The crucial role of hydrogen bonding in shaping the structures of zinc-based coordination polymers using tridentate N,N,O donor reduced Schiff base ligands and bridging acetates

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Hirshfeld surface analysis

Crystal Explorer 21.5[S1] software has been used to calculate Hirshfeld surfaces[S2-S4] and the related two-dimensional fingerprint plots.[S5,S6] The bond lengths to hydrogen atoms have been set to standard values. The distance from the point to the nearest nucleus external to the surface (d_e) and the distance to the nearest nucleus internal to the surface (d_i) are defined for each point on the Hirshfeld surface to calculate the normalized contact distance (d_{norm}) using the appropriate formula.[S7]

The d_{norm} value may be less than zero or more than zero depending on the relative values of intermolecular contacts and van der Waals separations. The Hirshfeld surface with a red-white-blue colour scheme is displayed with the d_{norm} parameter. Shorter contacts are indicated by the bright red spots. White areas represent contacts around the van der Waals separation and blue regions, on the other hand, signify absence of any close contacts. It is needless to say that the Hirshfeld surface is unique for a given CIF.[S8]

The details of crystallographic data and refinements have been given in Table **S1**. Important bond lengths and angles have been listed in Tables **S2** and **S3**, respectively. The details of the IR bands are gathered in Table S4 (**SI**).

Experimental Section

Synthesis of ligands

HL^1 {4-chloro-2-(((2-(methylamino)ethyl)amino)methyl)phenol}

A methanol solution (10 mL) of *N*-methyl-1,2-diaminoethane (~1 mmol, 0.09 mL) and 5-chlorosalicylaldehyde (~1 mmol, 157 mg) was refluxed for ca. 2 h to prepare a tridentate Schiff base, [4-chloro-2-(((2-(methylamino)ethyl)imino)methyl)phenol]. The methanol solution (10 mL) of the Schiff base was then cooled to 0°C and solid sodium borohydride (~2 mmol, 76 mg) was added to it slowly with constant stirring.[S9] Then the resulting solution was acidified with glacial acetic acid (1 mL) with constant stirring for 10 minutes. The solution was evaporated to dryness under reduced pressure in a rotary evaporator (the temperature was fixed to ~60°C). The residue was dissolved in water (5 mL) and extracted with dichloromethane (5 mL) using a separating funnel. A little amount of sodium bicarbonate solution was added to neutralize extra acids, if any. The organic phase was dried over anhydrous sodium acetate and then dichloromethane was evaporated under reduced pressure using a rotary evaporator to give the 'reduced Schiff base' ligand, HL^1 as the final product. It was not further purified, but was used directly for the preparation of complex **1**.

HL^2 {2,4-dibromo-6-(((3-(methylamino)propyl)amino)methyl)phenol}

HL^2 was synthesized in a similar procedure to that of HL^1, except *N*-methyl-1,3-propanediamine and 3,5-dibromosalicylaldehyde were used instead of N-methyl-1,2-diamine and 5-chlorosalicylaldehyde.[S10]

Electronic and Emission Spectra

Electronic spectra of complexes **1** and **2** have been recorded in acetonitrile. There are only three bands in the UV-vis spectra of complexes **1** and **2**. The bands at 212 and 209 nm may be attributed as $\pi\rightarrow\pi^*$ transition of complexes **1** and **2** respectively.[S11, S12] The bands 239 at 248 nm may be attributed to the $n\rightarrow\pi^*$ transition of complexes **1** and **2** respectively.[S12] The bands at ~292 and ~308 nm may be assigned as LMCT transition of complexes **1** and **2** respectively.[S13, S14] There is no band corresponding to d–d electronic transitions, as expected for zinc(II) complexes with d^{10} electronic configuration.[S15] The UV spectra of the complexes **1** and **2** is shown in Figs. **S5** and **S6** respectively.

Upon excitation of at 292 nm in acetonitrile solution, complex **1** shows strong emission around 329 nm. Emission of the complex may be tentatively attributed to the intra-ligand transitions modified by metal coordination. The fluorescence spectrum of complex **1** is shown in **Fig. S7**.

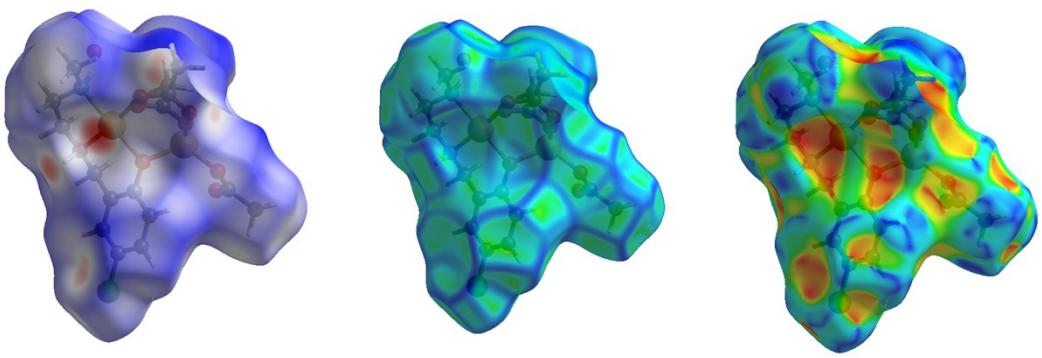

Fig S1. Hirshfeld surfaces of the complex **1** mapped over d_{norm} (left), curvedness (middle) and shape index (right).

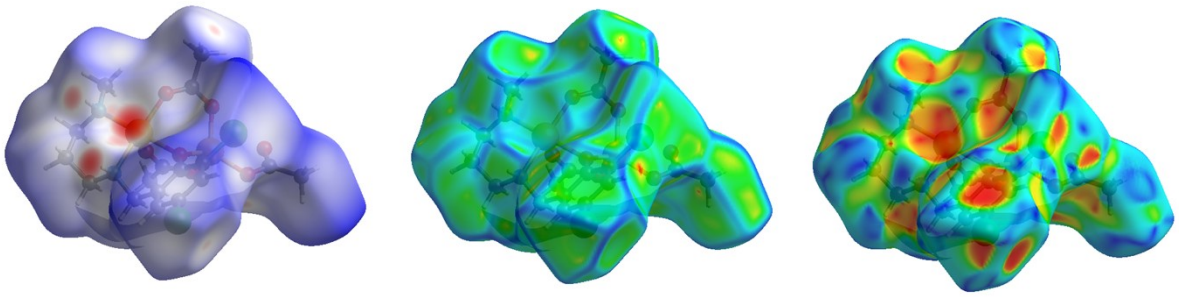

Fig S2. Hirshfeld surfaces of the complex **2** mapped over d_{norm} (left), curvedness (middle) and shape index (right).

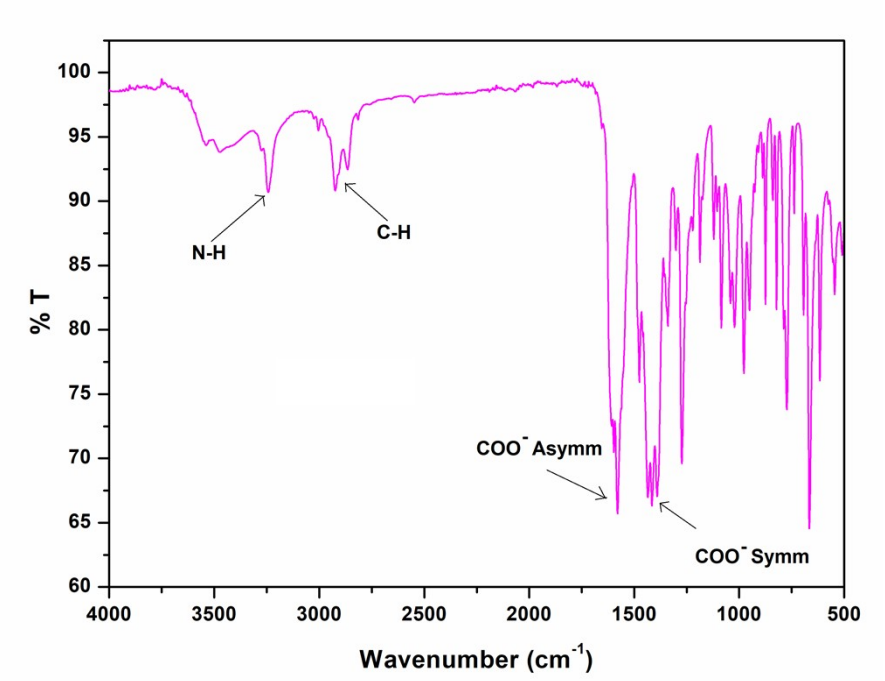

Fig. S3. IR spectrum of complex **1**.

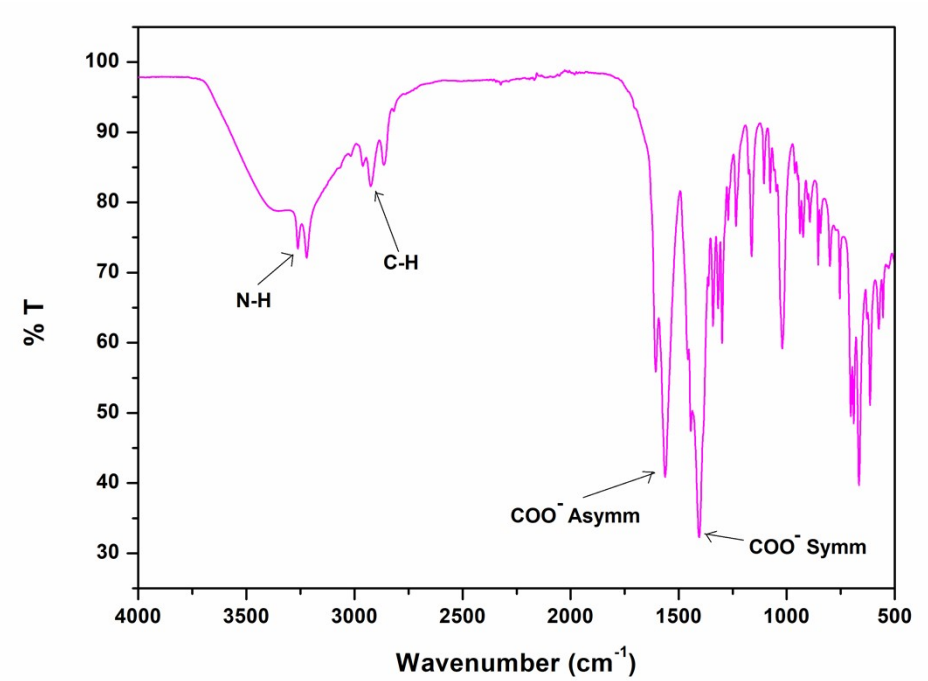

Fig. S4. IR spectrum of complex **2**.

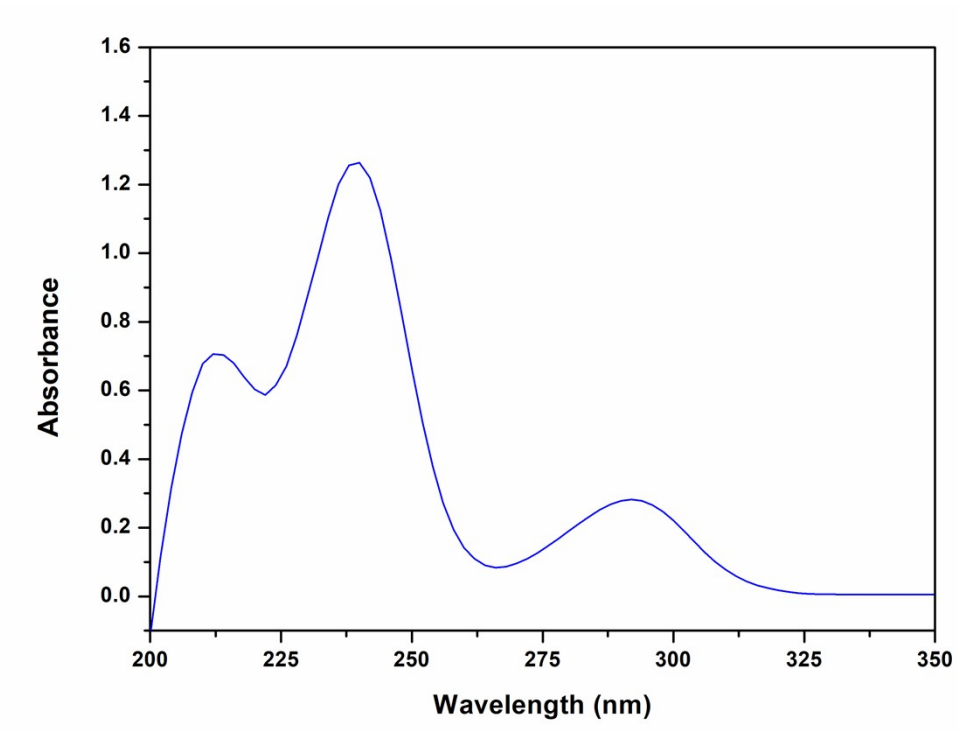

Fig. S5. UV spectrum of the complex **1**.

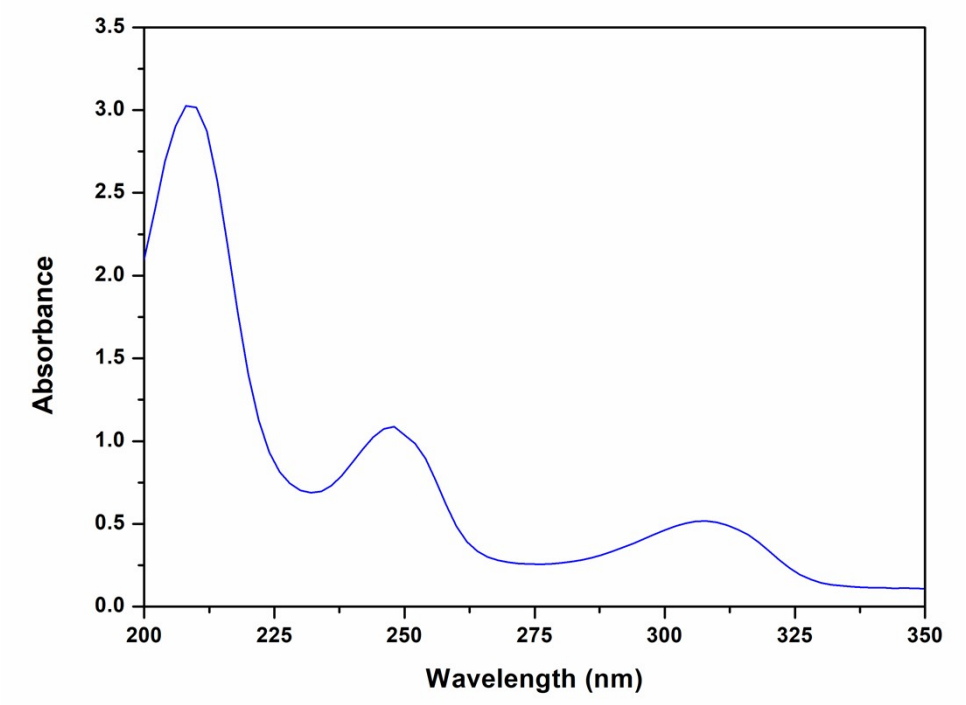

Fig. S6. UV spectrum of the complex **2**.

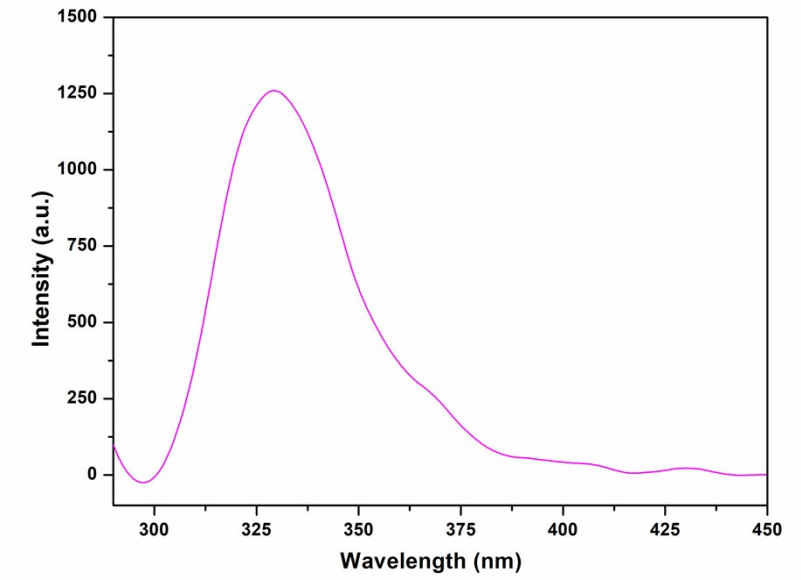

Fig. S7. Fluorescence spectrum of the complex **1**.

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Table S1: Crystal data and refinement details of complexes **1** and **2**.

Complex	**1**	**2**
Formula	$C_{16}H_{23}ClN_2O_8Zn_2$	$C_{17}H_{24}Br_2N_2O_7Zn_2$
Formula Weight	537.59	658.96
Temperature (K)	273	293(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	*Fdd2*	*Aba2*
a(Å)	25.653(16)	14.662(8)
b(Å)	38.97(2)	16.055(9)
c(Å)	8.972(6)	21.525(13)
Z	16	8
V(Å^3)	8969(9)	5067(5)
d_{calc} (g cm^{-3})	1.592	1.728
μ (mm^{-1})	2.300	5.083
F(000)	4384	2608.0
Total Reflections	33994	29619
Unique Reflections	4748	4166
Observed data [I >2 σ (I)]	4321	3427
No. of parameters	262	271
R(int)	0.0378	0.0359
$^{♪}R_1$, $^{♫}wR_2$ (all data)	0.0441, 0.1158	0.0476, 0.1134
$^{♪}R_1$, $^{♫}wR_2$ [I >2 σ (I)]	0.0378, 0.1044	0.0359, 0.1029
CCDC No.	2323492	2323493

(♪) $R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$; (♫) $wR_2 = \Sigma w(|Fo|^2-|Fc|^2)^2/\Sigma w|Fo|^2)^{1/2}$

Table S2: Selected bond lengths (Å) of the complexes **1** and **2**.

Complex	**1**	**2**
Zn(1)–O(1)	2.056(4)	2.083(6)
Zn(1)–O(2)	2.379(7)	2.183(7)
Zn(1)-O(4)	2.035(5)	2.082(6)
Zn(1)-O(7)	2.110(4)	2.170(6)
Zn(1)-N(1)	2.130(5)	2.153(8)
Zn(1)-N(2)	2.114(5)	2.134(8)
Zn(2)–O(1)	1.942(4)	1.949(6)
Zn(2)–O(6)	1.940(5)	1.952(7)
Zn(2)-O(5)	1.974(5)	1.959(6)
Zn(2)-O(3)	1.948(5)	1.987(8)

Table S3: Selected bond angles (°) of the complexes **1** and **2**.

Complex	**1**	**2**
O(1)-Zn(1)–O(4)	96.8(2)	86.4(2)
O(1)-Zn(1)-N(2)	164.9(2)	174.1(3)
O(4)-Zn(1)–N(2)	91.0(2)	92.1(4)
O(1)-Zn(1)–N(1)	88.90(18)	88.8(3)
O(4)-Zn(1)–N(1)	173.4(2)	170.7(3)
N(2)-Zn(1)-N(1)	82.8(2)	93.5(4)
O(1)-Zn(1)–O(7)	96.75(18)	100.0(3)
O(4)-Zn(1)-O(7)	96.0(2)	90.4(2)
N(2)-Zn(1)-O(7)	95.29(19)	85.8(3)
N(1)-Zn(1)-O(7)	88.57(18)	82.6(2)
O(1)-Zn(1)-O(2)	84.75(19)	87.9(3)
O(4)-Zn(1)-O(2)	86.6(3)	94.9(3)
N(2)-Zn(1)-O(2)	82.8(2)	86.5(3)
N(1)-Zn(1)-O(2)	90.6(2)	92.8(3)
O(7)-Zn(1)-O(2)	176.8(2)	170.8(3)
O(1)-Zn(2)-O(6)	114.6(2)	110.8(3)
O(1)-Zn(2)-O(5)	105.97(19)	101.9(3)
O(6)-Zn(2)-O(5)	96.7(2)	120.1(3)
O(1)-Zn(2)-O(3)	109.0(2)	107.0(3)
O(6)-Zn(2)-O(3)	120.6(2)	107.2(3)
O(5)-Zn(2)-O(3)	108.0(2)	109.1(4)

Table S4. IR stretching frequency of complexes **1** and **2**.

Assignment	St. frequency of complex **1** (cm^{-1})	St. frequency of complex **2** (cm^{-1})
ν(N-H)	3304-3241	3261-3220
ν(C-H)	2924-2864	2960-2863
$\nu(COO^-_{Asymmetric})$	1607-1567	1605-1562
$\nu(COO^-_{Symmetric})$	1434-1390	1405