Electronic Supplementary Information

for

Thioester hydrolysis reactivity of zinc hydroxide complexes: Investigating reactivity relevant to glyoxalase II enzymes

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$[(L^1Zn_2)(\mu\text{-}OH)](ClO_4)_2$ (1). A solution of L^1H (43 mg, 0.082 mmol) in acetonitrile (5 mL) was added to solid $Zn(ClO_4)_2{\cdot}6H_2O$ (61 mg, 0.16 mmol) and the mixture was stirred for ~5 minutes. Once the $Zn(ClO_4)_2{\cdot}6H_2O$ had fully dissolved, this solution was added to a slurry of $(CH_3)_4NOH{\cdot}5H_2O$ (30 mg, 0.16 mmol) in acetonitrile. The resulting mixture was stirred for 24 h at room temperature. The solvent was then removed under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 and filtered through a celite/glass wool plug. Recrystallization of this solid from CH_3CN:diethyl ether yielded the product as crystalline blocks suitable for single crystal X-ray crystallographic analysis (58 mg, 82%) (Found: C, 44.14; H, 3.95; N, 9.79. $C_{33}H_{34}N_6Zn_2Cl_2O_{10}$ requires C, 45.41; H, 3.93; N, 9.63%); ν_{max}/cm^{-1}: (OH) 3430 (br), (ClO_4) 1092, (ClO_4) 625 (KBr); δ_H (400 MHz, solvent CD_3CN): 2.15 (3H, s), 3.82 (4H, s), 3.92-4.08 (8H, m), 6.87 (2H, s), 7.52 (4H, d, J = 7.9 Hz), 7.65 (4H, m), 8.05 (4H, t, J = 7.7 Hz), 8.96 (4H, m), a resonance was not identified for the bridging hydroxyl proton; δ_C (100 MHz, solvent CD_3CN): 20.1, 57.5, 59.3, 122.9, 125.9, 126.0, 126.8, 134.0, 149.6, 156.7, 161.2 (12 signals expected, 11 observed; 1 aromatic resonance not observed, presumably due to overlap).

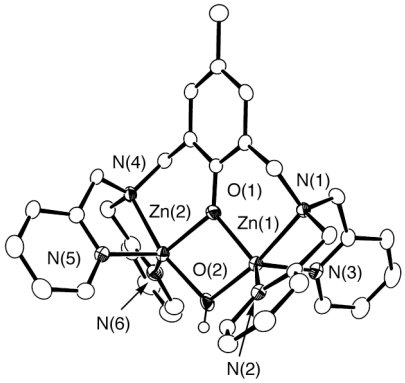


Fig. S1 ORTEP representation of the cationic portion of **1·3CH₃CN**. All hydrogen atoms except the hydroxyl proton have been omitted for clarity. All ellipsoids are plotted at the 50% probability level.

Table S1 Summary of X-ray data collection and refinement for **1·3CH$_3$CN**[a]

Empirical formula	$C_{39}H_{43}Cl_2N_9O_{10}Zn_2$
M	999.46
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.2290(2)
b/Å	10.10390(10)
c/Å	34.6544(7)
α/°	90
β/°	91.2424(5)
γ/°	90
V/ Å^3	4280.91(12)
Z	4
D_c/Mg m^{-3}	1.551
T/K	150(1)
Color	colorless
Crystal size/mm^3	0.25 x 0.15 x 0.13
Diffractometer[a]	Nonius KappaCCD
μ/mm^{-1}	1.313
$2\theta_{max}$/°	55.88
Completeness to θ = 27.94° (%)	99.4
Reflections collected	17587
Independent reflections	10200
R_{int}	0.0714
Variable parameters	579
$R1$/$wR2$[b]	0.0488/0.0854
Goodness-of-fit (F^2)	1.039
$\Delta\rho_{maxmin}$ /e Å^{-3}	0.626/-0.644

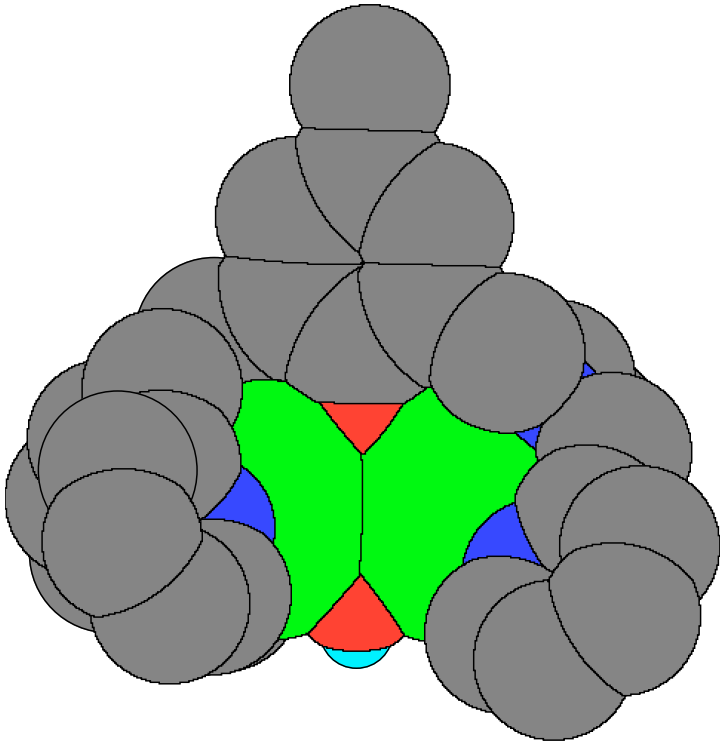
[a] Radiation used: Mo Kα (λ = 0.71073 Å). [b] $R1 = \sum | |F_o| - |F_c| | / \sum |F_o|$; $wR2 = [\sum[w(F_o^2-F_c^2)^2]/[\sum(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$.

Table S2 Selected bond lengths (Å) and angles (°) for **1·3CH$_3$CN**[a]

Zn(1)-O(2)	1.984(2)
Zn(1)-O(1)	2.0260(18)
Zn(1)-N(2)	2.062(2)
Zn(1)-N(3)	2.064(2)
Zn(1)-N(1)	2.183(2)
Zn(2)-O(2)	1.985(2)
Zn(2)-O(1)	2.0511(19)
Zn(2)-N(5)	2.052(2)
Zn(2)-N(6)	2.072(2)
Zn(2)-N(4)	2.186(2)
O(2)-Zn(1)-O(1)	81.20(8)
O(2)-Zn(1)-N(2)	103.43(9)
O(1)-Zn(1)-N(2)	126.26(8)
O(2)-Zn(1)-N(3)	106.52(9)
O(1)-Zn(1)-N(3)	113.26(8)
N(2)-Zn(1)-N(3)	116.12(9)
O(2)-Zn(1)-N(1)	170.26(8)
O(1)-Zn(1)-N(1)	89.26(8)
N(2)-Zn(1)N(1)	80.63(9)
N(3)-Zn(1)-N(1)	78.99(9)
O(2)-Zn(2)-O(1)	80.57(8)
O(2)Zn(2)-N(5)	113.10(8)
O(1)-Zn(2)-N(5)	113.08(9)
O(2)-Zn(2)-N(6)	98.64(9)
O(1)-Zn(2)-N(6)	127.42(8)
N(5)-Zn(2)-N(6)	115.12(9)
O(2)-Zn(2)-N(4)	165.29(8)
O(1)-Zn(2)-N(4)	88.48(8)
N(5)-Zn(2)-N(4)	80.19(8)
N(6)-Zn(2)-N(4)	80.21(9)

[a] Estimated standard deviations indicated in parentheses.

Figure S2 Space-filling model for the cationic portion of **1** (prepared using Chem3D).



Zinc (green)
Nitrogen (blue)
Oxygen (red)
Carbon (gray)
Hydrogen (light blue)

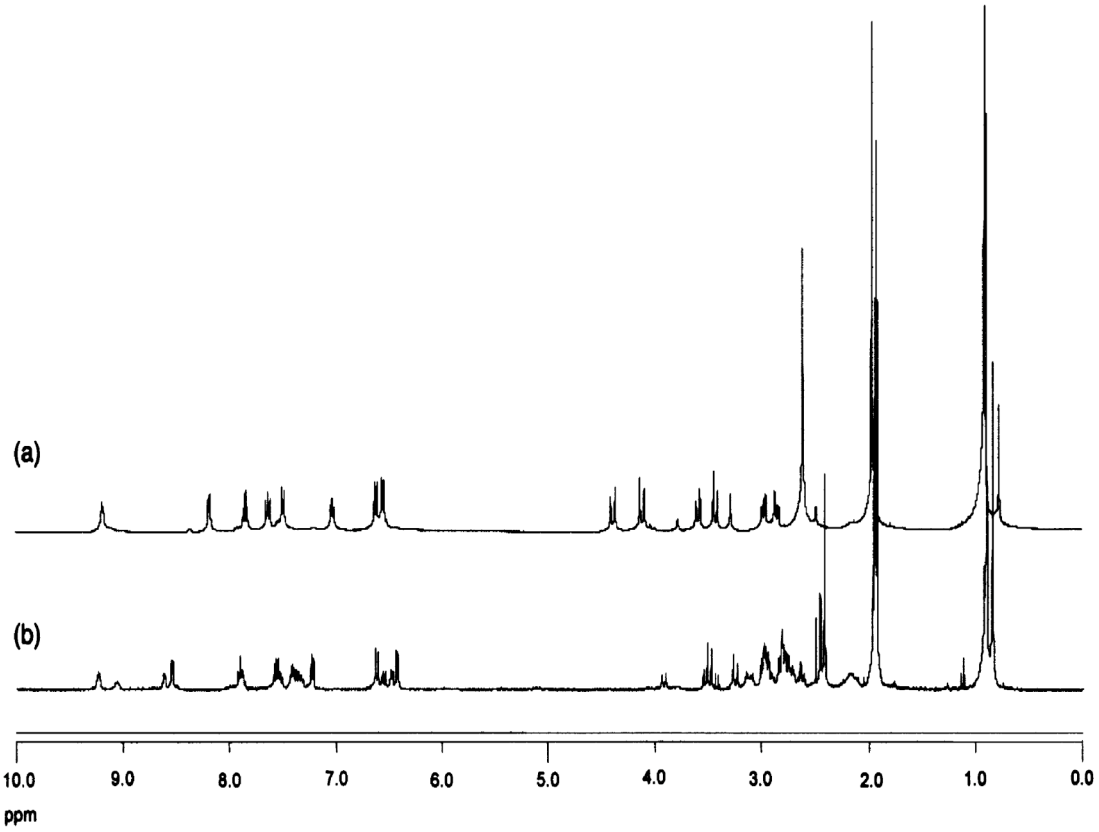


Figure S3. ^{1}H NMR spectra of **2** (a) and **3** (b) in CD_3CN at 25(1) °C