Electronic supplementary information (ESI)

Dinuclear metal(II)-acetato complexes based on bicompartmental 4-chlorophenolate: syntheses, structures, magnetic properties, DNA interactions and phosphodiester hydrolysis†

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Table S1. Crystallographic data and processing parameters for compounds **1**-**6**.

Compound	**1**	**2**	**3**
Empirical formula	$C_{36}H_{42}ClF_6N_6Ni_2O_8P$	$C_{39}H_{42}Cl_2N_6Ni_2O_{10}$	$C_{34}H_{33}Cl_3Cu_2N_6O_{11}$
Formula mass	984.56	943.07	935.11
System	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	10.4453(3)	10.1039(2)	10.6949(4)
b (Å)	20.6559(6)	14.0417(2)	20.3869(9)
c (Å)	19.7889(6)	28.0477(5)	17.5905(7)
α (°)	90	90	90
β (°)	103.241(1)	91.895(1)	105.489(2)
γ (°)	90	90	90
V (Å^3)	4156.1(2)	3977.12(12)	3696.1(3)
Z	4	4	4
T (K)	100(2)	100(2)	100(2)
μ (mm^{-1})	1.093	1.148	1.437
D_{calc} (Mg/m^3)	1.574	1.575	1.681
Data collected	101401	76473	81476
Unique refl. / R_{int}	12155 / 0.0399	11605 / 0.0506	9835 / 0.0482
Parameters / restraints	598 / 6	536 / 0	506 / 0
Goodness-of-Fit on F^2	1.135	1.123	1.105
R1 / wR2 (all data)	0.0403 / 0.1243	0.0318 / 0.0995	0.0419 / 0.1363
Residual extrema (e/Å^3)	1.07 / -0.67	0.63 / -0.64	1.33 / -0.68

Table S1. cont. Crystallographic data and processing parameters

Compound	**4**	**5**	**6**
Empirical formula	$C_{36}H_{38}ClCu_2F_6N_6O_6P$	$C_{36}H_{36}ClF_6N_6O_5PZn_2$	$C_{36}H_{36}Cl_2Mn_2N_6O_{10}$
Formula mass	958.24	943.91	893.49
System	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	P-1	$P2_1/c$
a (Å)	11.0390(2)	10.2050(14)	10.2227(2)
b (Å)	27.5883(6)	12.0710(17)	13.9012(4)
c (Å)	12.7990(3)	16.930(2)	28.2107(7)
α (°)	90	90.53(2)	90
β (°)	90.327(1)	106.84(2)	91.499(1)
γ (°)	90	104.35(2)	90
V (Å^3)	3897.84(14)	1926.4(5)	4007.59(17)
Z	4	2	4
T (K)	100(2)	100(2)	100(2)
μ (mm^{-1})	1.284	1.436	0.826
D_{calc} (Mg/m^3)	1.633	1.627	1.481
Data collected	44754	15176	111141
Unique refl. / R_{int}	10374 / 0.0412	7674 / 0.0259	10643 / 0.0293
Parameters / restraints	533 / 0	516 / 0	525 / 12
Goodness-of-Fit on F^2	1.081	1.197	1.041
R1 / wR2 (all data)	0.0336 / 0.0988	0.0532 / 0.1101	0.0296 / 0.0798
Residual extrema (e/Å^3)	0.80 / -0.70	0.79 / -0.44	0.93 / -0.48

Table S2. Selected bond distances (Å) and angles (°) for compound **1**.

Ni(1)-O(4)	2.0512(16)	Ni(2)-O(1)	2.0216(15)
Ni(1)-O(1)	2.0097(15)	Ni(2)-O(3)	2.0334(16)
Ni(1)-O(2)	2.0569(17)	Ni(2)-O(5)	2.0568(16)
Ni(1)-N(2)	2.087(2)	Ni(2)-N(5)	2.0870(19)
Ni(1)-N(3)	2.0780(19)	Ni(2)-N(4)	2.1049(19)
Ni(1)-N(1)	2.1169(18)	Ni(2)-N(6)	2.106(2)
Cl(3)-C(4)	1.747(2)	O(3)-C(33)	1.267(3)
O(4)-C(35)	1.265(2)	O(2)-C(33)	1.248(3)
O(1)-C(1)	1.328(3)	O(5)-C(35)	1.254(3)
O(4)-Ni(1)-O(1)	96.63(6)	O(3)-Ni(2)-O(1)	97.39(6)
O(4)-Ni(1)-O(2)	91.82(7)	O(3)-Ni(2)-O(5)	92.26(7)
O(1)-Ni(1)-O(2)	89.86(7)	O(1)-Ni(2)-O(5)	90.02(6)
O(4)-Ni(1)-N(2)	92.82(7)	O(3)-Ni(2)-N(5)	92.85(7)
O(1)-Ni(1)-N(2)	169.82(7)	O(1)-Ni(2)-N(5)	169.17(7)
O(2)-Ni(1)-N(2)	86.05(7)	O(5)-Ni(2)-N(5)	86.05(7)
O(4)-Ni(1)-N(3)	95.60(7)	O(3)-Ni(2)-N(6)	92.58(7)
O(1)-Ni(1)-N(3)	88.06(7)	O(1)-Ni(2)-N(6)	86.30(7)
O(2)-Ni(1)-N(3)	172.48(7)	O(5)-Ni(2)-N(6)	174.26(7)
N(2)-Ni(1)-N(3)	94.79(8)	O(3)-Ni(2)-N(4)	170.03(7)
O(4)-Ni(1)-N(1)	170.77(7)	O(1)-Ni(2)-N(4)	90.69(7)
O(1)-Ni(1)-N(1)	91.89(6)	O(5)-Ni(2)-N(4)	93.59(7)
O(2)-Ni(1)-N(1)	91.72(7)	N(6)-Ni(2)-N(4)	82.07(7)
N(2)-Ni(1)-N(1)	78.93(7)	N(5)-Ni(2)-N(6)	96.79(7)
N(3)-Ni(1)-N(1)	81.12(7)	N(5)-Ni(2)-N(4)	79.51(7)
C(33)-O(3)-Ni(2)	129.54(15)	C(35)-O(4)-Ni(1)	131.20(15)
C(33)-O(2)-Ni(1)	129.18(15)	C(1)-O(1)-Ni(2)	122.42(14)
C(1)-O(1)-Ni(1)	121.87(13)	Ni(2)-O(1)-Ni(1)	115.70(7)
C(35)-O(5)-Ni(2)	127.24(15)		

Table S3. Selected bond distances (Å) and angles (°) for compound **2**.

Ni(1)-O(4)	2.0157(12)	Ni(2)-O(3)	2.0174(12)
Ni(1)-O(1)	2.0209(12)	Ni(2)-O(1)	2.0198(12)
Ni(1)-O(2)	2.0463(15)	Ni(2)-O(5)	2.0453(12)
Ni(1)-N(2)	2.0948(14)	Ni(2)-N(5)	2.0845(15)
Ni(1)-N(3)	2.1133(15)	Ni(2)-N(6)	2.1198(14)
Ni(1)-N(1)	2.1297(14)	Ni(2)-N(4)	2.1254(15)
Cl(1)-C(4)	1.7447(17)	O(3)-C(33)	1.265(2)
O(4)-C(35)	1.265(2)	O(2)-C(33)	1.258(2)
O(1)-C(1)	1.322(2)	O(5)-C(35)	1.255(2)
O(4)-Ni(1)-O(1)	96.92(5)	O(3)-Ni(2)-O(1)	95.51(5)
O(4)-Ni(1)-O(2)	94.17(5)	O(3)-Ni(2)-O(5)	96.09(5)
O(1)-Ni(1)-O(2)	90.72(5)	O(1)-Ni(2)-O(5)	89.82(5)
O(4)-Ni(1)-N(2)	95.39(5)	O(3)-Ni(2)-N(5)	94.85(5)
O(1)-Ni(1)-N(2)	167.29(5)	O(1)-Ni(2)-N(5)	168.90(5)
O(2)-Ni(1)-N(2)	85.25(5)	O(5)-Ni(2)-N(5)	85.14(5)
O(4)-Ni(1)-N(3)	92.07(5)	O(3)-Ni(2)-N(6)	91.23(5)
O(1)-Ni(1)-N(3)	87.02(5)	O(1)-Ni(2)-N(6)	86.38(5)
O(2)-Ni(1)-N(3)	173.58(5)	O(5)-Ni(2)-N(6)	172.06(5)
N(2)-Ni(1)-N(3)	95.68(5)	O(3)-Ni(2)-N(4)	169.50(5)
O(4)-Ni(1)-N(1)	170.09(5)	O(1)-Ni(2)-N(4)	90.83(5)
O(1)-Ni(1)-N(1)	89.74(5)	O(5)-Ni(2)-N(4)	92.29(5)
O(2)-Ni(1)-N(1)	93.07(5)	N(6)-Ni(2)-N(4)	80.80(6)
N(2)-Ni(1)-N(1)	78.47(5)	O(5)-Ni(2)-N(4)	92.29(5)
N(3)-Ni(1)-N(1)	80.92(6)	N(5)-Ni(2)-N(6)	97.36(5)
C(33)-O(3)-Ni(2)	132.69(11)	C(35)-O(4)-Ni(1)	129.65(11)
C(33)-O(2)-Ni(1)	131.10(11)	C(1)-O(1)-Ni(2)	121.82(10)
C(1)-O(1)-Ni(1)	121.70(10)	Ni(2)-O(1)-Ni(1)	116.43(6)
C(35)-O(5)-Ni(2)	132.18(11)		

Table S4. Selected bond distances (Å) and angles (°) for compound **3**.

Cu(2)-O(2)	1.971(2)	Cu(1)-O(3)	1.941(2)
Cu(2)-N(5)	1.993(2)	Cu(1)-N(3)	1.994(3)
Cu(2)-N(6)	2.204(2)	Cu(1)-N(2)	2.008(2)
Cu(2)-N(4)	2.067(2)	Cu(1)-N(1)	2.033(2)
Cu(2)-O(1)	1.9362(19)	Cu(1)-O(1)	2.2089(19)
O(1)-C(1)	1.335(3)	Cl(1)-C(4)	1.746(3)
O(1)-Cu(2)-O(2)	92.51(8)	O(3)-Cu(1)-N(3)	94.85(9)
O(1)-Cu(2)-N(5)	176.11(10)	O(3)-Cu(1)-N(2)	96.23(9)
O(2)-Cu(2)-N(5)	90.06(10)	N(3)-Cu(1)-N(2)	158.05(10)
O(1)-Cu(2)-N(4)	94.57(9)	O(3)-Cu(1)-N(1)	170.10(9)
O(2)-Cu(2)-N(4)	163.74(9)	N(3)-Cu(1)-N(1)	83.02(10)
N(5)-Cu(2)-N(4)	82.21(10)	N(2)-Cu(1)-N(1)	82.82(10)
N(6)-Cu(2)-O(1)	84.13(9)	O(3)-Cu(1)-O(1)	94.61(8)
N(6)-Cu(2)-O(2)	114.23(9)	N(3)-Cu(1)-O(1)	82.93(8)
N(6)-Cu(2)-N(5)	97.47(10)	N(2)-Cu(1)-O(1)	114.89(9)
N(4)-Cu(2)-N(6)	81.11(9)	N(1)-Cu(1)-O(1)	94.72(8)
C(1)-O(1)-Cu(1)	117.34(16)	C(1)-O(1)-Cu(2)	123.71(17)
Cu(2)-O(1)-Cu(1)	118.83(9)	C(33)-O(2)-Cu(2)	123.96(19)
C(33)-O(3)-Cu(1)	123.07(19)		

Table S5. Selected bond distances (Å) and angles (°) for compound **4**.

Cu(2)-O(4)	1.9385(16)	Cu(1)-O(2)	1.9384(15)
Cu(2)-N(5)	1.9843(18)	Cu(1)-N(3)	1.9913(19)
Cu(2)-N(6)	1.9888(18)	Cu(1)-N(2)	1.9959(18)
Cu(2)-N(4)	2.0678(18)	Cu(1)-N(1)	2.0599(18)
Cu(2)-O(1)	2.1826(14)	Cu(1)-O(1)	2.1972(14)
O(1)-C(1)	1.317(3)	Cl(1)-C(4)	1.752(2)
O(4)-Cu(2)-N(5)	99.15(7)	O(2)-Cu(1)-N(3)	93.19(7)
O(4)-Cu(2)-N(6)	93.54(7)	O(2)-Cu(1)-N(2)	98.93(7)
N(5)-Cu(2)-N(6)	159.77(8)	N(3)-Cu(1)-N(2)	160.06(8)
O(4)-Cu(2)-N(4)	169.96(7)	O(2)-Cu(1)-N(1)	169.51(7)
N(5)-Cu(2)-N(4)	82.87(7)	N(3)-Cu(1)-N(1)	82.12(8)
N(6)-Cu(2)-N(4)	82.02(8)	N(2)-Cu(1)-N(1)	83.23(8)
O(4)-Cu(2)-O(1)	96.90(6)	O(2)-Cu(1)-O(1)	98.05(6)
N(5)-Cu(2)-O(1)	89.25(6)	N(3)-Cu(1)-O(1)	106.50(7)
N(6)-Cu(2)-O(1)	104.88(6)	N(2)-Cu(1)-O(1)	87.51(6)
N(4)-Cu(2)-O(1)	92.96(6)	N(1)-Cu(1)-O(1)	92.29(6)
C(1)-O(1)-Cu(2)	115.49(13)	C(1)-O(1)-Cu(1)	116.37(13)
Cu(2)-O(1)-Cu(1)	128.13(7)	C(33)-O(2)-Cu(1)	114.01(14)
C(35)-O(4)-Cu(2)	119.49(14)		

Table S6. Selected bond distances (Å) and angles (°) for compound **5**.

Zn(1)-O(4)	2.014(3)	Zn(2)-O(3)	2.005(3)
Zn(1)-O(2)	2.083(3)	Zn(2)-O(1)	2.013(2)
Zn(1)-N(3)	2.218(3)	Zn(2)-N(5)	2.118(3)
Zn(1)-O(1)	2.040(2)	Zn(2)-O(5)	2.190(3)
Zn(1)-N(2)	2.150(3)	Zn(2)-N(4)	2.219(3)
Zn(1)-N(1)	2.235(3)	Zn(2)-N(6)	2.228(3)
O(1)-C(10)	1.323(4)	O(2)-C(1)	1.245(4)
O(3)-C(1)	1.269(4)	O(4)-C(7)	1.258(4)
O(5)-C(7)	1.254(4)		
O(4)-Zn(1)-O(1)	99.85(10)	O(3)-Zn(2)-O(1)	99.60(10)
O(4)-Zn(1)-O(2)	97.33(11)	O(3)-Zn(2)-N(5)	95.41(11)
O(1)-Zn(1)-O(2)	91.64(10)	O(1)-Zn(2)-N(5)	163.98(11)
O(4)-Zn(1)-N(2)	96.02(11)	O(3)-Zn(2)-O(5)	100.95(10)
O(1)-Zn(1)-N(2)	164.11(11)	O(1)-Zn(2)-O(5)	87.03(10)
O(2)-Zn(1)-N(2)	85.44(11)	N(5)-Zn(2)-O(5)	84.66(11)
O(4)-Zn(1)-N(3)	92.41(12)	O(3)-Zn(2)-N(4)	166.08(11)
O(1)-Zn(1)-N(3)	86.36(11)	O(1)-Zn(2)-N(4)	89.12(11)
O(2)-Zn(1)-N(3)	170.25(11)	N(5)-Zn(2)-N(4)	77.26(12)
N(2)-Zn(1)-N(3)	93.89(11)	O(5)-Zn(2)-N(4)	90.25(11)
O(4)-Zn(1)-N(1)	166.94(11)	O(3)-Zn(2)-N(6)	92.01(11)
O(1)-Zn(1)-N(1)	87.76(10)	O(1)-Zn(2)-N(6)	87.40(10)
O(2)-Zn(1)-N(1)	93.01(11)	N(5)-Zn(2)-N(6)	97.66(11)
N(2)-Zn(1)-N(1)	76.82(11)	O(5)-Zn(2)-N(6)	166.59(10)
N(3)-Zn(1)-N(1)	77.39(11)	N(4)-Zn(2)-N(6)	77.48(11)
C(10)-O(1)-Zn(2)	122.0(2)	C(10)-O(1)-Zn(1)	124.1(2)
Zn(2)-O(1)-Zn(1)	113.71(11)	C(1)-O(2)-Zn(1)	134.3(2)
C(1)-O(3)-Zn(1)	129.9(2)	C(7)-O(4)-Zn(1)	128.1(2)
C(7)-O(5)-Zn(2)	132.2(2)		

Table S7. Selected bond distances (Å) and angles (°) for compound **6**.

Mn(1)-O(4)	2.1803(11)	Mn(2)-O(5)	2.0964(11)
Mn(1)-O(2)	2.0903(11)	Mn(2)-O(1)	2.1216(10)
Mn(1)-N(3)	2.3319(12)	Mn(2)-N(5)	2.2721(12)
Mn(1)-O(1)	2.1150(10)	Mn(2)-O(3)	2.1448(11)
Mn(1)-N(2)	2.2499(12)	Mn(2)-N(4)	2.3352(12)
Mn(1)-N(1)	2.3228(13)	Mn(2)-N(6)	2.2995(12)
O(1)-C(10)	1.323(4)	O(2)-C(33)	1.2660(18)
O(1)-C(1)	1.3303(16)	O(4)-C(35)	1.2571(19)
O(5)-C(35)	1.2615(19)	O(3)-C(33)	1.2556(18)
Cl(1)-C(4)	1.7484(15)		
O(4)-Mn(1)-O(1)	89.66(4)	O(3)-Mn(2)-O(1)	92.84(4)
O(4)-Mn(1)-O(2)	102.58(4)	O(3)-Mn(2)-N(5)	84.94(4)
O(1)-Mn(1)-O(2)	98.89(4)	O(1)-Mn(2)-N(5)	157.35(4)
O(4)-Mn(1)-N(2)	83.85(4)	O(3)-Mn(2)-O(5)	99.10(5)
O(1)-Mn(1)-N(2)	159.26(4)	O(1)-Mn(2)-O(5)	99.19(4)
O(2)-Mn(1)-N(2)	101.74(5)	N(5)-Mn(2)-O(5)	103.43(4)
O(4)-Mn(1)-N(3)	166.89(4)	O(3)-Mn(2)-N(4)	93.89(4)
O(1)-Mn(1)-N(3)	84.58(4)	O(1)-Mn(2)-N(4)	85.01(4)
O(2)-Mn(1)-N(3)	89.96(4)	N(5)-Mn(2)-N(4)	72.69(4)
N(2)-Mn(1)-N(3)	97.46(4)	O(5)-Mn(2)-N(4)	166.10(4)
O(4)-Mn(1)-N(1)	93.60(4)	O(3)-Mn(2)-N(6)	168.35(5)
O(1)-Mn(1)-N(1)	86.40(4)	O(1)-Mn(2)-N(6)	84.60(4)
O(2)-Mn(1)-N(1)	162.95(4)	N(5)-Mn(2)-N(6)	93.04(4)
N(2)-Mn(1)-N(1)	74.41(5)	O(5)-Mn(2)-N(6)	92.52(5)
N(3)-Mn(1)-N(1)	74.33(4)	N(4)-Mn(2)-N(6)	74.59(4)
C(33)-O(3)-Mn(2)	134.61(10)	C(33)-O(2)-Mn(1)	131.80(9)
Mn(2)-O(1)-Mn(1)	109.11(4)	C(1)-O(1)-Mn(1)	124.51(8)
C(1)-O(1)-Mn(2)	126.36(8)	C(35)-O(4)-Mn(1)	134.22(10)
C(35)-O(3)-Mn(2)	130.38(10)		

Table S8. Possible hydrogen bonding system for compounds **1** and **4**

D-H..A[a]	Symmetry of A	D..A (Å)	D-H..A (°)
Compound **1**			
O(6)-H(91)...O(4)		2.923(4)	171
O(7)-H(93)…O(8)		2.835(5)	169
O(7)-H(94)…O(8)	[1-x,1-y,1-z]	2.765(6)	172
O(8)-H(95)…O(3)		2.864(3)	162
O(8)-H(96)....O(6)		2.724(5)	170
Compound **4**			
O(6)-H(1)…O(3)	[1+x,-y,-z]	2.776(3)	162
O(6)-H(2)…O(5)		2.750(3)	166

[a] D = Donor, A = Acceptor

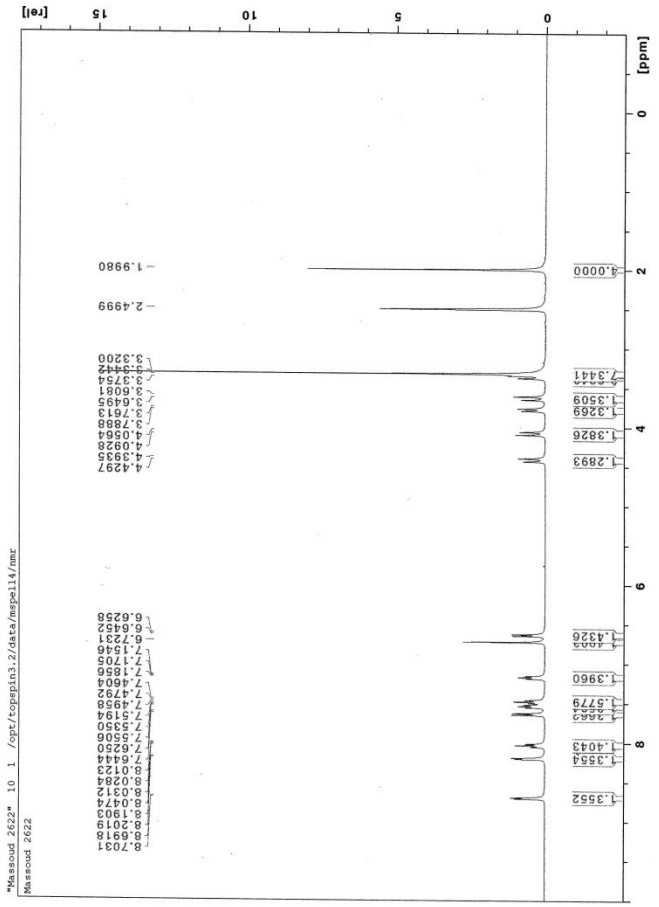


Figure S1. ^{1}H NMR of $[Zn_2(\mu\text{-}L^{Cl}O)(\mu_2\text{-}OAc)_2](PF_6)$ (**5**) in DMSO-d_6.

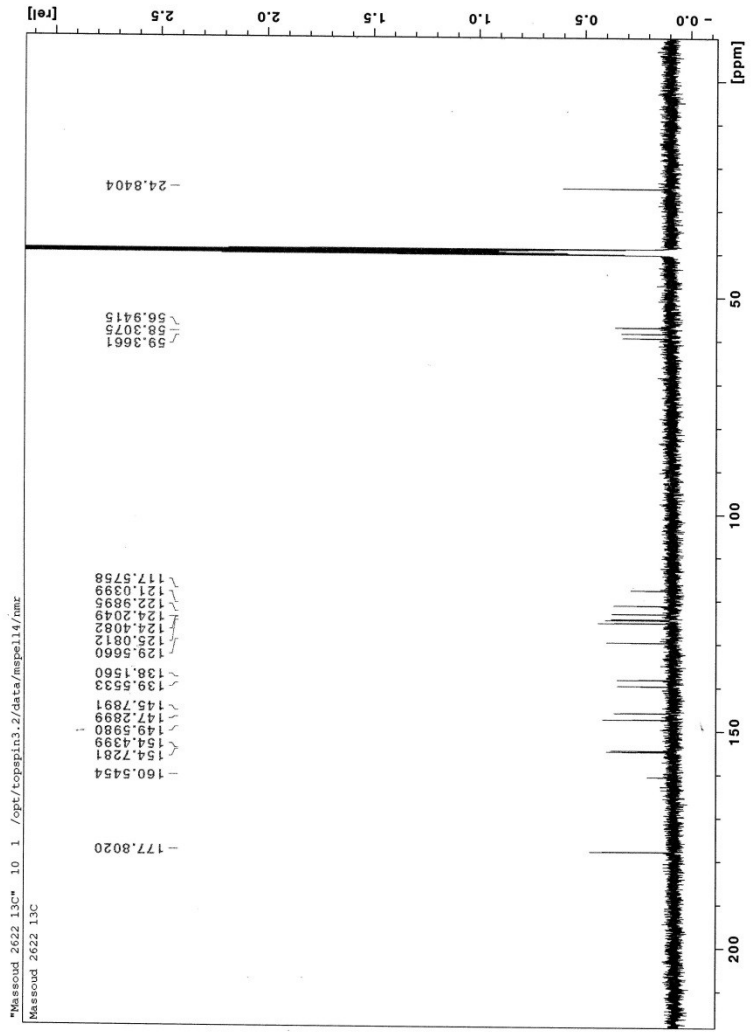
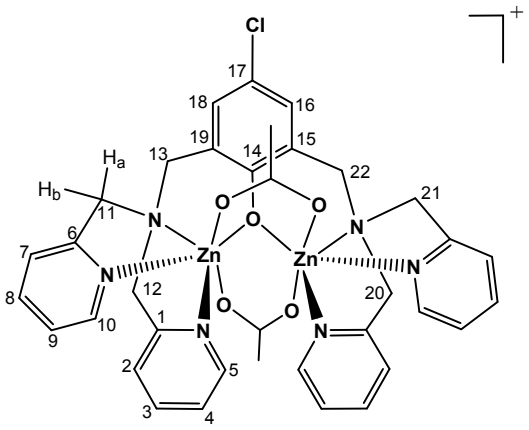


Figure S2. ^{13}C NMR of $[Zn_2(\mu\text{-}L^{Cl}O)(\mu_2\text{-}OAc)_2](PF_6)$ (**5**) in DMSO-d_6.

Chart S1. Structure formula of $[Zn_2(\mu\text{-}L^{Cl}O)(\mu_2\text{-}OAc)_2]^+$ ion and atom numbering scheme (for clarity only the split of the methylene protons at C11 is shown but similar splits also exist at C12, C13, C20 and C21).



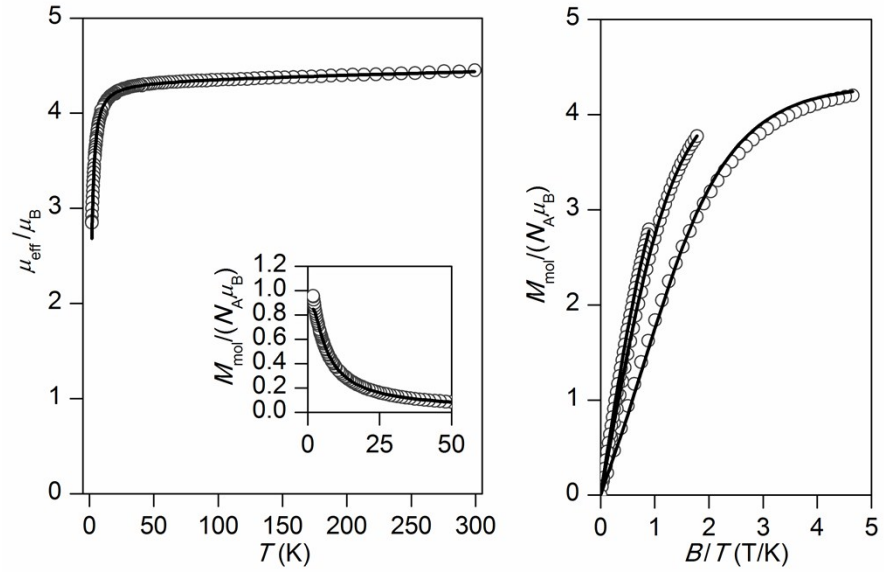


Figure S3. The magnetic data for **2**. *Left*: the temperature dependence of the effective magnetic moment and molar magnetization measured at $B = 1$ T. *Right*: the isothermal magnetizations measured at $T = 2$, 5 and 10 K. Empty circles – experimental data, red full lines – calculated data using the equation 1, with J = -1.20 cm^{-1}, D = +2.80 cm^{-1}, g = 2.17, $\chi_{TIP} = 4.77\text{x}10^{-9}$ m^{3}mol^{-1}.

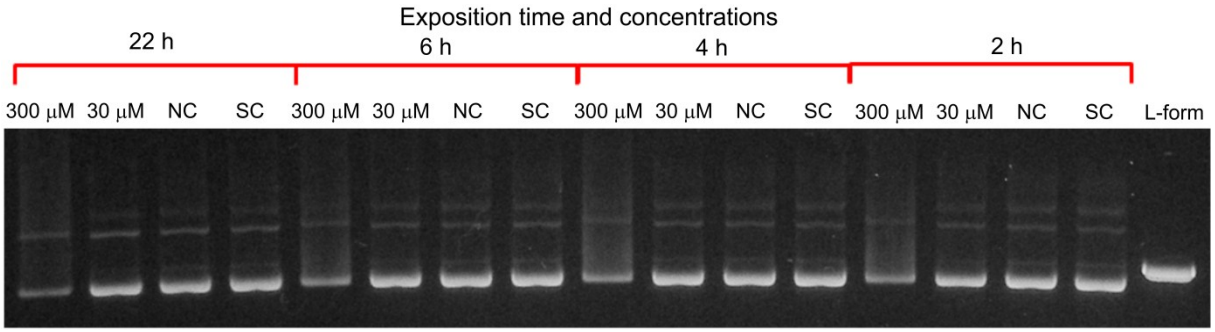


Figure S4. . Agarose gel (in TBE buffer with pH 8.4 at room temperature) electrophoretic pattern for Cu(II) complex **3** showing the effect of incubation time (2-22 h) and complex concentrations (30 and 300 μM) on the native pUC19 plasmid DNA [the calculated concentration of base pairs (bp) = 23 μM]. NC denotes to the negative control, and SC the supercoiled plasmid DNA, and L-form (*right*) represents the sample of native plasmid linearized by *HIndIII* endonuclease.

Isolation of plasmid DNA

The efficiency of metal complexes to act as chemical nucleases was evaluated on pUC19 plasmid (2686 bp). Plasmids were isolated from the transformed bacteria *Escherichia coli* TOP10F' by the QIAprep Spin Miniprep Kit (Qiagen, Hilden, Germany) according to the manufacture's instruction. Plasmids were eluted from the column by nuclease-free ultrapure water. The quantity and purity of isolated DNA was measured spectrophotometrically at 260 nm using ε_{260} = 6600 $M^{-1}cm^{-1}$ (calcd. to base pairs), and the absorbance ratio A_{260}/A_{280} was in the range between 1.75 and 1.85, which confirmed that the DNA was free of proteins.