiya, K. *Inorg. Chem.* **2006**, *45*, 8108.

(2) Sokolov, M. N.; Izarova, N. V.; Peresypkina, E. V.; Mainichev, D. A.; Fedin, V. P. *Inorganica Chimica Acta* **2009**, *362*, 3756.

(3) Saku, Y.; Sakai, Y.; Nomiya, K. *Inorganica Chimica Acta* **2010**, *363*, 967.