The interplay between coordination and non-covalent interactions in three zinc coordination polymers

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Physical measurement

An elemental analyzer (Perkin-Elmer 240C) was used to do elemental analysis (carbon, hydrogen, and nitrogen). IR spectrum acquired with RX-1 FTIR spectrophotometer in KBr (4500-500 cm^{-1}). A UV-1900 i Shimadzu absorbance spectrophotometer was used to record the absorption spectra in a methanol solution. Powder X-ray diffraction data of the complexes were collected using a Bruker AXS D8 Advanced SWAX diffractometer (Cu K_α, $\lambda = 0.15406$ nm).

X-ray crystallography

Utilizing adequate crystals of the complexes with the right dimensions, "Bruker D8 QUEST area detector" diffractometer with graphite-monochromated Mo-Kα radiation (λ= 0.71073 Å) has been utilized to acquire (single crystal) XRD data. The structures were solved directly, and the F^2 full-matrix least squares using the SHELXL-18/1 program were utilized for refinement.[S1] Anisotropic thermal parameters were used to refine non-hydrogen atoms. By using several Fourier maps, the hydrogen atoms that were bound to the nitrogen atoms were found and maintained in their fixed locations. Every other hydrogen atom was confined to ride on its parent atom after being positioned in their geometrically idealized places. Multi-scan empirical absorption corrections were applied to the data using the program SADABS.[S2] The details of crystallographic data and refinements have been given in Table **1**. Important bond lengths and angles have been listed in Tables **2** and **3**, respectively.

Hirshfeld surface analysis

Crystal Explorer 21.5[S3] software has been used to calculate Hirshfeld surfaces[S4-S6] and the related two-dimensional fingerprint plots.[S7,S8] 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.[S9]

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 the absence of any close contacts. It is needless to say that the Hirshfeld surface is unique for a given CIF.[S10]

Experimental Section

Synthesis of Ligands

HL^1 {2-(((2-(diethylamino)ethyl)amino)methyl)phenol}

A methanol solution (10 mL) of *N,N*-diethyl-1,2-diaminoethane (~1 mmol, 0.14 mL) and salicylaldehyde (~1 mmol, 0.11 mL) was refluxed for ca. 2 h to prepare a tridentate Schiff base, [2-(((2-(diethylamino)ethyl)imino)methyl)phenol] (HL^a). The methanol solution (10 mL) of the Schiff base was then cooled to 0°C and solid sodium borohydride (~4 mmol, 152 mg) was added to it slowly with constant stirring. 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 produce 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 {4-chloro-2-(((3-(dimethylamino)propyl)amino)methyl)phenol}

HL^2 was prepared in a similar procedure to HL^1, except N,N-dimethyl-1,3-propanediamine and 5-chlorosalicylaldehyde was used instead of N,N-dimethyl-1,2-diaminoethane and salicylaldehyde.

HL^3 {4-bromo-2-(((3-(dimethylamino)propyl)amino)methyl)phenol

HL^3 was prepared in a similar procedure to HL^1, except N,N-dimethyl-1,3-propanediamine and 5-bromosalicylaldehyde were used instead of N,N-dimethyl-1,2-diaminoethane and salicylaldehyde.

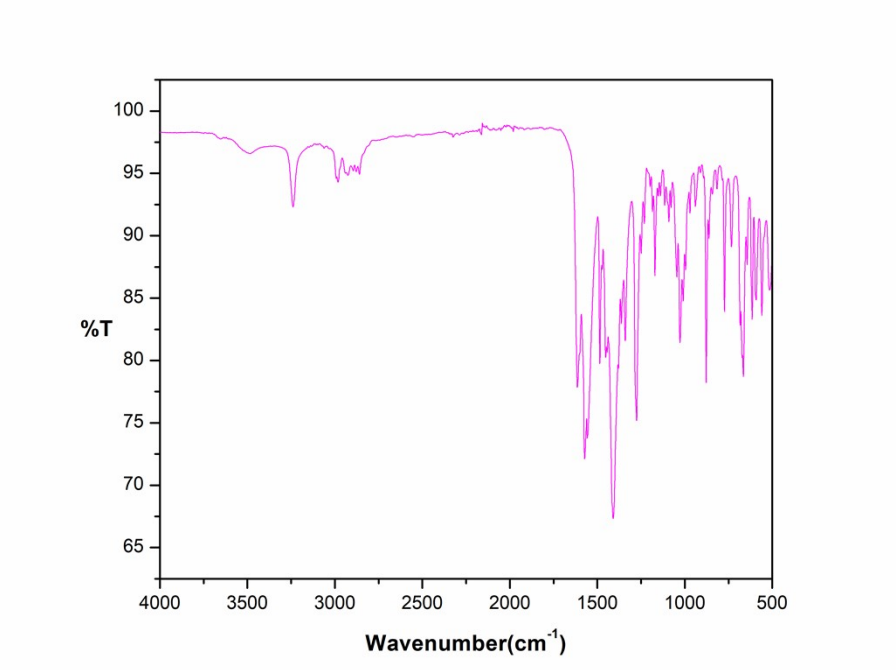

Fig. S1. IR spectrum of complex **1**.

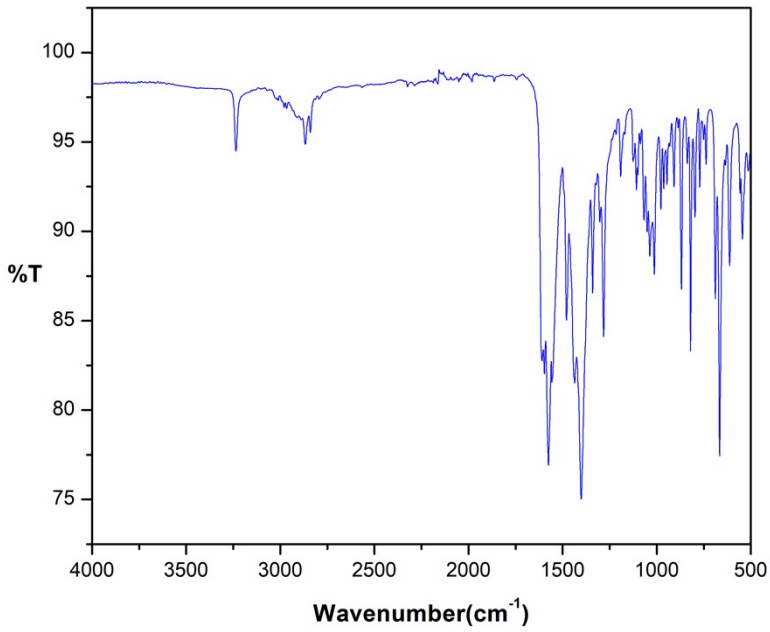

Fig. S2. IR spectrum of complex **2**.

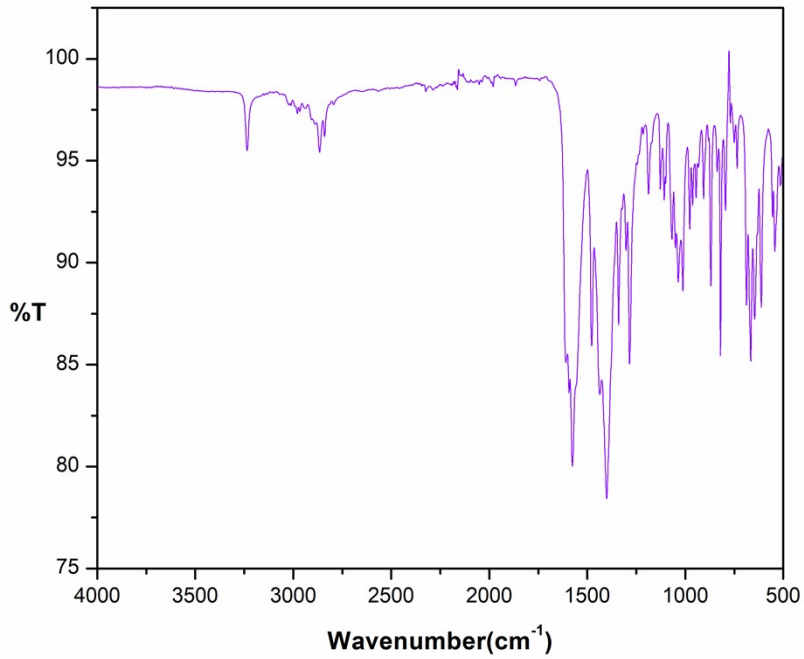

Fig. S3. IR spectrum of complex **3**.

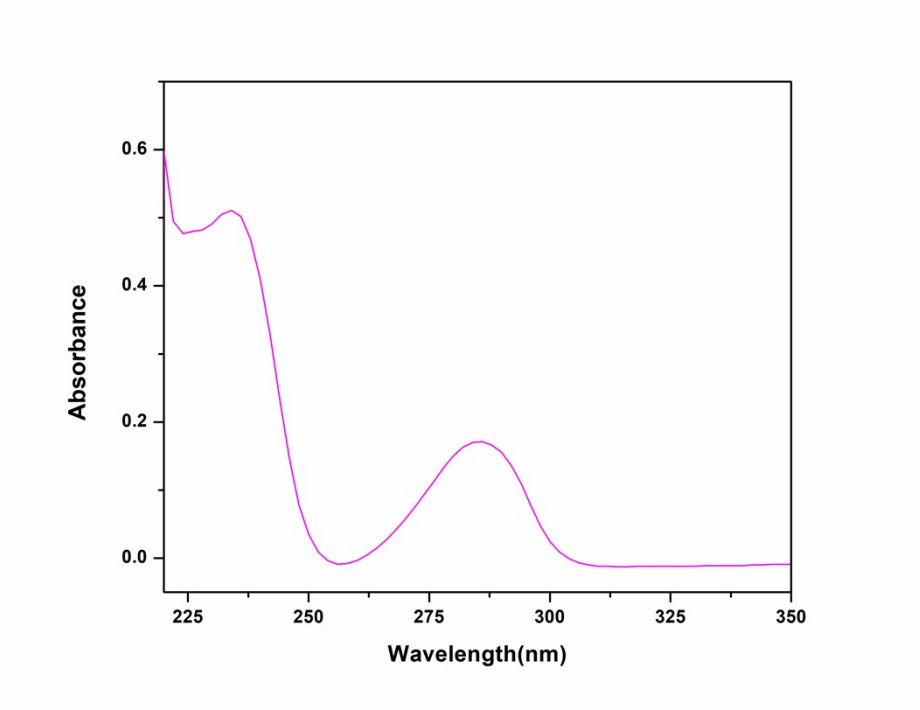

Fig. S4. UV-Vis spectrum of complex **1** in 10^{-4} M methanol solution.

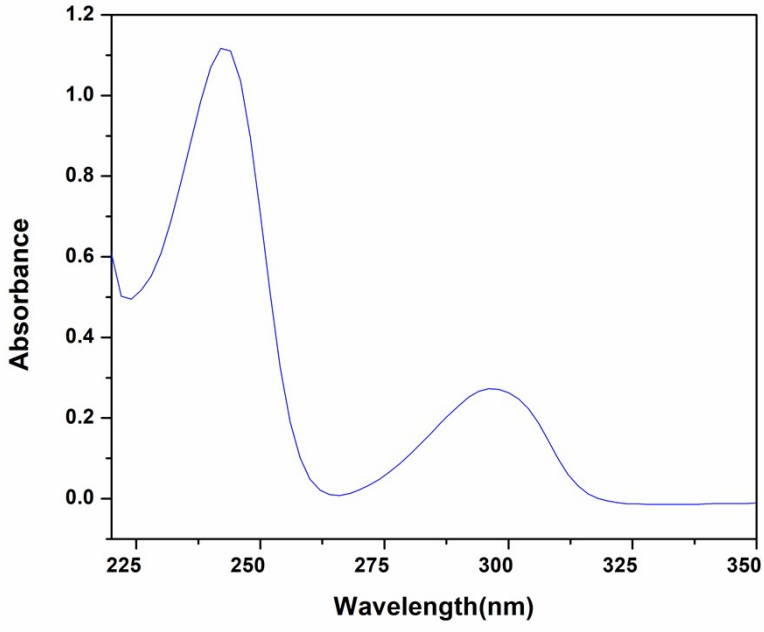

Fig. S5. UV-Vis spectrum of complex **2** in 10^{-4} M methanol solution.

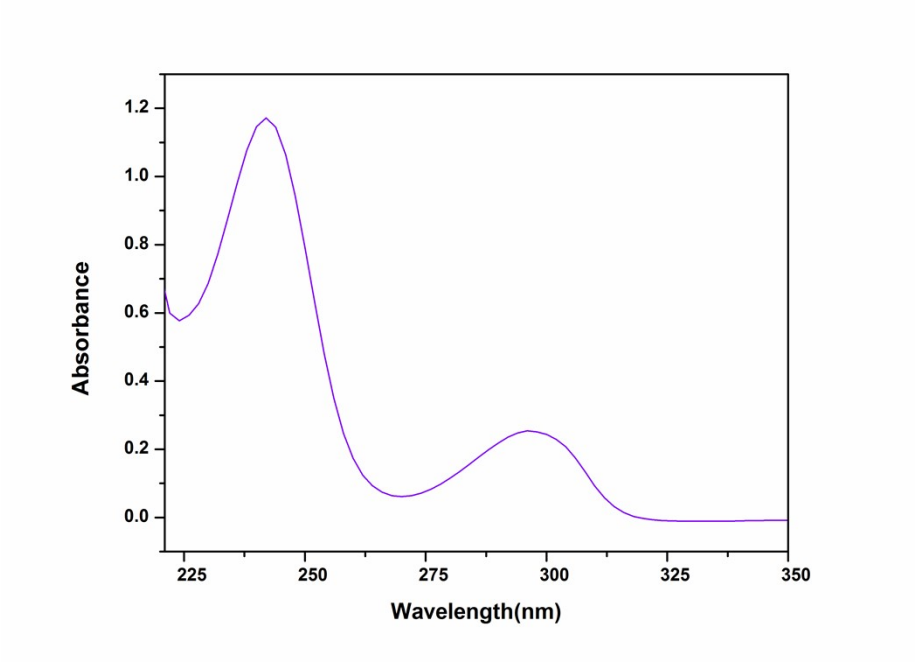

Fig. S6. UV-Vis spectrum of complex **3** in 10^{-4} M methanol solution.

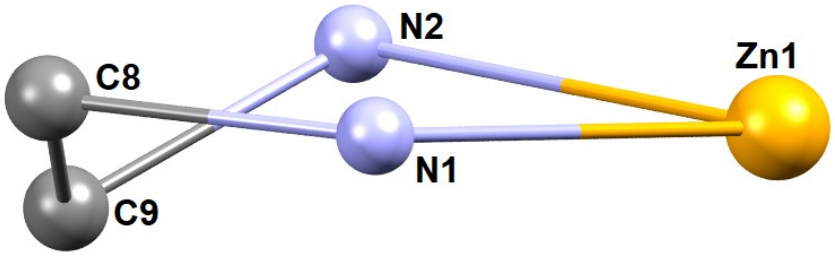

Fig. S7. Perspective view of saturated five member chelate ring [Zn(1)-N(1)-C(8)-C(9)-N(2)] of complex **1**.

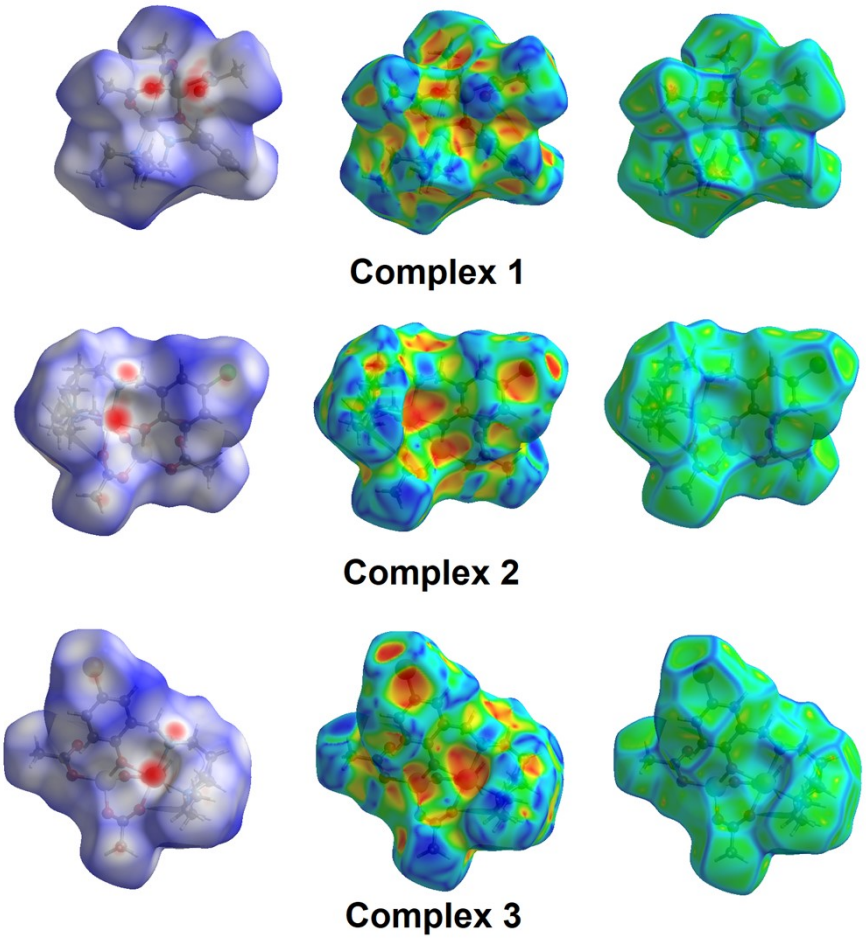

Fig. S8. Hirshfeld surfaces of complexes **1-3**, mapped over d_{norm} (left), shape index (middle), curvedness (right).

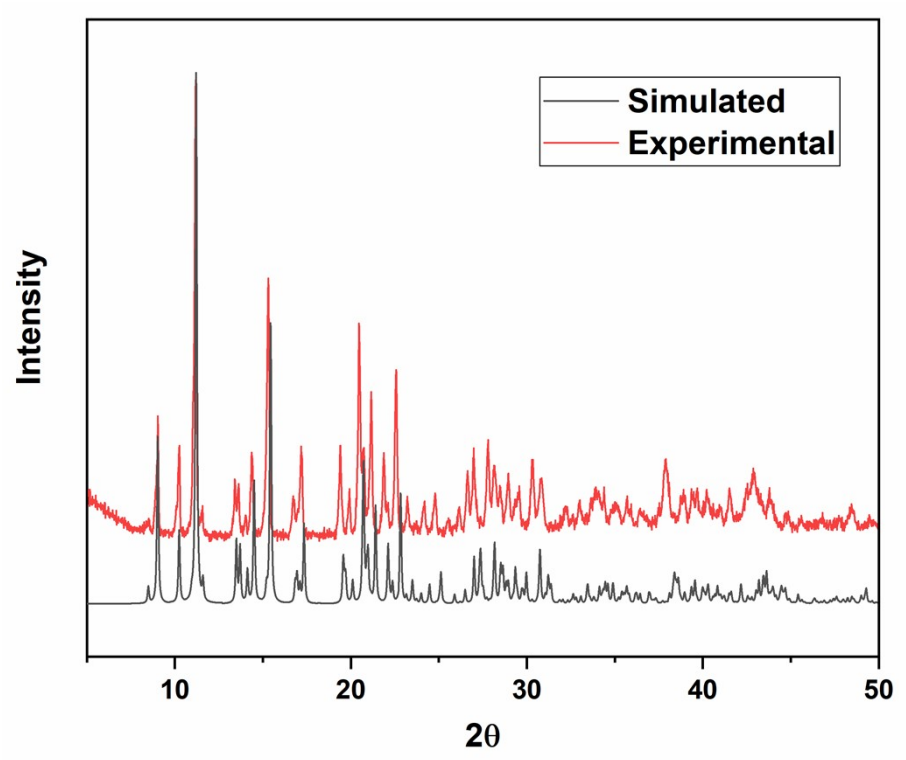

Fig. S9. Experimental and simulated PXRD patterns of complex **3** confirming purity of the bulk material.

References

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