Synthesis, X-ray, Hirshfeld, and AIM studies on Zn(II) and Cd(II) complexes with pyridine ligands

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Method S1 Crystal structure determination

The crystal structures of the studied complexes were determined using a Bruker APEX II diffractometer using graphite monochromated MoKα radiation. SADABS was used for absorption corrections [74], and all calculations were performed using the SHELXTL program package [75]. The positions of the heavy atoms were detected by the direct methods of SHELXS. The hydrogen atoms bonded to carbon atoms were refined according to the riding model implemented in SHELX. The hydrogen atoms in the crystal structure bonded to oxygen were refined with DFIX restraints and with a fixed thermal parameter at a value of 1.5 times the displacement parameters of the respective oxygen atoms. Details regarding the crystallographic measurements are included in **Table S1**.

Table S1 Crystallographic details of complexes **1–3**.

CCDC	2162606	21626067	2162608
Empirical formula	$C_{16}H_{18}Cl_2N_2O_4Zn$	$C_{10}H_{24}N_2O_{10}SZn$	$C_{16}H_{22}CdN_4O_4$
Formula weight	438.59 g/mol	429.74 g/mol	446.77 g/mol
Temperature/K	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P\ 2_1\ 2_1\ 2_1$	$P2_1/n$
a/Å	14.1940(9)	7.6541(3)	8.4025(4)
b/Å	19.8380(11)	9.9244(4)	17.1565(15)
c/Å	14.3957(9)	23.1526(10)	12.9867(9)
α/°	90	90°	90
β/°	111.432(3)	90°	94.661(3)
γ/°	90	90°	90
Volume	3773.3(4) $Å^3$	1758.73(12) $Å^3$	1865.9(2) $Å^3$
Z	8	4	4
Density (calculated)	1.544 g/cm^3	1.623 g/cm^3	1.590 g/cm^3
Absorption coefficient	1.607 mm^{-1}	1.566 mm^{-1}	1.197 mm^{-1}
F(000)	1792	896	904
Crystal size	0.07 x 0.11 x 0.17 mm^3	0.26 x 0.29 x 0.31 mm^3	0.10 x 0.20 x 0.27 mm^3
Theta range for data collection	1.83 to 27.50°	2.23 to 33.20°	2.71 to 33.21°
Index ranges	$-18 \le h \le 18$, $-23 \le k \le 25$, $-18 \le l \le 18$	$-11 \le h \le 11$, $-15 \le k \le 15$, $-24 \le l \le 35$	$-12 \le h \le 12$, $-26 \le k \le 26$, $-19 \le l \le 20$
Reflections collected	63161	42805	48272
Independent reflections	8539 (R(int) = 0.0625)	6683 (R(int) = 0.0339)	7115 (R(int) = 0.0366)
Completeness to θ = 66.67°	98.50%	99.90%	99.70%
Absorption correction	Multiscan	Multiscan	Multiscan
Max. and min. transmission	0.8960 and 0.7720	0.6860 and 0.6420	1.000 and 0.9216
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	8539 / 0 / 455	6683 / 9 / 281	7115 / 0 / 246
Goodness of fit on F^2	1.08	1.068	1.025
Final R indices (I >2sigma(I))	R1 = 0.0362, wR2 = 0.0810	R1 = 0.0178, wR2 = 0.0458	R1 = 0.0162, wR2 = 0.0421
R indices (all data)	R1 = 0.0852, wR2 = 0.1112	R1 = 0.0183, wR2 = 0.0459	R1 = 0.0179, wR2 = 0.0431
Largest diff. peak and hole	0.873 and -0.881	0.626 and -0.591	0.554 and -0.345

Table S2 Hydrogen bond parameters (Å, °) in **1**.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)	Symm. Code
C7-H7A···O5	0.99	2.58	3.076(5)	111	1+x,1/2-y,1/2+z
C31-H31B···O4	0.99	2.55	3.055(6)	111	1+x,1/2-y,1/2+z

Table S3 AIM topology parameters (a.u.) at bond critical points (BCPs) as well as the bond distances of the coordinated bonds in complexes **1, 2,** and **3**.

Atoms	BD	ϱ	G(r) [a]	V(r) [b]	H(r)	$\nabla^2\varrho$
			Complex **1** (Zn1 unit)			
Zn1-Cl2	2.2225	0.0506	0.0995	-0.1062	-0.0067	0.3715
Zn1-Cl1	2.2243	0.0503	0.0989	-0.1056	-0.0066	0.3692
Zn1-N3	2.0580	0.0636	0.1195	-0.1322	-0.0127	0.4274
Zn1-N4	2.0566	0.0639	0.1203	-0.1331	-0.0128	0.4302
			(Zn2 unit)			
Zn2-Cl3	2.2224	0.0506	0.0997	-0.1064	-0.0067	0.3718
Zn2-Cl4	2.2256	0.0502	0.0985	-0.1051	-0.0066	0.3674
Zn2-N1	2.0607	0.0633	0.1187	-0.1313	-0.0126	0.4246
Zn2-N2	2.0590	0.0636	0.1194	-0.1320	-0.0127	0.4267
			Complex **2** (Part A)			
Zn1-O9	2.1283	0.0473	0.0838	-0.0911	-0.0073	0.3060
Zn1-O2	2.1145	0.0476	0.0853	-0.0925	-0.0072	0.3127
Zn1-O4	2.0657	0.0529	0.1009	-0.1082	-0.0073	0.3744
Zn1-O3	2.0797	0.0508	0.0948	-0.1015	-0.0067	0.3525
Zn1-O5	2.1011	0.0472	0.0872	-0.0931	-0.0059	0.3252
Zn1-N1	2.1388	0.0568	0.0937	-0.1072	-0.0135	0.3207
			(Part B)			
Zn1-O9	2.1283	0.0473	0.0837	-0.0910	-0.0073	0.3058
Zn1-O2	2.1145	0.0476	0.0853	-0.0924	-0.0072	0.3125
Zn1-O4	2.0657	0.0529	0.1008	-0.1080	-0.0073	0.3741
Zn1-O3	2.0797	0.0508	0.0947	-0.1014	-0.0067	0.3522
Zn1-O5	2.1011	0.0474	0.0878	-0.0939	-0.0061	0.3266
Zn1-N1	2.1388	0.0567	0.0936	-0.1070	-0.0133	0.3212
			Complex **3**			
Cd1-O1	2.2993	0.0454	0.0768	-0.0799	-0.0032	0.2946
Cd1-O2	2.4483	0.0308	0.0485	-0.0481	0.0005	0.1960
Cd1-O3	2.3813	0.0363	0.0594	-0.0599	-0.0005	0.2356
Cd1-O4	2.3355	0.0423	0.0692	-0.0719	-0.0027	0.2660
Cd1-N1	2.3210	0.0512	0.0782	-0.0845	-0.0063	0.2877
Cd1-N2	2.2723	0.0578	0.0905	-0.0998	-0.0093	0.3248

[a] V(r) is the potential energy density and [b] G(r) is the kinetic energy density.

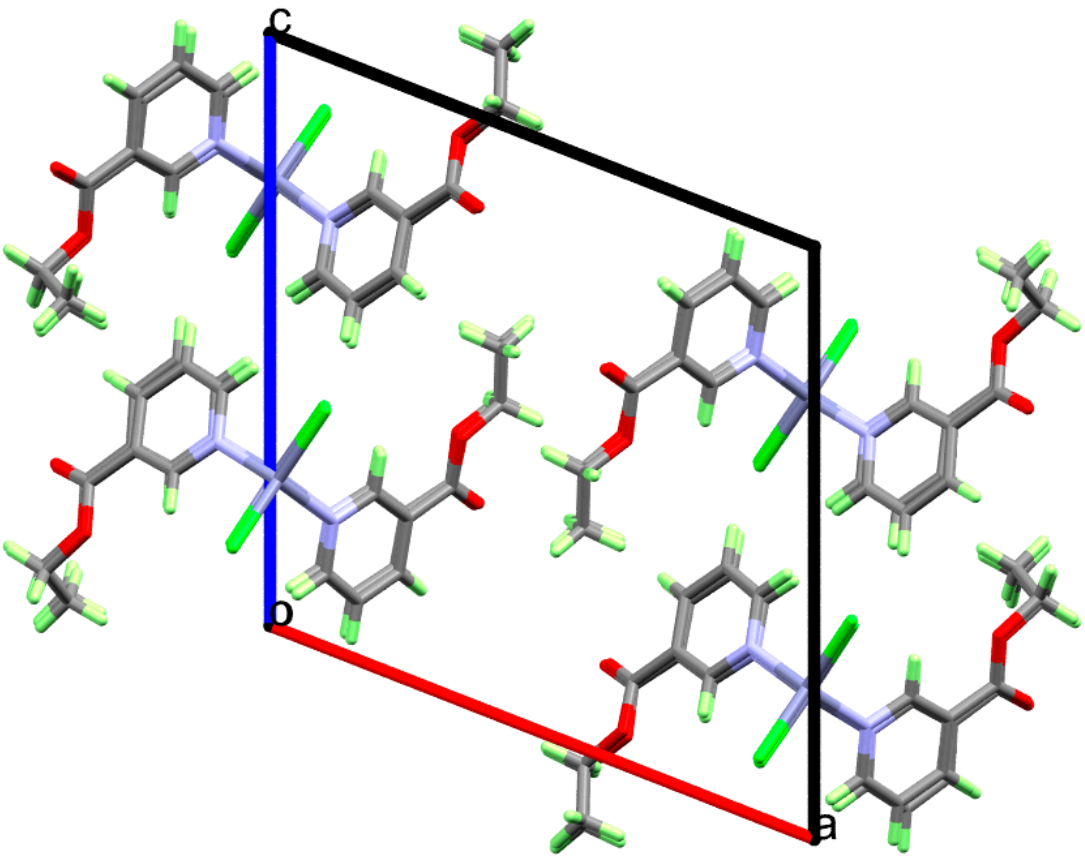

Figure S1 View of the unit cell of **1** along the *ac* plane.

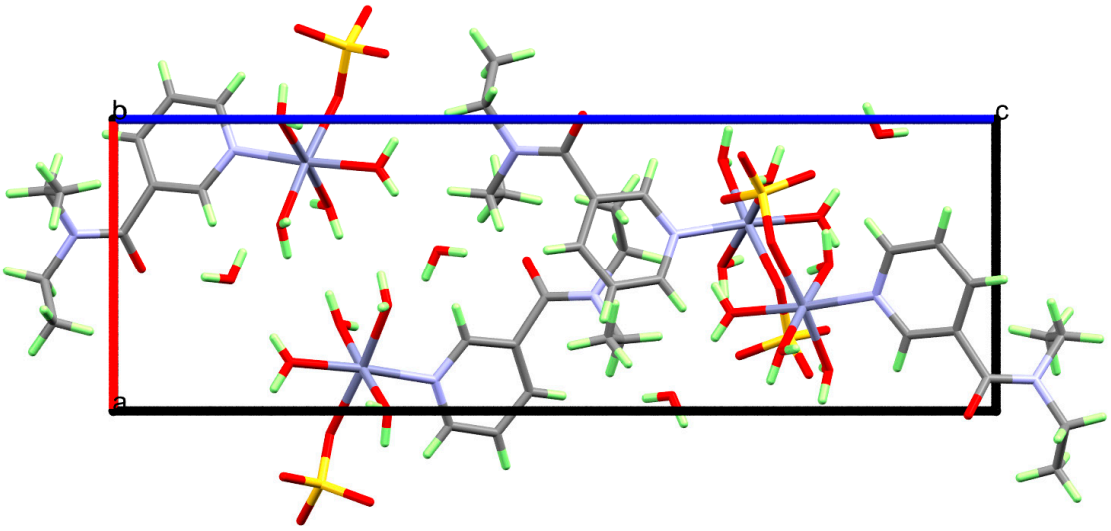

Figure S2 View of the unit cell of **2** along the *ac* plane.

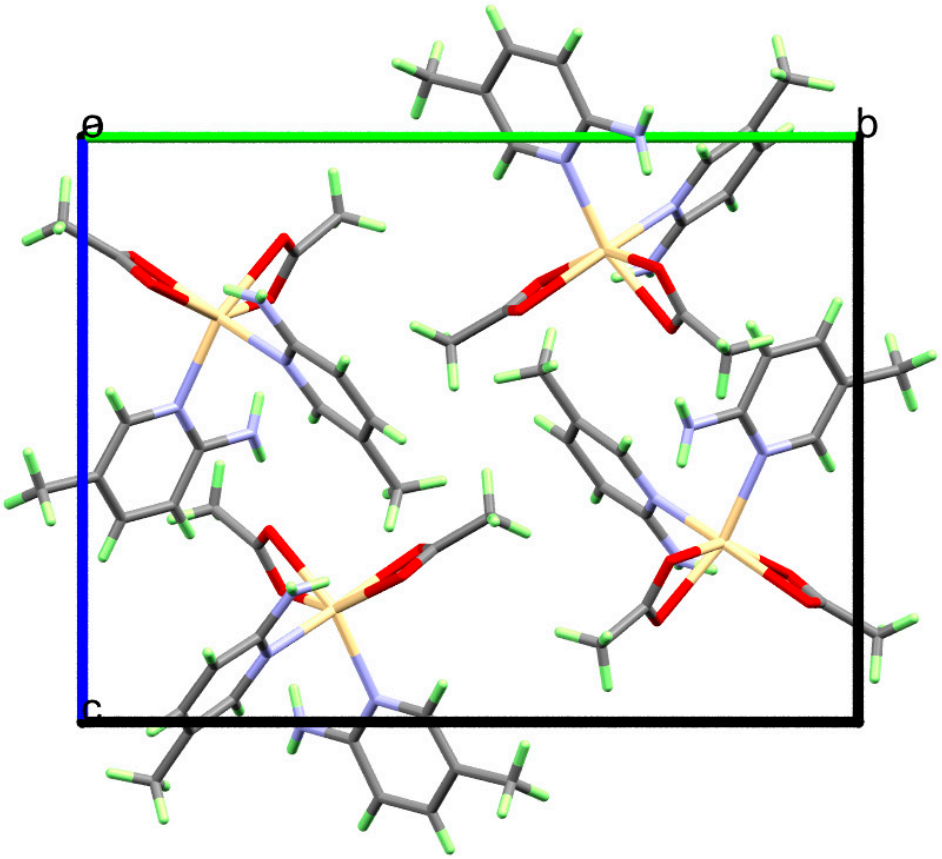

Figure S3 View of the unit cell of **3** along the *bc* plane.

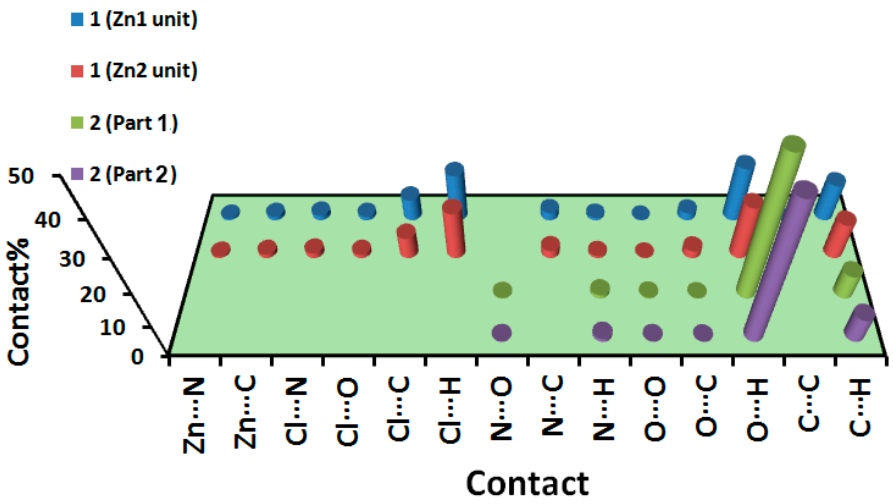

Figure S4 Distribution of all contacts in complexes **1** and **2**.

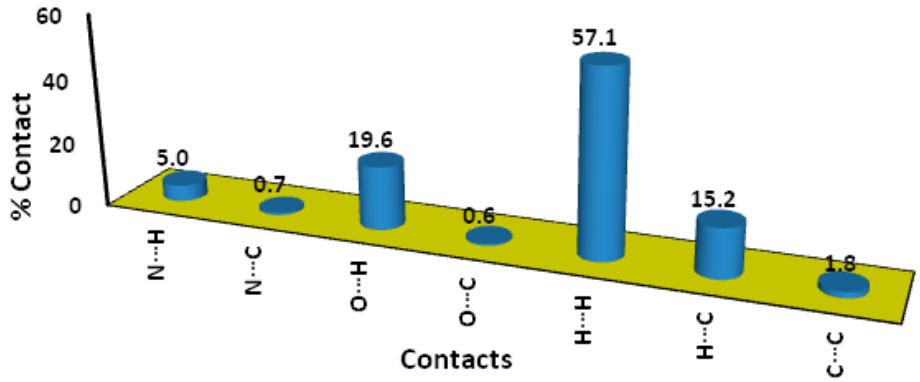

Figure S5 Intermolecular interactions in **3** and their percentages.