Electronic Supplementary Material

Metallohydrolase biomimetics with catalytic and structural flexibility

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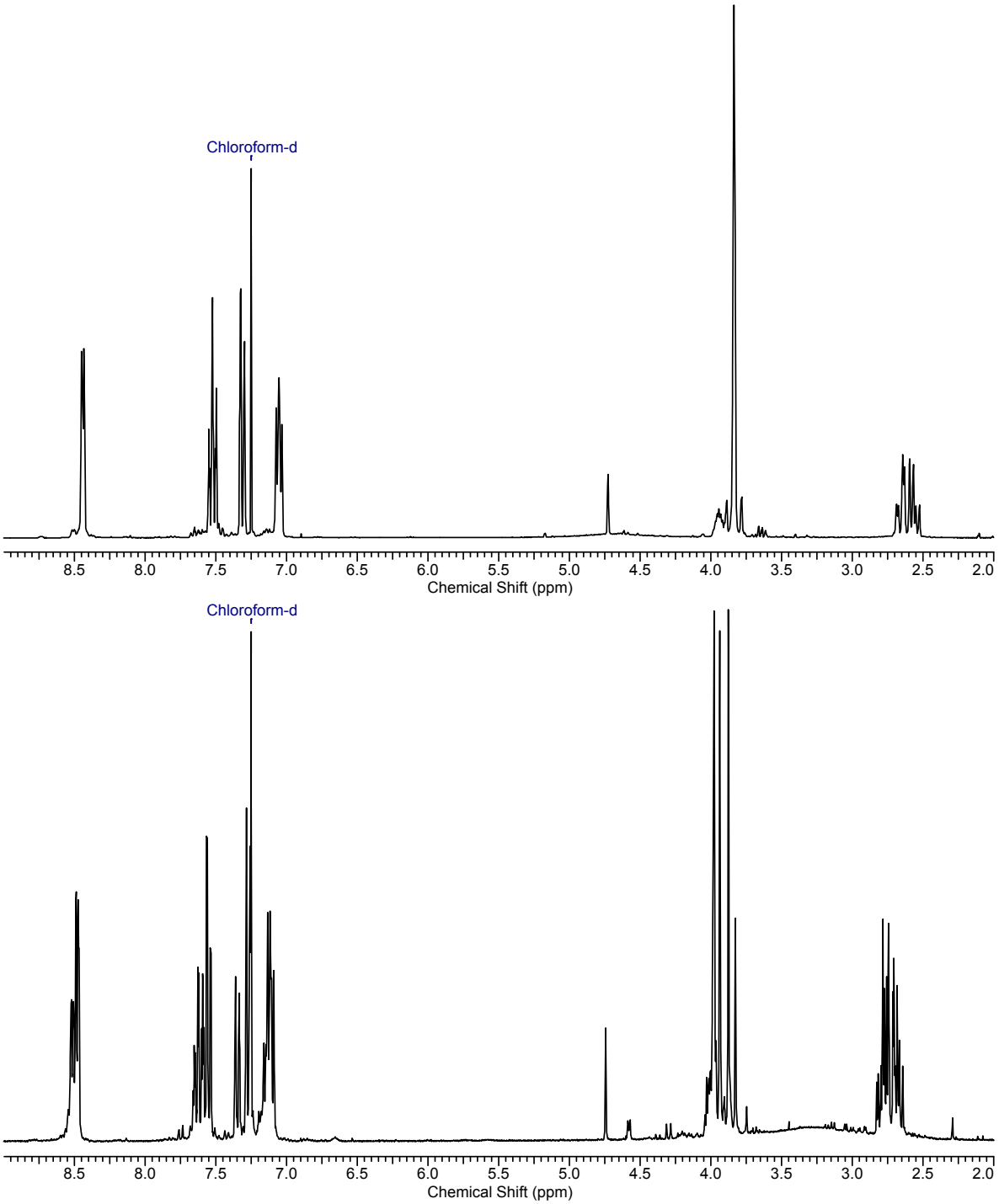

Figure S1. ^{1}H NMR spectra of the ligands HL1 (top) and HL2 (bottom).

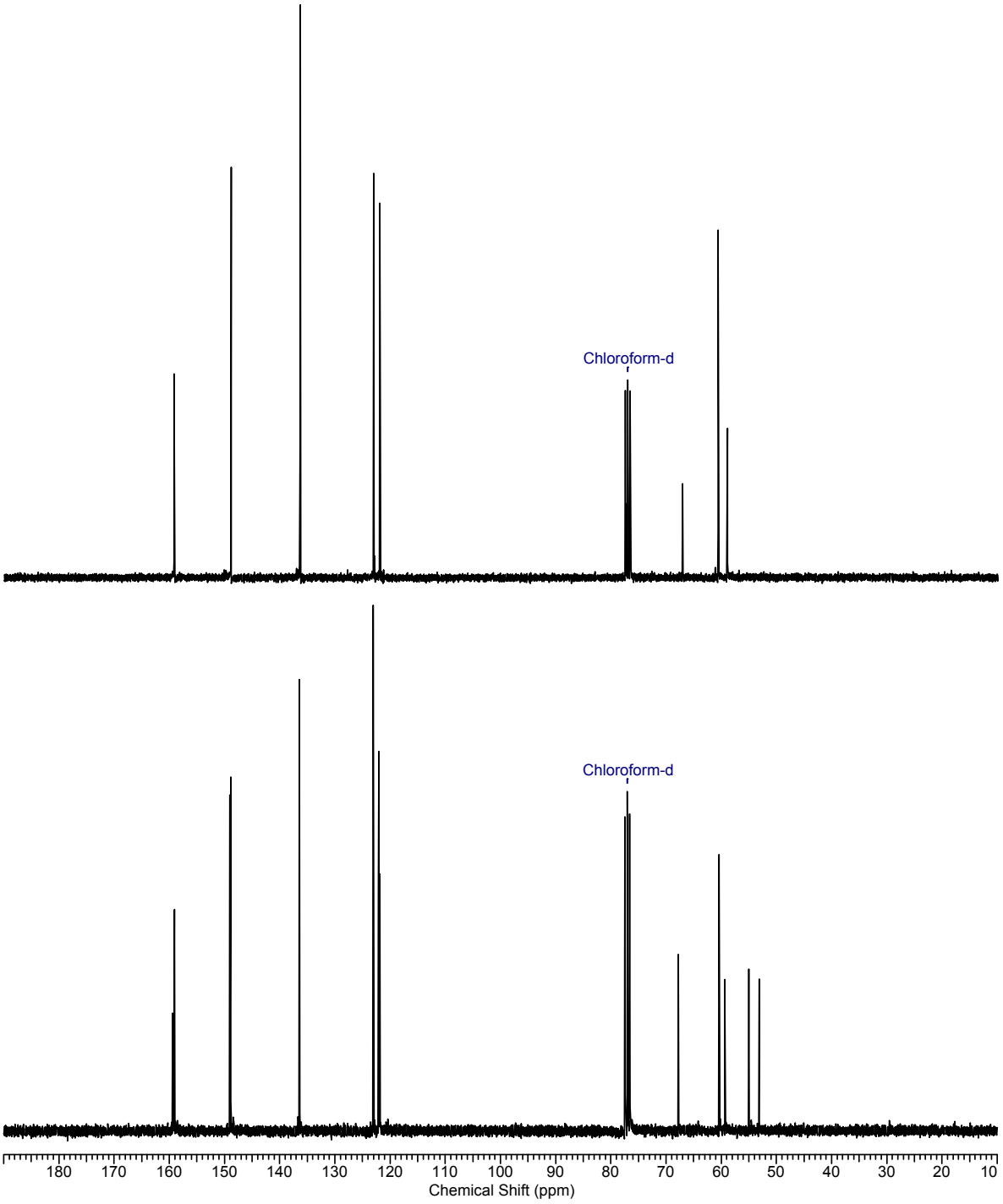

Figure S2. ^{13}C NMR spectra of the ligands HL1 (top) and HL2 (bottom).

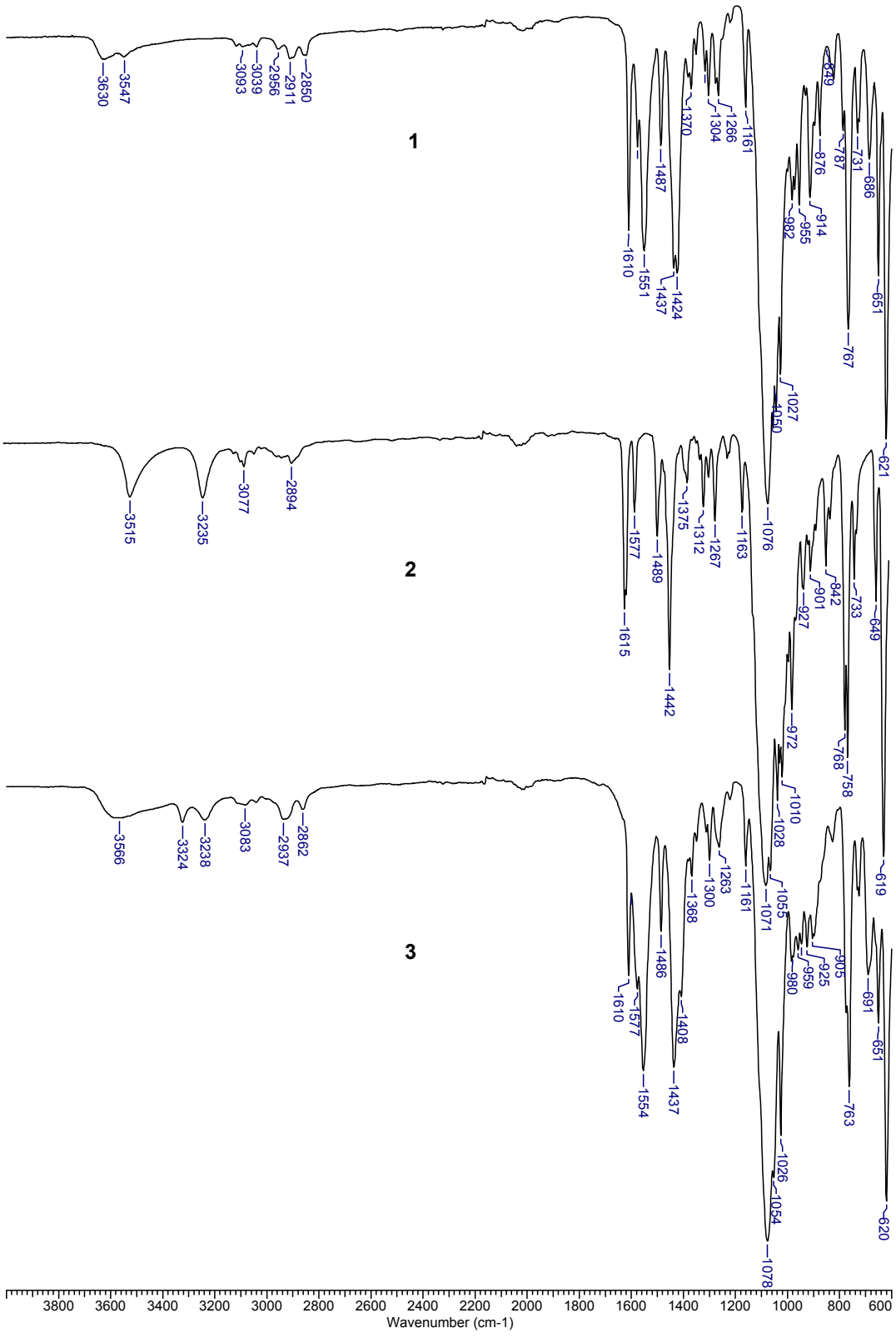

Figure S3. Infrared spectra of the complexes **1**, **2** and **3**.

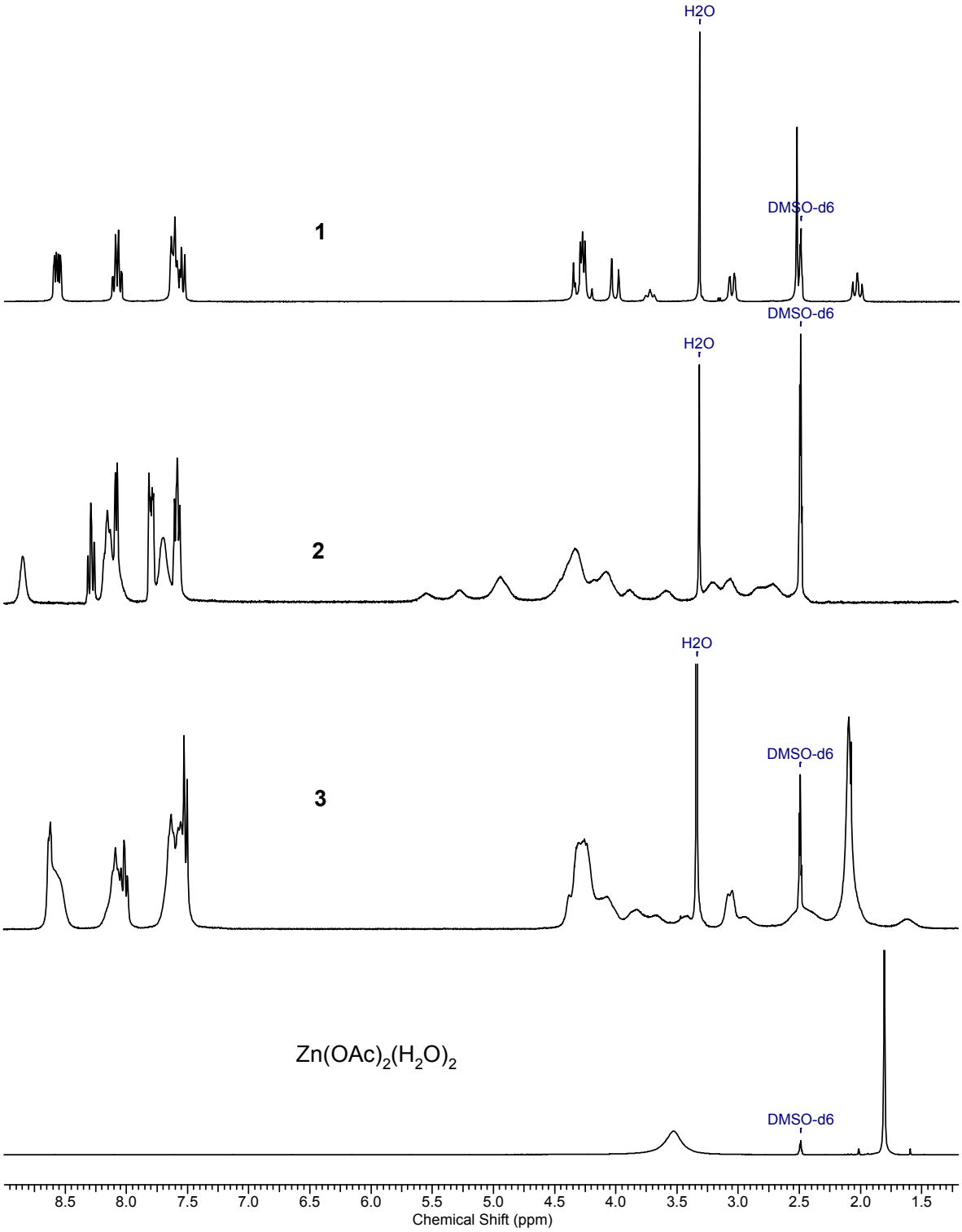

Figure S4. ^{1}H NMR of the complexes **1**, **2**, **3** and $Zn(OAc)_2(H_2O)$ in DMSO-d6.

Table S1. Crystal data for $[Zn(HL2)](ClO_4)_2$, **2**, $[Zn_4(L2)_2(OAc)_3](ClO_4)_3$, **3,** and $[Zn_4(L2)_2(DNPP)_2](ClO_4)_2$, **4**.

	$[Zn(HL2)](ClO_4)_2$	$[Zn_4(L2)_2(OAc)_3](ClO_4)_3$ .H_2O	$[Zn_4(L2)_2(DNPP)_2](ClO_4)_2$
	2	**3**	**4**
Empirical Formula	$C_{21}H_{25}C\square_2N_5O_9Zn$	$C_{48}H_{59}C\square_3N_{10}O_{21}Zn_4$	$C_{54}H_{54}C\square_2N_{14}O_{26}P2Zn_4$
Formula weight	627.73	1479.88	1709.43
Temperature (K)	190(2)	190(2)	190(2)
wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Triclinic
Space Group	I 1 2/a 1	P -1	P -1
Unit Cell dimensions			
a	16.5042(7) Å	13.7210(7) Å	8.8153(10) Å
b	9.3346(4) Å	15.4894(7) Å	14.3078(18) Å
c	32.7148(14) Å	17.1435(8) Å	14.6939(18) Å
α	90°	66.918(4) °	67.511(12) °
β	95.369(4)°	67.606(5) °	72.975(11) °
γ	90°	75.704(4) °	82.475(10) °
Volume	5017.9(4) $Å^3$	3078.6(3) $Å^3$	1636.9(3) $Å^3$
Z	8	2	1
Density (*calc*)	1.662 Mg/m^3	1.594 Mg/m^3	1.734 Mg/m^3
Absorption coefficient	1.254 mm^{-1}	1.750 mm^{-1}	1.673 mm^{-1}
F(000)	2576	1508	868
Crystal size	0.4 x 0.2 x 0.2 mm^3	0.2 x 0.2 x 0.2 mm^3	0.3 x 0.2 x 0.2 mm^3
Theta range for data collection	3.35 to 25°	3.579 to 22.872 °	3.503 to 26.269°
Index ranges	-19<=*h*<=19, -11<=*k*<=10, -38<=*l*<=32	-16<=*h*<=16, -18<=*k*<=17, -20<=*l*<=20	-10<=*h*<=10, -16<=*k*<=16, -17<=*l*<=17
Reflections	11450	24058	12010

collected			
Independent reflections	4412[R(int)=0.0319]	10844 [R(int)= 0.0581]	5756[R(int)= 0.0367]
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least Squares on F^2
Data/restraints/parameters	4412/0/344	10844/6/815	5756/0/460
Goodness-of-fit on F^2	1.035	1.029	1.051
Final R indices [$I>2\sigma(I)$]	R1=0.0346, wR2=0.0785	R1=0.0684, wR2=0.1552	R1=0.0435, wR2=0.0923
R indices (all data)	R1=0.0446, wR2=0.0845	R1=0.1183, wR2=0.183	R1=0.062, wR2=0.1007
Largest diff. peaks and hole	0.482 and -0.308 e.Å^{-3}	0.872 and -0.464 e.Å^{-3}	0.63 and -0.362 e.Å^{-3}

Table S2. Selected bond lengths [Å] for compounds **2**, **3** and **4**.

Bond	Compound		
	2	**3**	**4**[#]
N(1)-Zn(1)	2.059(2)	2.059(6)	2.068(3)
N(2)-Zn(1)	2.197(2)	2.227(5)	2.250(3)
N(3)-Zn(1)	2.063(2)	2.057(6)	2.088(4)
N(4)-Zn(1)	2.065(2)	-	-
N(5)-Zn(1)	2.128(2)	-	-
O(1)-Zn(1)	-	1.929(4)	1.969(3)
O(2)-Zn(1)	-	1.984(5) [a]	1.961(3) [b]
N(4)-Zn(2)	-	2.204(5)	2.212(3)
N(5)-Zn(2)	-	2.078(6)	2.100(3)
O(1)-Zn(2)	-	1.952(4)	2.003(3)
O(3)-Zn(2)	-	2.092(4)[a]	2.005(3)[b]
O(4)-Zn(2)	-	2.069(5)	-
O(4)[i]-Zn(2)	-	-	1.950(3)
O(5)-Zn(2)	-	2.408(4)	-
N(10)-Zn(3)	-	2.053(5)	-
N(9)-Zn(3)	-	2.180(5)	-
O(5)-Zn(3)	-	1.989(4)	-
O(6)-Zn(3)	-	1.959(4)	-
O(7)-Zn(3)	-	2.034(4)	-
N(6)-Zn(4)	-	2.042(6)	-
N(7)-Zn(4)	-	2.256(6)	-
N(8)-Zn(4)	-	2.061(5)	-
O(6)-Zn(4)	-	1.945(4)	-
O(8)-Zn(4)	-	2.022(5)	-
Zn(1)-Zn(2)	-	3.465(5)	3.612(3)
Zn(3)-Zn(4)	-	3.484(5)	-
Zn(2)-Zn(3)	-	4.106(5)	-
Zn(1)-Zn(2)[i]	-	-	5.670(3)
Zn(1)-Zn(1)[i]	-	-	8.170(3)
Zn(2)-Zn(2)[i]	-	-	4.863(3)

[#] Symmetry transformations used to generate equivalent atoms: 1 -x+1,-y+1,-z

[a] oxygen from acetate group, [b] oxygen from phosphate group.

Table S3. Selected bond angles [°] for compounds **2**, **3** and **4**.

Bond	Compound		
	2	**3**	**4**[#]
N(1)-Zn(1)-N(3)	123.09(10)	113.7(2)	107.97(13)
N(1)-Zn(1)-N(4)	121.16(10)	-	-
N(3)-Zn(1)-N(4)	113.34(9)	-	-
N(1)-Zn(1)-N(5)	106.20(9)	-	-
N(3)-Zn(1)-N(5)	96.47(9)	-	-
N(4)-Zn(1)-N(5)	81.31(9)	-	-
N(1)-Zn(1)-N(2)	79.74(9)	78.9(2)	77.96(13)
N(3)-Zn(1)-N(2)	79.75(9)	79.7(2)	78.74(14)
N(4)-Zn(1)-N(2)	95.91(9)	-	-
N(5)-Zn(1)-N(2)	174.06(9)	-	-
O(1)-Zn(1)-O(2)	-	101.77(18)[a]	100.28(11)[b]
O(1)-Zn(1)-N(3)	-	112.4(2)	117.50(13)
O(2)-Zn(1)-N(3)	-	97.7(2)	102.37(14)
O(1)-Zn(1)-N(1)	-	125.4(2)	124.41(12)
O(2)-Zn(1)-N(1)	-	99.4(2)[a]	99.43(13)[b]
O(1)-Zn(1)-N(2)	-	82.2(2)	81.18(11)
O(2)-Zn(1)-N(2)	-	175.9(2)	177.38(13)
Zn(1)-O(1)-Zn(2)	-	126.5(2)	130.87(13)
N(5)-Zn(2)-N(4)	-	78.4(2)	77.63(12)
O(1)-Zn(2)-O(4)	-	102.3(2)	-
O(1) -Zn(2)- O(4)[i]	-	-	120.62(13)
O(1)-Zn(2)-N(5)	-	111.7(2)	122.35(12)
O(4)-Zn(2)-N(5)	-	142.2(2)	-
O(4)[i]-Zn(2)-N(5)	-	-	113.53(13)
O(1)-Zn(2)-O(3)	-	95.04(17)	92.53(10)
O(4)-Zn(2)-O(3)	-	97.08(19)	-
O(4)[i]-Zn(2)-O(3)	-	-	102.11(12)
N(5)-Zn(2)-O(3)	-	95.91(19)[a]	94.35(12)[b]
O(1)-Zn(2)-N(4)	-	81.9(2)	81.58(11)
O(4)-Zn(2)-N(4)	-	90.9(2)	-
O(4)[i]-Zn(2)-N(4)	-	-	92.60(13)
O(3)-Zn(2)-N(4)	-	171.9(2)[a]	165.14(13)[b]
O(1)-Zn(2)-O(5)	-	159.14(19)	-
O(4)-Zn(2)-O(5)	-	56.88(16)	-

N(5)-Zn(2)-O(5)	-	88.76(18)	-
O(3)-Zn(2)-O(5)	-	86.49(16)	-
N(4)-Zn(2)-O(5)	-	99.01(19)	-
O(6)-Zn(3)-O(5)	-	118.99(18)	-
O(6)-Zn(3)-O(7)	-	95.59(18)	-
O(5)-Zn(3)-O(7)	-	97.98(19)	-
O(6)-Zn(3)-N(10)	-	121.8(2)	-
O(5)-Zn(3)-N(10)	-	116.2(2)	-
O(7)-Zn(3)-N(10)	-	93.6(2)	-
O(6)-Zn(3)-N(9)	-	81.78(18)	-
O(5)-Zn(3)-N(9)	-	91.37(19)	-
O(7)-Zn(3)-N(9)	-	170.36(19)	-
N(10)-Zn(3)-N(9)	-	80.1(2)	-
O(6)-Zn(4)-O(8)	-	100.50(18)	-
O(6)-Zn(4)-N(6)	-	116.7(2)	-
O(8)-Zn(4)-N(6)	-	99.7(3)	-
O(6)-Zn(4)-N(8)	-	123.27(19)	-
O(8)-Zn(4)-N(8)	-	101.1(2)	-
N(6)-Zn(4)-N(8)	-	110.3(2)	-
O(6)-Zn(4)-N(7)	-	81.32(19)	-
O(8)-Zn(4)-N(7)	-	178.16(19)	-
N(6)-Zn(4)-N(7)	-	79.1(3)	-
N(8)-Zn(4)-N(7)	-	78.1(2)	-
P(1)-O(2)-Zn(1)	-	-	132.81(17)
P(1)-O(3)-Zn(2)	-	-	131.19(16)
P(1)-O(4)-Zn(2)^{i}	-	-	153.5(2)
O(4)-P(1)-O(3)	-	-	116.17(17)
O(4)-P(1)-O(2)	-	-	113.63(19)
O(3)-P(1)-O(2)	-	-	114.79(16)
O(4)-P(1)-O(5)	-	-	103.94(17)
O(3)-P(1)-O(5)	-	-	101.20(15)
O(2)-P(1)-O(5)	-	-	104.82(17)

[#] Symmetry transformations used to generate equivalent atoms: 1 -x+1,-y+1,-z

[a] oxygen from acetate group; [b] oxygen from phosphate group.