

Supporting Information

Bioactive Heterometallic Cu^{II}-Zn^{II} Complexes with Potential Biomedical Applications

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EXPERIMENTAL SECTION

Synthesis of the Schiff-base Ligand (N,N'-bis(5-chloro-2-hydroxybenzylidene)-2,2-dimethylpropane-1,3-diamine) (H₂L). This di-Schiff base ligand used for our present work was synthesized according to the standard procedure reported in literature.^{S1} 2 mmol of 5-Chloro salicylaldehyde (0.312 g) was dissolved in 5 mL of methanol to which 1 mmol of N,N'-dimethylethelenediammine (120 µlit) in 5 mL methanolic solution was added in a drop wise

manner. Then the resulting mixture was refluxed for 30 mins and allowed to cool to room temperature. Yellow colored solid product precipitated out from the solution as the desired ligand. It was then filtered, washed with methanol, and dried in a vacuum desiccator.

Preparation of the ‘metalloligand’ [CuL]. 1 mmol of the ligand was dissolved in 10 mL of methanol then to this mixture 5 mL methanolic solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 0.375g) is added in a drop wise manner with constant stirring. Then the solution is filtered and the filtrate is then kept overnight in a calcium chloride dessicator. Deep brown crystals suitable for X-ray data collection were obtained from the filtrate (yield 70%). Elemental analysis calcd (%) for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{Cl}_2\text{Cu}_1$ (440.79): C, 51.72%; H, 4.11%; N, 6.35%; found: C, 51.17%; H, 4.26%; N, 6.19%; FT-IR data (KBr pellet): $\nu(\text{C}=\text{N}) = 1623 \text{ cm}^{-1}$; $\nu(\text{skeletal vibration}) = 1533 \text{ cm}^{-1}$. UV/vis (DMSO): $\lambda_{\text{max}}(\epsilon) = 376(1062 \text{ L mol}^{-1} \text{ cm}^{-1})$.

Synthesis of Complexes. A general stepwise or sequential method was adapted for the synthesis of the heterometallic complexes. Firstly the metalloligand was dissolved in methanol, to which the methanolic solution of the second metal is added followed by addition of the bridging ligand in case of complex **1** and **4**.

Synthesis of Complex [(CuL)₂Zn(dca)₂], (1). 1 mmol of the metalloligand (CuL) (0.44 g) was firstly dissolved in 10 mL of methanol, to which 5mL methanolic solution of 0.5 mmol $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.18 g) was added in a drop wise manner with continuous stirring for 20 mins. To this resulting mixture again 5 mL aqueous solution of 1 mmol sodium dicyanamide (0.09 g) was added. It was then filtered and the filtrate was kept overnight in open atmosphere for evaporation. Light green square shaped crystals appropriate for X-ray diffraction was obtained from the filtrate (yield 65%). Elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{36}\text{N}_{10}\text{O}_4\text{Cl}_4\text{Cu}_2\text{Zn}$ (1079.06): C, 46.70%; H, 3.36%; N, 12.97%; found: C, 46.79%; H, 3.10%; N, 12.11%; FT-IR data (KBr pellet): $\nu(\text{C}=\text{N}) = 1634 \text{ cm}^{-1}$; $\nu(\text{skeletal vibration}) = 1513 \text{ cm}^{-1}$; $\nu(\text{dca}^-) = 2150 \text{ cm}^{-1}$. UV/vis (DMSO): $\lambda_{\text{max}}(\epsilon) = 375(1332 \text{ L mol}^{-1} \text{ cm}^{-1})$.

Synthesis of Complex [(CuL)₂Zn(NO₃)₂], (2). Complex **2** was prepared by same method as that of **1** just by adding 0.5 mmol methanolic solution of $\text{Zn}(\text{NO}_3)_2$ (0.148 g) instead of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Then the resulting mixture was filtered and the filtrate was kept overnight. X-ray quality crystals were obtained from the filtrate (yield 65%). Elemental analysis calcd (%) for

$C_{38}H_{36}N_6O_{11}Cl_4Cu_2Zn$ (1086.98): C, 41.95%; H, 3.33%; N, 7.72%; found: C, 41.09%; H, 3.97%; N, 7.11%; FT-IR data (KBr pellet): ν (C=N) = 1634 cm^{-1} ; ν (skeletal vibration) = 1511 cm^{-1} ; ν (NO_3^-) = 2150 cm^{-1} . UV/vis (DMSO): $\lambda_{max}(\epsilon)$ = 376 (1664 L mol $^{-1}$ cm $^{-1}$).

Synthesis of Complex [(CuL)₂Zn₂(Cl)₄], (3). Complex **3** was also prepared as same method as **1**. Here 0.5 mmole methanolic solution of ZnCl₂ (0.136 g) is added instead of Zn(ClO₄)₂·6H₂O. Then the resulting mixture was filtered and the filtrate was kept overnight. X-ray quality single crystals were obtained from the filtrate (yield 65%). Elemental analysis calcd (%) for $C_{38}H_{36}N_4O_4Cl_8Cu_4Zn_2$ (1154.13): C, 39.51%; H, 3.14%; N, 4.85%; found: C, 39.66%; H, 3.81%; N, 4.25%; FT-IR data (KBr pellet): ν (C=N) = 1647 cm^{-1} ; ν (skeletal vibration) = 1528 cm^{-1} ; UV/vis (DMSO): $\lambda_{max}(\epsilon)$ = 376 (2014 L mol $^{-1}$ cm $^{-1}$).

Synthesis of Complex [(CuL)₂Zn₂(NO₂)₄], (4). Complex **4** was also prepared as similar method to that of **1**. Here 1 mmol aqueous solution of NaNO₂ (0.07 g) is added instead of Na-dca. X-ray quality single crystals were obtained from the filtrate (yield 65%). Elemental analysis calcd (%) for $C_{38}H_{36}N_8O_{12}Cl_4Cu_2Zn_2$ (1196.37): C, 38.11%; H, 3.03%; N, 9.36%; found: C, 38.24%; H, 3.14%; N, 9.47%; FT-IR data (KBr pellet): ν (C=N) = 1638 cm^{-1} ; ν (skeletal vibration) = 1516 cm^{-1} ; ν (NO_2^-) = 1414 cm^{-1} . UV/vis (DMSO): $\lambda_{max}(\epsilon)$ = 376 (2134 L mol $^{-1}$ cm $^{-1}$).

Table S1. Crystallographic Data and Details of Refinements for ML and complexes **1-4**.

	ML	1	2	3	4
empirical formula	C ₁₉ H ₁₈ Cl ₂ CuN ₂ O ₂	C ₄₂ H ₃₆ Cl ₄ Cu ₂ N ₁₀ O ₄ Zn	C ₃₈ H ₃₆ Cl ₄ Cu ₂ N ₆ O ₁₁ Zn	C ₃₈ H ₃₆ Cl ₈ Cu ₂ N ₄ O ₄ Zn ₂	C ₃₈ H ₃₆ Cl ₄ Cu ₂ N ₈ O ₁₂ Zn ₂
fw	440.79	1079.06	1086.98	1154.13	1196.37
cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	<i>P</i> 2 ₁ /n	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ /c
<i>a</i> (Å)	6.9256(3)	10.3783(18)	10.0431(9)	9.7807(16)	10.0800(4)
<i>b</i> (Å)	23.3181(10)	20.893(4)	19.9558(19)	16.605(3)	17.9664(8)
<i>c</i> (Å)	11.7998(5)	10.1906(18)	11.4121(11)	13.616(2)	12.4991(6)
β (°)	103.829(2)	106.224(2)	111.678(3)	90.203(2)	96.773(2)
V/(Å ³)	1850.33(14)	2121.7(6)	2125.4(3)	2211.4(6)	2247.81(17)

Z	4	2	2	2	2
D _{calcd} (mg/m ³)	1.582	1.689	1.698	1.733	1.768
μ (Mo- Kα) (mm ⁻¹)	1.485	1.863	1.869	2.548	2.295
F(000)	900	1092	1100	1156	1204
θ range (°)	1.75 - 27.04	1.95 - 26.56	2.04 - 21.55	1.93 - 26.59	1.99-25.10
collected reflections	22163	14929	17187	15575	24392
indep reflections	3989	4088	2460	4254	3970
R _{int}	0.0522	0.0652	0.0741	0.0453	0.0398
Obs reflections [I> 2σ(I)]	3125	2824	1857	3105	3302
parameters	237	286	285	264	300
R ₁ [I> 2σ(I)] ^[a]	0.0455	0.0452	0.0402	0.0425	0.0330
wR ₂ [I> 2σ(I)] ^[a]	0.1261	0.1111	0.0911	0.1000	0.0826
GOF on F ²	1.033	1.009	1.045	1.042	1.030
residuals (e Å ⁻³)	0.689, - 0.623	0.719, -0.640	0.590, -0.290	1.352, -0.985	0.716, -0.348

$$^{[a]}R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$$

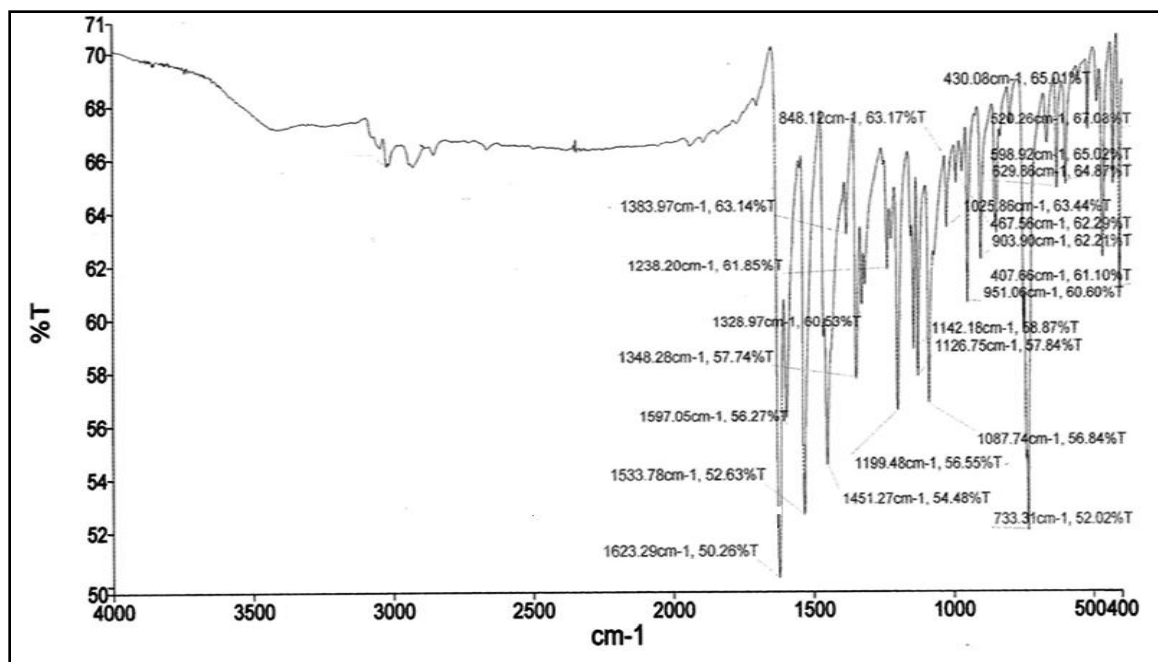


Figure S1. FTIR spectrum of ML.

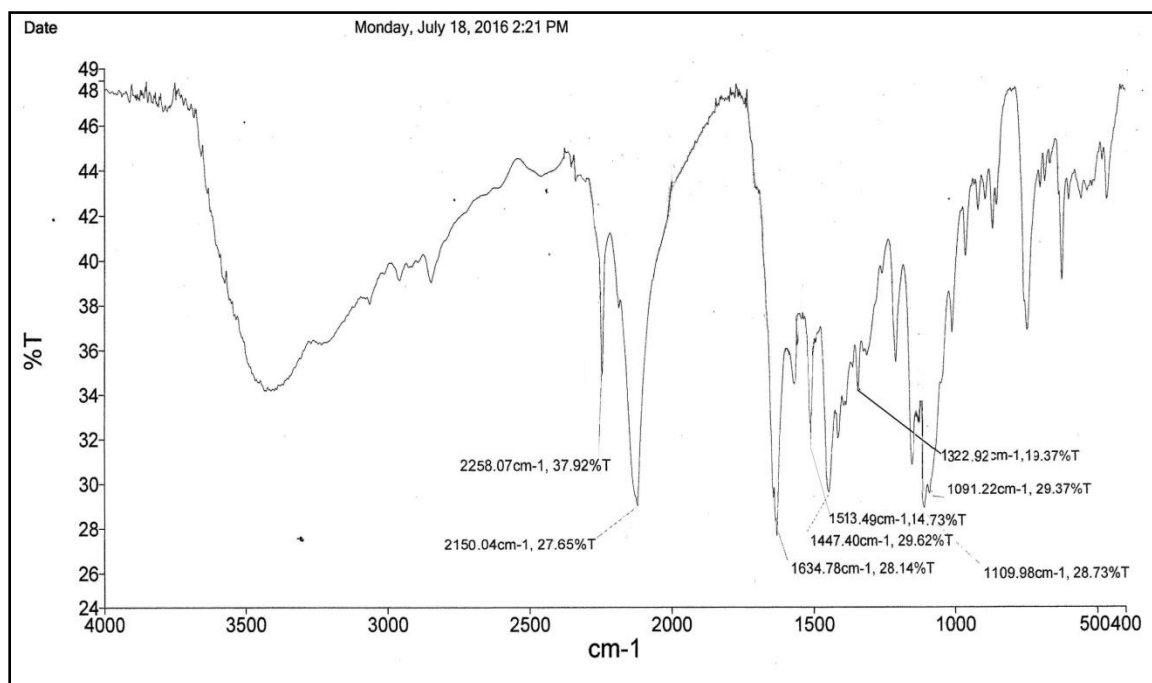


Figure S2. FTIR spectrum of complex 1.

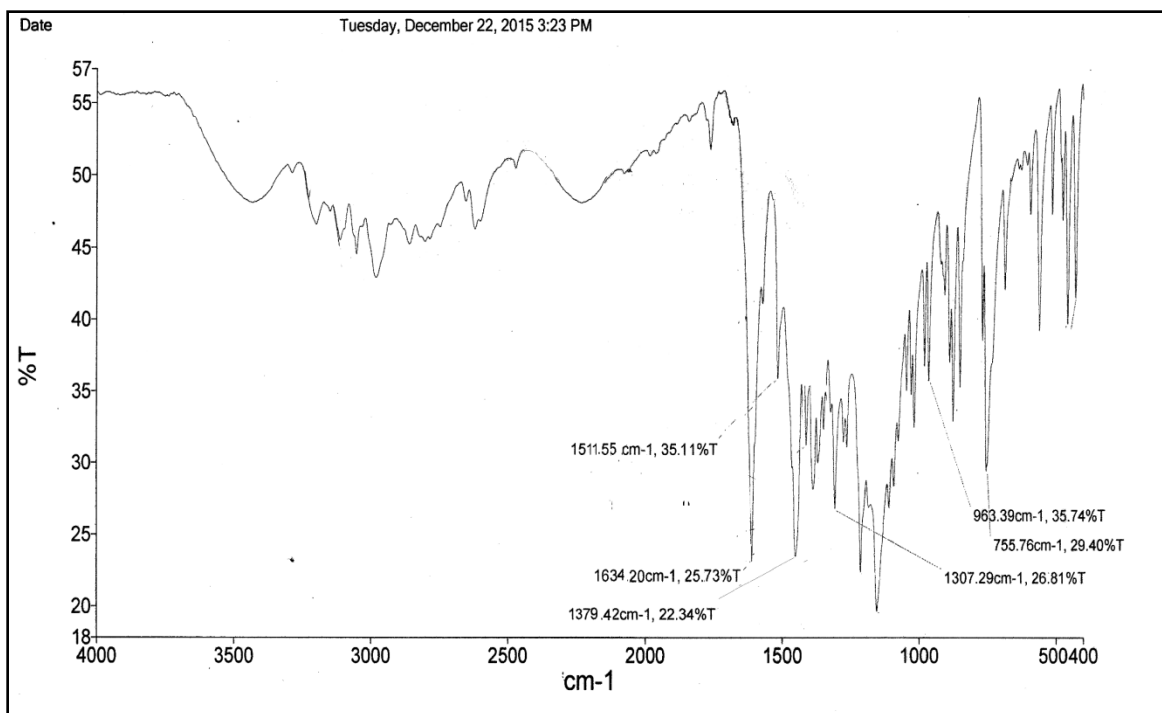


Figure S3. FTIR spectrum of complex **2**.

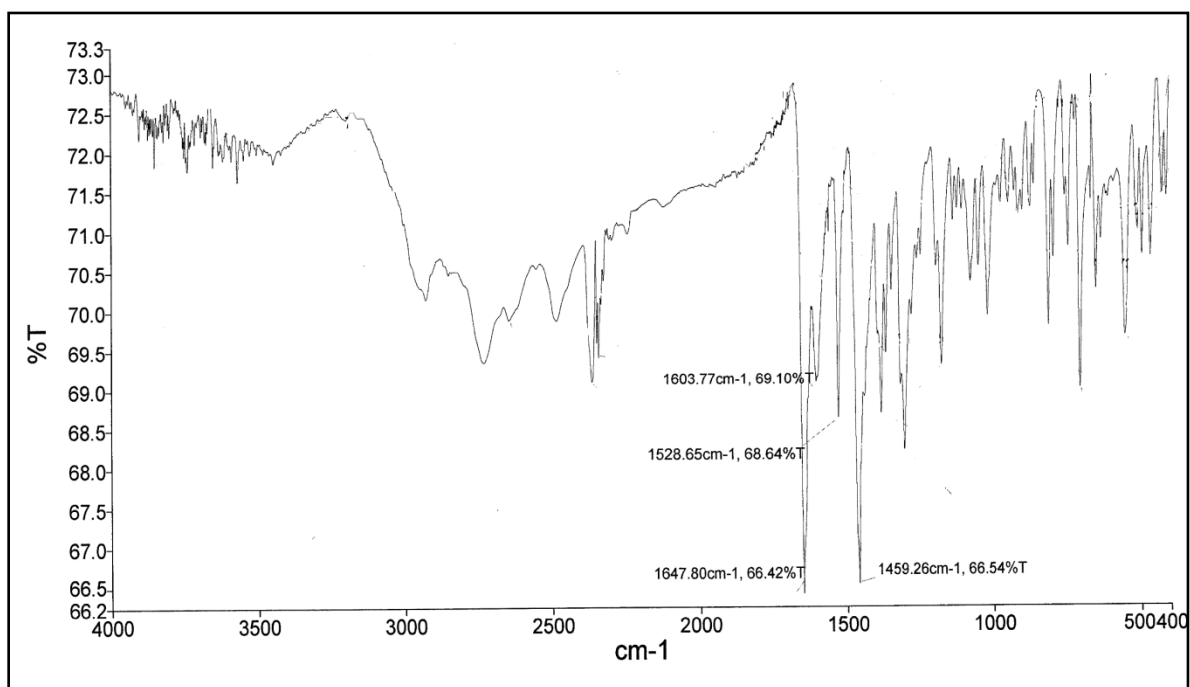


Figure S4. FTIR spectrum of complex **3**.

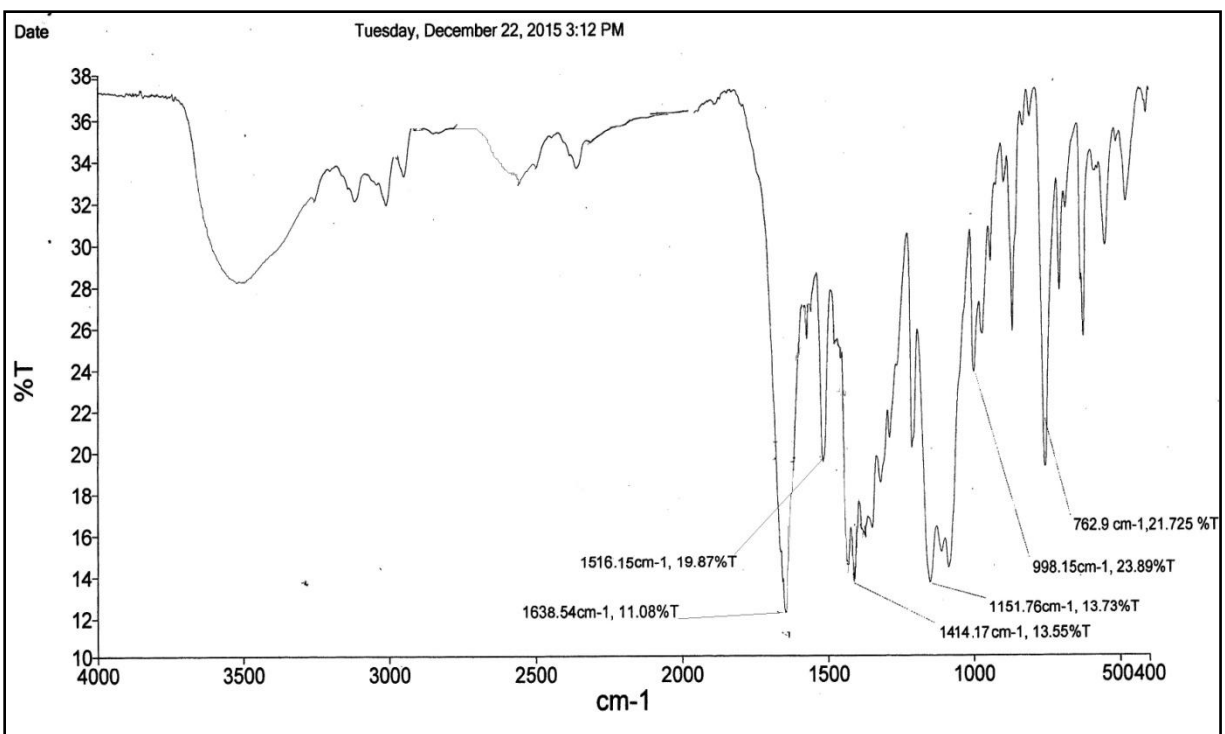


Figure S5. FTIR spectrum of complex 4.

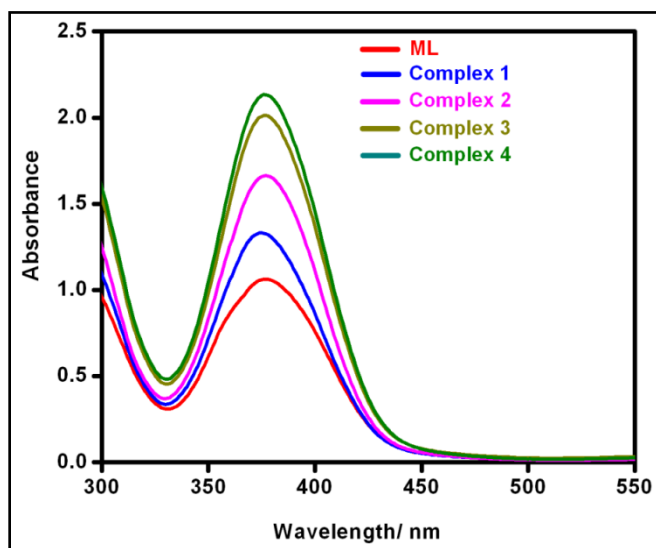


Figure S6. UV-VIS spectra of ML and Complexes 1-4 in DMSO.

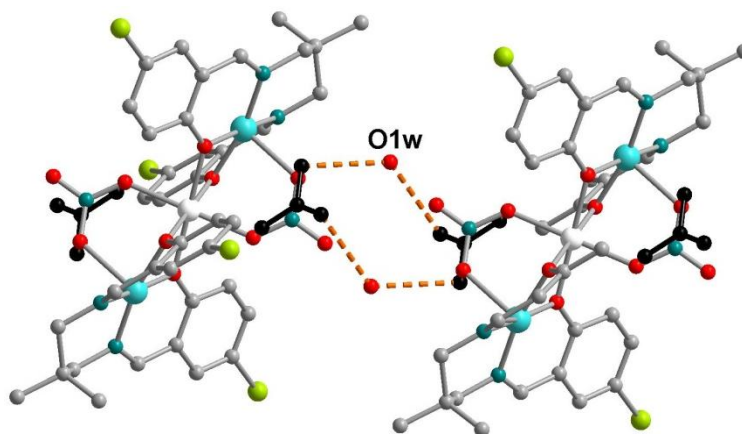


Figure S7. The picture displays the disordered nitrate anions in compound **2**: the species depicted in black (N3b/O3b/O4b/O5b), which is loosely bound to the Zn ion, forms a H-bonding scheme with the lattice water Ow1.

Table S2. Coordination Bond Lengths (Å) and Angles (deg) for complex **ML**.

Cu-O(1)	1.905(2)	Cu-N(1)	1.947(3)
Cu-O(2)	1.903(2)	Cu-N(2)	1.953(3)
O(1)-Cu-O(2)	85.85(10)	O(2)-Cu-N(1)	174.06(12)
N(1)-Cu-N(2)	91.82(11)	O(1)-Cu-N(2)	174.14(11)
O(1)-Cu-N(1)	91.22(10)	O(2)-Cu-N(2)	91.56(10)

Table S3. Coordination bond lengths (Å) and angles (°) for complex **1**.

Cu-O(1)	1.962(3)	Zn-O(1)	2.183(3)
Cu-O(2)	1.962(3)	Zn-O(2)	2.177(3)
Cu-N(1)	1.982(3)	Zn-N(3)	2.031(4)
Cu-N(2)	1.983(3)	Cu-Zn	3.1891(8)
Cu-N(5)#1	2.479(5)		
O(2)-Cu-O(1)	81.87(11)	N(1)-Cu-N(2)	92.83(13)
O(2)-Cu-N(1)	170.62(13)	O(1)-Cu-N(5')	109.80(14)
O(1)-Cu-N(1)	91.10(12)	O(2)-Cu-N(5')	99.10(14)
O(2)-Cu-N(2)	92.17(12)	N(1)-Cu-N(5')	89.09(15)
O(1)-Cu-N(2)	162.98(12)	N(2)-Cu-N(5')	86.83(15)

N(3)-Zn-N(3'')	180.0	N(3)-Zn-O(2)	90.71(13)
O(1)-Zn-O(1'')	180.0	N(3)-Zn-O(1'')	88.50(12)
O(2)-Zn-O(2'')	180.0	N(3)-Zn-O(1)	91.50(12)
O(2)-Zn-N(3'')	89.29(13)	O(2)-Zn-O(1)	72.27(9)
		O(1)-Zn-O(2'')	107.73(9)

Symmetry transformations used to generate equivalent atoms: (') x,y,z-1; (") -x, -y, -z+1.

Table S4. Coordination bond lengths (Å) and angles (°) for complex **2**.

Cu-O(1)	1.954(3)	Zn-O(1)	2.068(3)
Cu-O(2)	1.936(3)	Zn-O(2)	2.045(3)
Cu-N(1)	1.951(4)	Zn-O(4)	2.084(10)
Cu-N(2)	1.966(4)	Zn-O(4b)	2.279(11)
Cu-O(3)	2.356(11)	Cu-Zn	3.0178(6)
Cu-O(3b)	2.323(12)		
O(1)-Cu-O(2)	81.50(15)	O(2)-Cu-N(2)	92.59(17)
N(1)-Cu-N(2)	95.11(18)	O(1)-Cu-O(3)	92.0(3)
O(1)-Cu-N(1)	90.34(16)	O(2)-Cu-O(3)	87.6(3)
O(1)-Cu-N(2)	167.95(17)	N(1)-Cu-O(3)	94.4(3)
O(2)-Cu-N(1)	171.65(17)	N(2)-Cu-O(3)	98.2(3)
O(1)-Zn-O(1')	180.0	O(1)-Zn-O(4)	88.3(3)
O(2)-Zn-O(2')	180.0	O(1)-Zn-O(4')	91.7(3)
O(4)-Zn-O(4')	180.0	O(2)-Zn-O(4)	97.1(3)
O(1)-Zn-O(2)	76.26(13)	O(2)-Zn-O(4')	82.9(3)
O(1)-Zn-O(2')	103.74(13)		

Primed atoms at -x+2,-y,-z+2. Bond angles involving atoms O(3b) and O(4b), pertaining to the second fragment of the disordered nitrate anion, not reported.

Table S5. Coordination bond lengths (Å) and angles (°) for complex **3**.

Cu-O(1)	1.929(3)	Zn-O(1)	1.990(3)
Cu-O(2)	1.939(3)	Zn-O(2)	1.999(3)

Cu-N(1)	1.975(3)	Zn-Cl(3)	2.1929(12)
Cu-N(2)	1.935(4)	Zn-Cl(4)	2.2057(12)
Cu-Cl(4')	2.8484(15)	Cu-Zn	3.0526(8)
O(1)-Cu-O(2)	79.43(12)	O(2)-Cu-N(2)	92.06(14)
N(1)-Cu-N(2)	97.47(15)	O(1)-Cu-Cl(4')	87.01(9)
O(1)-Cu-N(1)	92.82(13)	O(2)-Cu-Cl(4')	111.75(9)
O(1)-Cu-N(2)	168.62(14)	N(1)-Cu-Cl(4')	84.25(9)
O(2)-Cu-N(1)	161.54(14)	N(2)-Cu-Cl(4')	89.19(12)
O(1)-Zn-O(2)	76.56(11)	O(1)-Zn-Cl(4)	118.98(9)
O(1)-Zn-Cl(3)	112.50(9)	O(2)-Zn-Cl(4)	110.56(10)
O(2)-Zn-Cl(3)	120.12(10)	Cl(3)-Zn-Cl(4)	113.55(5)

Primed atom at 1-x, -y, 1-z.

Table S6. Coordination bond lengths (Å) and angles (°) for complex **4**.

Cu-N(1)	1.937(3)	Zn-O(1)	2.030(2)
Cu-N(2)	1.979(3)	Zn-O(2)	2.018(2)
Cu-O(1)	1.951(2)	Zn-O(3)	2.223(3)
Cu-O(2)	1.925(2)	Zn-O(4)	2.171(3)
Cu-O(3')	2.593(3)	Zn-O(5)	2.160(3)
Cu-Zn	3.0709(5)	Zn-O(6)	2.143(3)
O(1)-Cu-O(2)	80.27(9)	O(2)-Cu-N(2)	92.73(10)
N(1)-Cu-N(2)	95.33(11)	O(1)-Cu-O(3')	99.20(9)
O(1)-Cu-N(1)	93.19(10)	O(2)-Cu-O(3')	83.69(9)
O(1)-Cu-N(2)	163.11(11)	N(1)-Cu-O(3')	90.76(10)
O(2)-Cu-N(1)	170.61(10)	N(2)-Cu-O(3')	95.26(10)
O(3)-Zn-O(4)	56.07(10)	O(2)-Zn-O(3)	97.36(9)
O(5)-Zn-O(6)	57.67(12)	O(2)-Zn-O(4)	152.37(10)
O(1)-Zn-O(2)	76.23(8)	O(2)-Zn-O(5)	96.77(10)
O(1)-Zn-O(3)	111.58(10)	O(2)-Zn-O(6)	117.93(11)
O(1)-Zn-O(4)	104.82(10)	O(3)-Zn-O(6)	138.99(11)
O(1)-Zn-O(5)	147.75(11)	O(3)-Zn-O(5)	100.47(11)
O(1)-Zn-O(6)	97.36(11)	O(4)-Zn-O(5)	95.72(11)
		O(4)-Zn-O(6)	89.53(12)

Primed atom at 1-x, 2-y, -z.

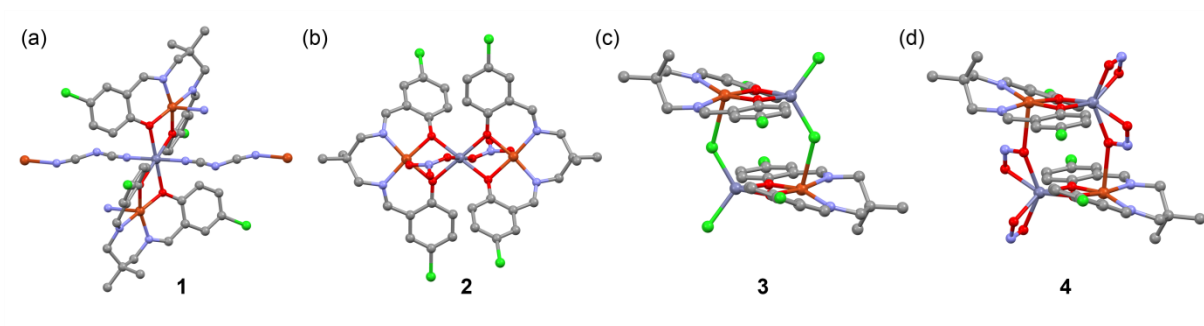


Figure S8. X-ray structures of compounds **1–4**.

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(S1) Karakas, A.; Elmali, A.; Yahsi, Y.; Kara, H. Third-order Nonlinear Optic and Optical Limiting Properties of a Mn(III) Transition Metal Complex. *J. Nonlinear Opt. Phys. Mater.* **2007**, *16*, 505.