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Electronic Supplementary Information

Large interaction energy for the homodimer and the heterodimer extracted from the supramolecular chain of a bent trinuclear zinc(II) complex with a reduced Schiff base ligand

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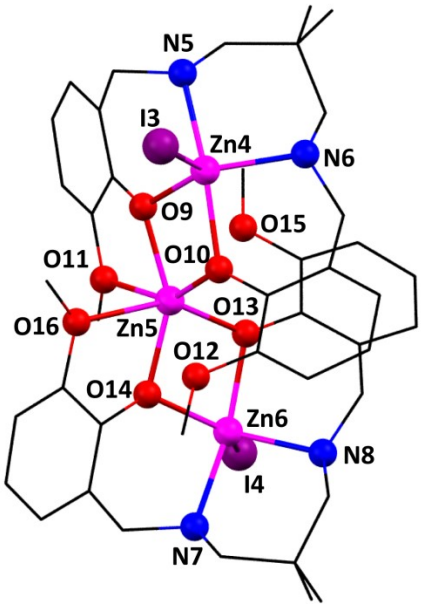
Description of crystal structures of subunit 'B' of *[Zn{Zn(I)L}$_2$].DMF*

Subunit 'B' has an identical structure with that of subunit 'A' as mentioned in main manuscript. Perspective view of subunit 'B' with selective atom numbering scheme is shown in Fig. **S1**. Required bond lengths and angles are listed in Tables **S1** and **S2** respectively. This subunit also contains three zinc centers {Zn(4), Zn(5), and Zn(6)}, two units of deprotonated reduce Schiff base ligand (L^{-2}) and two iodides. The three zinc centers are not in linear arrangement which is obvious from Zn(4)–Zn(5)–Zn(6) angle of 144.15(2)° of. The distances between the zinc centers are 3.1863(7) Å {Zn(4)–Zn(5)} and 3.183(7) Å {Zn(5)–Zn(6)}.



Subunit 'B'

Fig. S1 Perspective view of subunit 'A' of the complex with selective atom numbering schemes. Solvent molecules and hydrogen atoms have been omitted for clarity.

Two zinc centers, {Zn(4) and Zn(6), are situated at the inner N_2O_2 compartment of each unit of reduced Schiff base ligand. One iodide is bonded to each zinc centre situated in the inner compartment. Thus, both zinc centers in inner compartments are penta-coordinated being bonded to two secondary amine nitrogen atoms {N(5), N(6) for Zn(4) and N(7), N(8) for Zn(6)} and two phenolate oxygen atoms {O(9), O(10) for Zn(4) and O(13), O(14) for Zn(6)} of the deprotonated reduced Schiff base ligand (L^{-2}) and one terminal iodide atom {I(3) and I(4) for Zn(4) and Zn(6), respectively}. Trigonality indices for terminal zinc centers [τ = 0.55 and 0.47 for Zn(4) and Zn(6), respectively] are far away from the ideal value for square pyramidal geometry, suggesting that the coordination geometry of each penta-coordinated zinc is intermediate between square pyramid and trigonal bipyramid. The central Zn center, Zn(5), has six-

coordinate distorted octahedral geometry, being bonded with four phenolate oxygen atoms {O(9),O(10), O(13) and O(14)} and two methoxy oxygen atoms {O(11) and O(16)} of two outer O_4 compartments of two reduced Schiff base units. The ligand may be best considered as a pentadentate one, as it has used five donor atoms out of its total six possible donor atoms (N_2O_4) for binding zinc.

The saturated six membered chelate rings, Zn(4)−N(5)−C(72)–C(73)–C(76)–N(6) and Zn(6)−N(7)−C(51)–C(52)–C(55)–N(8), assume half chair conformation (Fig. **S2**) with puckering parameters, q= 0.562(4), Θ=166.5(4)°, ϕ= 14.1(18)° and q= 0.564(4), Θ=168.9(4)°, ϕ= 353(2)°, respectively.

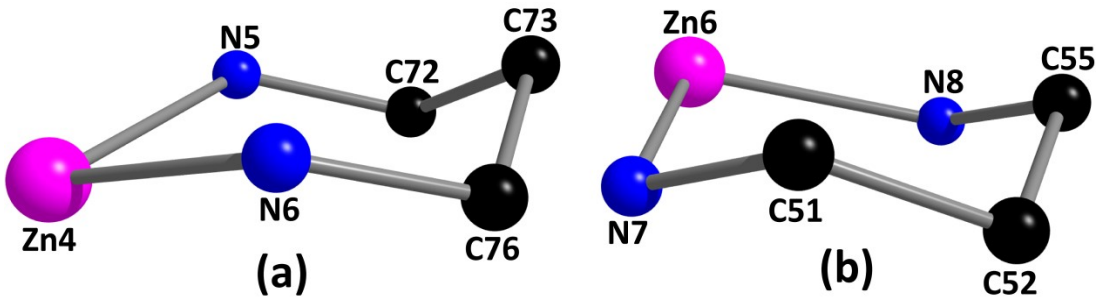


Fig S2 Chair conformations of the six member saturated chelate rings, (a) Zn(4)−N(5)−C(72)–C(73)–C(76)–N(6) and (b) Zn(6)−N(7)−C(51)–C(52)–C(55)–N(8).

Table S1: Selected bond lengths (Å) of the complex**.**

Zn(4)-I(3)	2.6354(6)	Zn(5)-O(13)	2.027(3)
Zn(4)-N(5)	2.169(3)	Zn(5)-O(14)	1.998(2)
Zn(4)-N(6)	2.085(3)	Zn(5)-O(16)	2.352(3)
Zn(4)-O(9)	2.035(2)	Zn(6)-I(4)	2.6667(6)

Zn(4)-O(10)	2.052(2)	Zn(6)-N(7)	2.127(3)
Zn(5)-O(9)	2.007(2)	Zn(6)-N(8)	2.113(3)
Zn(5)-O(10)	2.000(2)	Zn(6)-O(13)	2.049(2)
Zn(5)-O(11)	2.312(3)	Zn(6)-O(14)	2.050(3)

Table S2: Selected bond angles (°) of the complex.

O(9)-Zn(4)-N(5)	88.62(10)	O(10)-Zn(5)-O(16)	91.88(10)
O(9)-Zn(4)-N(6)	128.18(12)	O(11)-Zn(5)-O(13)	94.94(11)
O(9)-Zn(4)-O(10)	75.15(9)	O(11)-Zn(5)-O(14)	86.29(10)
I(3)-Zn(4)-0(9)	118.74(8)	O(11)-Zn(5)-O(16)	89.59(10)
I(3)-Zn(4)-0(10)	101.68(7)	O(13)-Zn(5)-O(14)	77.44(10)
I(3)-Zn(4)-N(5)	93.43(8)	O(13)-Zn(5)-O(16)	149.75(9)
I(3)-Zn(4)-N(6)	112.93(9)	O(14)-Zn(5)-O(16)	73.03(9)
O(10)-Zn(4)-N(5)	161.71(11)	I(4)-Zn(6)-O(13)	101.40(8)
O(10)-Zn(4)-N(6)	91.44(11)	I(4)-Zn(6)-O(14)	125.14(8)
N(5)-Zn(4)-N(6)	92.10(12)	I(4)-Zn(6)-N(7)	96.16(8)
O(9)-Zn(5)-O(10)	76.93(9)	I(4)-Zn(6)-N(8)	102.22(9)
O(9)-Zn(5)-O(11)	73.52(10)	O(13)-Zn(6)-O(14)	75.79(10)
O(9)-Zn(5)-O(13)	124.57(10)	O(13)-Zn(6)-N(7)	161.13(11)
O(9)-Zn(5)-O(14)	150.57(10)	O(13)-Zn(6)-N(8)	91.21(11)
O(9)-Zn(5)-O(16)	85.39(10)	O(14)-Zn(6)-N(7)	88.51(11)
O(10)-Zn(5)-O(11)	150.19(10)	O(14)-Zn(6)-N(8)	132.34(11)
O(10)-Zn(5)-O(13)	98.58(11)	N(7)-Zn(6)-N(8)	91.77(12)
O(10)-Zn(5)-O(14)	122.52(10)	-	-

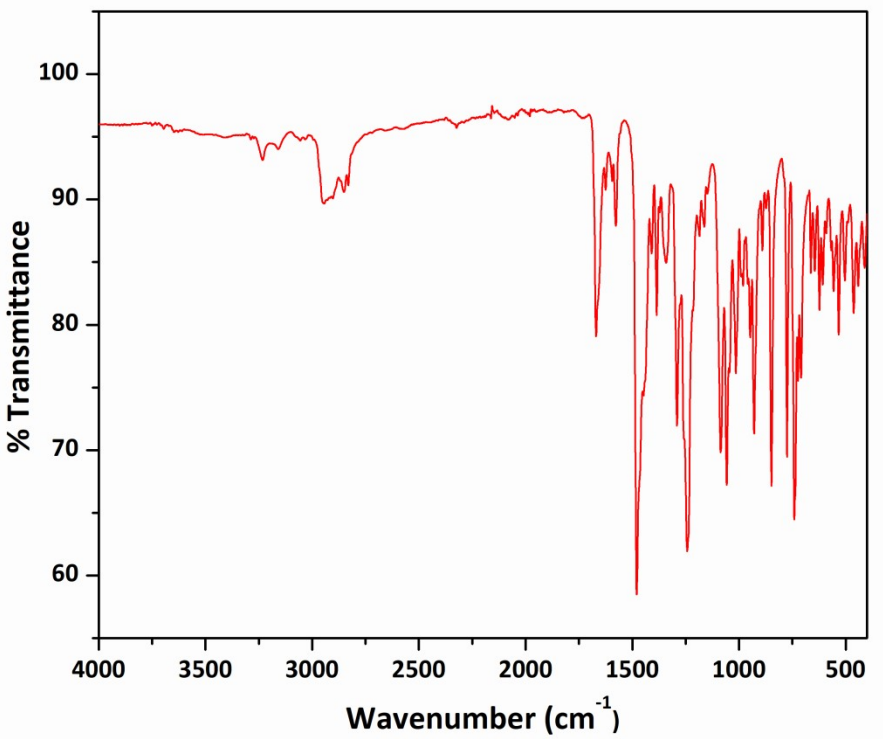


Fig. S3 IR spectrum of the complex.

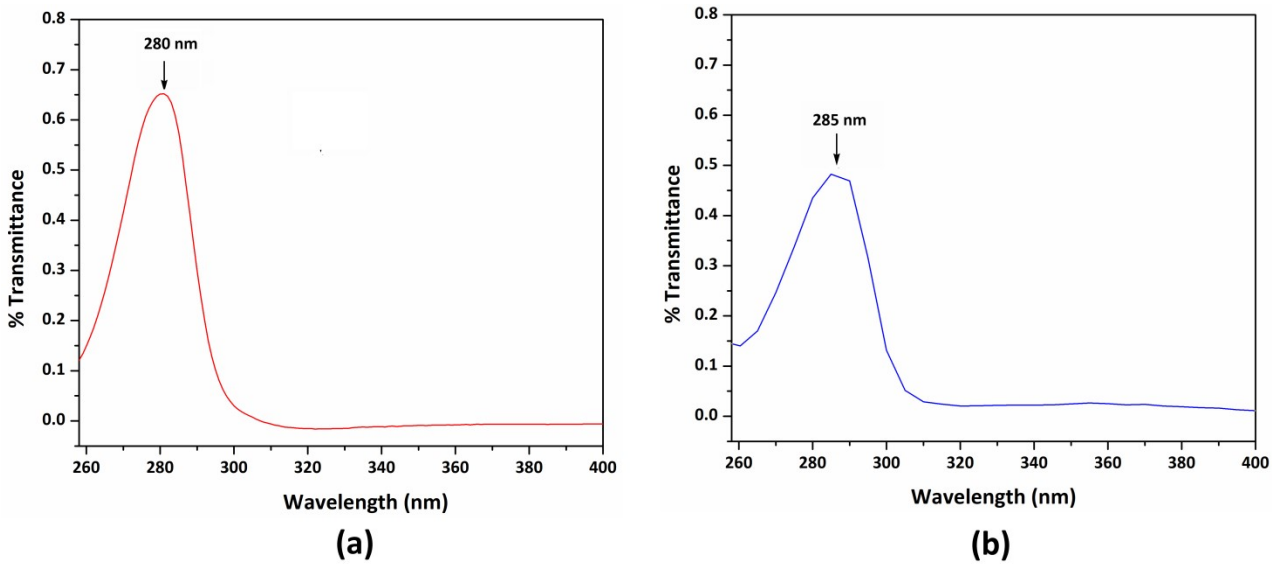


Fig. S4 Electronic spectra of **(a)** the ligand and **(b)** the complex.

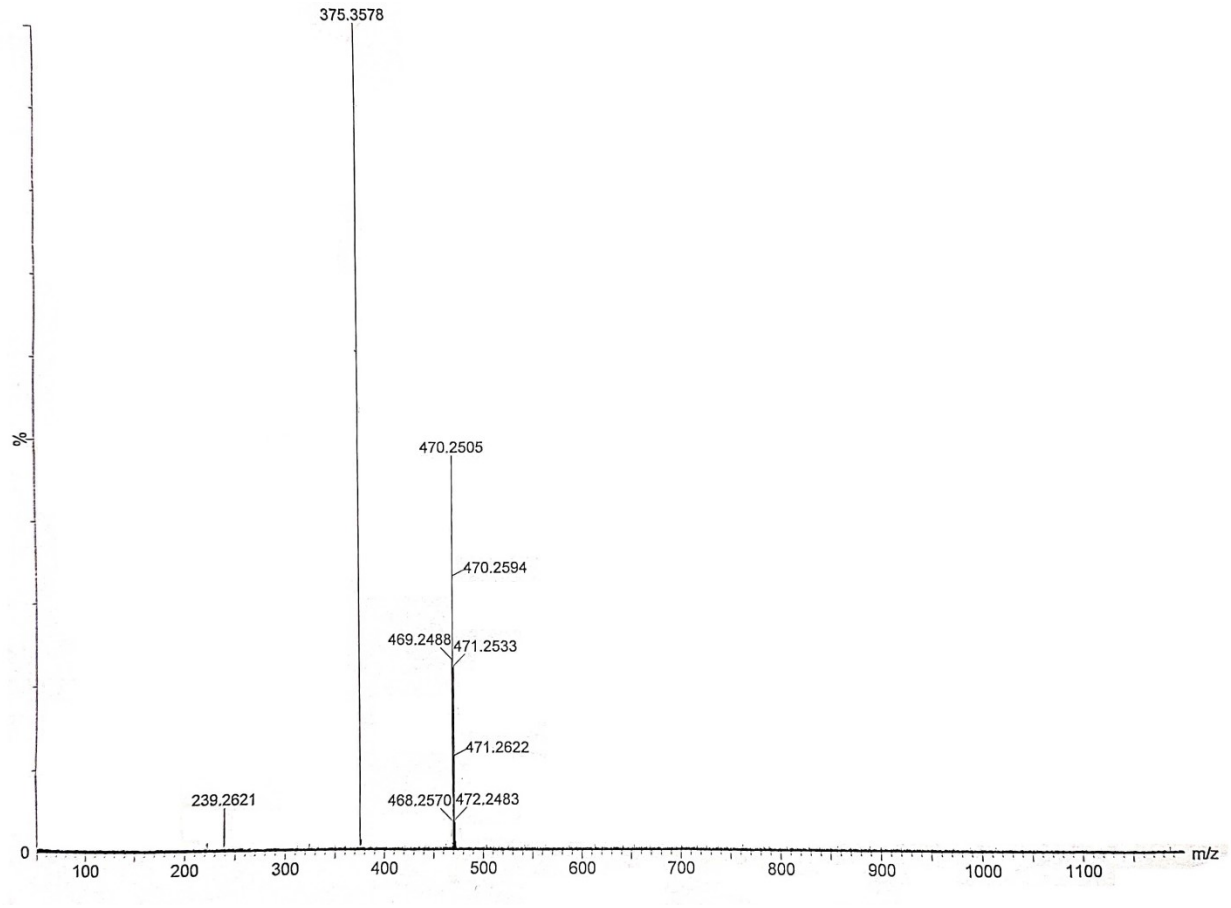


Fig. S5 Mass spectrum of the complex in CH_3OH.

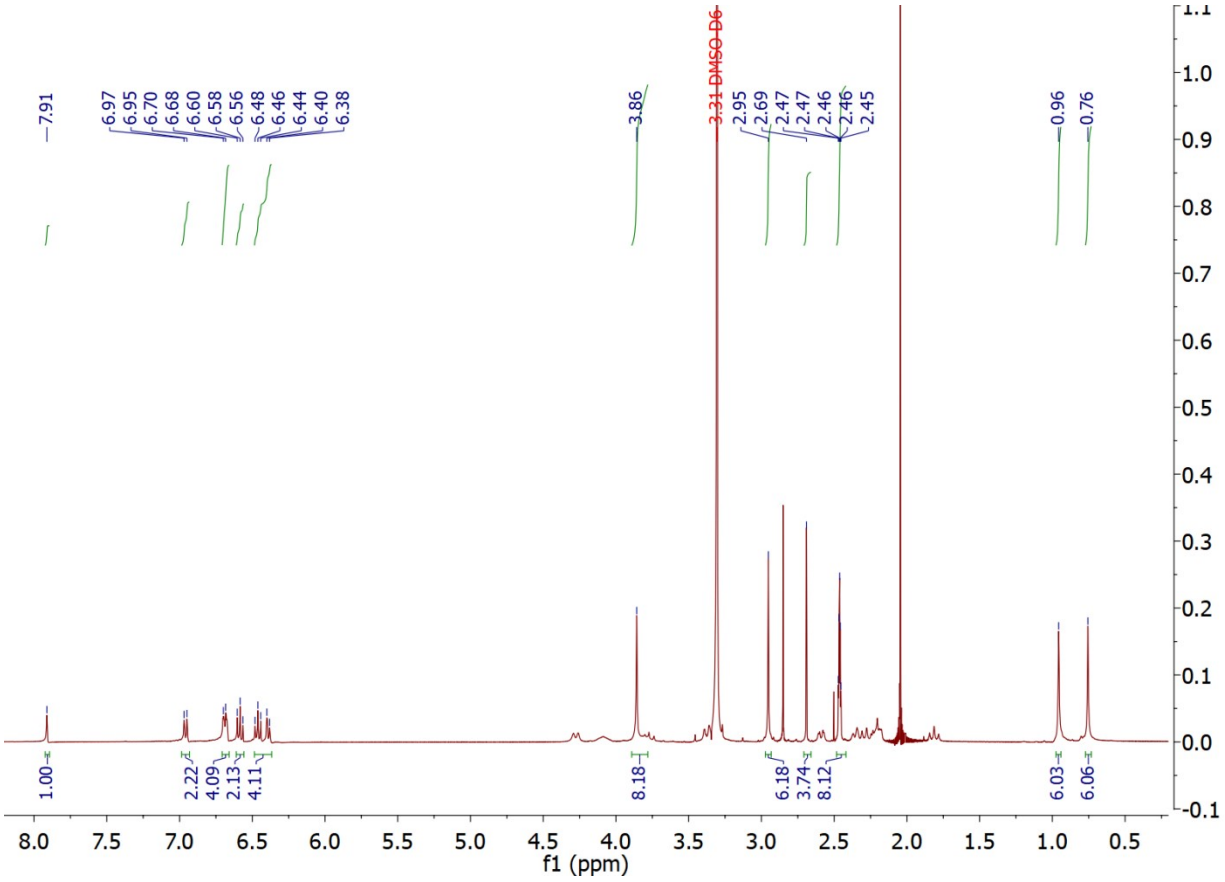


Fig. S6 ^{1}H NMR spectrum of the complex in DMSO-d_6.

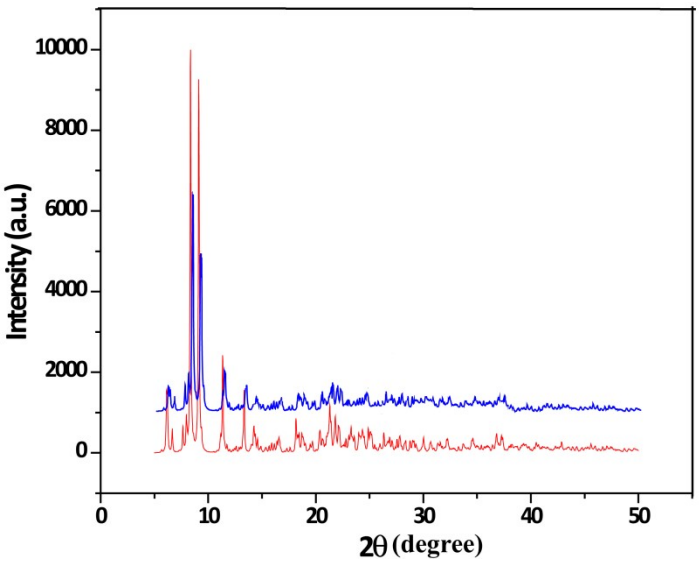


Fig. S7 Experimental and simulated powder XRD patterns of the complex confirming the purity of the bulk materials.

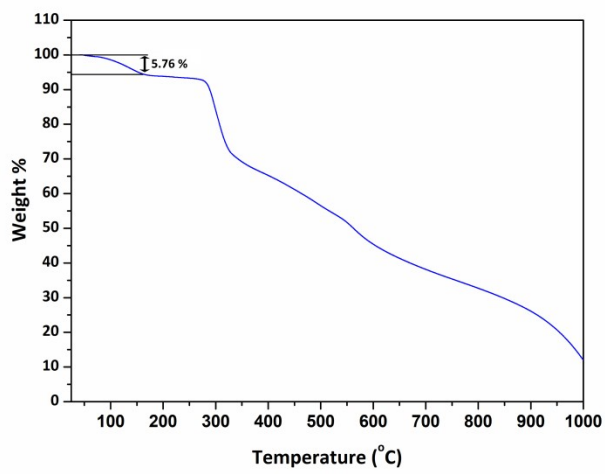


Fig. S8 TGA plot of the complex.