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A new end-on $(\mu_{1,1})$ azido bridged $[Zn_2(L)_2(Na)N_3]_n$ 1D chain derived from a trinuclear zinc complex: syntheses, crystal structures, photoluminescence properties and DFT study

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ABSTRACT

A bicompartmental N_2O_4 donor symmetric Schiff base ligand has been deployed to synthesize a trinuclear zinc complex $[Zn_3(L)_2Cl_2]$, which upon treatment with sodium azide produces a new $\mu_{1,1}$ -azido-bridged 1-D polymer $[Zn_2(L)_2(Na)N_3]_n$. Both complexes have been characterized using IR, NMR, UV-vis, and X-ray diffraction techniques. In order to have better understanding of electronic transitions of the complexes, a time-dependent DFT study has been performed. Lifetime measurements have also been performed to learn about the stability of excited states of both complexes. The average fluorescence decay lifetime has been found to be 1.42 and 0.59 ns for **1** and **2**, respectively. In Hirshfeld surface mapping, X···H/H···X (X = O, Cl) contacts are found to be only 2.7% of the total surface, which indicates that no significant X···H/H···X contacts are present in either of the complexes. Unconventional interactions such as C–H··· π and π ··· π stacking interactions are found in supramolecular architectures of both complexes.



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1. Introduction

The synthesis of coordination polymers and metal-organic frameworks (MOFs) using compartmental ligands [1] have drawn an enormous amount of attention in crystal engineering and molecular modeling,

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owing to robust structural topologies and potential applications in gas storage, separation science, luminescence, catalysis, adsorption, host-quest chemistry, electrofunctional materials, non-linear optics, magnetism, etc. [2–6]. MOFs involving d¹⁰ metal complexes are of special interest due to their structural diversity [7] and application in non-linear optics, luminescence, biological modeling, etc. [8–14]. The ligand field stabilization energy of Zn(II) complexes is zero, and thus, a delicate balance between bond energies and repulsion among the ligands governs the coordination chemistry of such complexes. Schiff bases derived from condensation of diamines e.g. 1,2-diaminoethane, 1,3-diaminopropane, and salicylaldehyde or its derivatives are a group of N $_2O_4$ donor ligands termed compartmental ligands. These react readily with transition metals to form mono-, di-, or trinuclear complexes depending upon the coligands and substituents present in the ligands. For example, a dinuclear complex can be obtained by azide bridging of two mononuclear units [15]. Also, a number of diphenoxo-bridged dinuclear compounds [16, 17] and phenoxo-bridged trinuclear compounds [18–20] have been reported using these compartmental ligands. Bridging ligands give enormous structural diversity to facilitate polymeric complexes. Bridging ligands such as azide ions are commonly used due to their diverse bridging capabilities for synthesizing metal complexes with various nuclearities. Metal-azido complexes have attracted interest for many years mainly due to their potential applications as functional materials. There are nine types of bridging modes of an azide ion commonly known as $\mu_{1,1}$ (end-on), $\mu_{1,3}$ (end-end), $\mu_{3-1,1,1}, \mu_{3-1,1,3}, \mu_{4-1,1,1,1}, \mu_{4-1,1,3,3}, \mu_{6-1,1,1,3,3,3}$, etc. [21]. A CSD (CSD version 5.36, year 2014) search with $N_{0}O_{4}$ donor compartmental ligands revealed that only five examples [22–26] have been found where exclusively and only μ_{11} bridging is taking place to bind two metal ions. Most importantly, of these five examples, only two examples have been found where a single azide ion is bridging through the $\mu_{1,1}$ mode to create a 1-D network [22, 23]. These two examples are very similar involving Mn(III) ions with the only difference being the substituents present in the ligand system. Actually, the scope of formation of metal complexes of higher nuclearity supported by only one $\mu_{1,1}$ bridging azide seems to be very difficult mainly due to steric congestion and electronic factors between two adjoining asymmetric units. In our present work, we reported an unusual single end-on azido-bridged ($\mu_{1,1}$)Zn-polymer derived from a trinuclear zinc complex.

2. Experimental

2.1. Materials and physical measurements

1,3-Diaminopropane was purchased from TCI. *o*-Vanillin, zinc chloride, and sodium azide were purchased from Alfa Aesar. Methanol, triethylamine, and DMF were purchased from Sigma–Aldrich. All reagent or analytical grade chemicals and solvents were used without purification. *Caution!* Azide salts are potentially explosive especially in the presence of organic ligands. Only a small amount of material should be prepared, and it should be handled with great care.

Elemental analysis for C, H, and N was carried out using a PerkinElmer 240C elemental analyzer. Infrared spectra (400–4000 cm⁻¹) were recorded from KBr pellets on a Nicolet Magna IR 750 series-II FTIR spectrophotometer. Absorption spectra were measured using a UV-2450 spectrophotometer (Shimadzu) with a 1-cm-path-length quartz cell. Measurements of ¹H NMR spectra were conducted using a Bruker 300 spectrometer in DMSO-d₆. Emission was examined by a LS 55 PerkinElmer spectrofluorimeter at room temperature (298 K) in degassed DMF. Fluorescence lifetimes were measured using a time-resolved spectrofluorimeter from IBH, UK.

2.2. Syntheses

2.2.1. Synthesis of Schiff base $(H_{L} = N, N' - bis(3 - methoxysalicylidene) propylene - 1, 3 - diamine)$

The tetradentate Schiff base (**H**₂**L**) was prepared by the standard method [27], and the purity was confirmed by ESI-Mass and ¹H NMR. Yield: 0.339 g (99%). Anal. Calcd for $C_{19}H_{22}N_2O_4$: C, 66.65%; H, 6.25%; N, 8.18%. Found: C, 66.05%; H, 5.97%; N, 8.09%. ESI-MS (positive) in MeOH: The base peak was detected

at m/z = 343.11, corresponding to $[H_2L + 1]^+$. IR (cm⁻¹, KBr): v(C=N) 1629 m; v(C-N) 1243 s; v(C-H) 730 s. UV–vis, λ_{max} (nm), (ϵ (dm³ mol⁻¹ cm⁻¹)) in DMF: 220 (40,556), 260 (20,055), 295 (10,808) 420 (3782). ¹H NMR (DMSO-d₆, 300 MHz) δ ppm: 2.04–1.99 (–CH₂) (bs, 2H), 3.70–3.66 (–CH₂) (m, 4H), 3.77 (–OCH₃) (s, 6H), 6.82–6.77 (Ar-H) (m, 2H), 7.03–7.00 (Ar–H) (m, 4H), 8.56 (–CH=N) (bs, 2H).

2.2.2. Synthesis of [Zn₃(L)₂Cl₂] (1)

A 10-mL methanolic solution of zinc chloride (6.0 mmol, 0.818 g) was added to a methanolic solution of H_2L (4.0 mmol, 1.370 g) followed by addition of triethylamine (8.0 mmol, ~1.5 mL), and the resultant reaction mixture was heated to reflux for 4 h. The solution was then cooled and filtered. Deep yellow plate-shaped crystals resulted from slow evaporation of the methanolic solution of the complex at room temperature. Yield: 1.56 g (82%). Anal. Calcd for $C_{38}H_{40}Cl_2N_4O_8Zn_3$: C, 48.15%; H, 4.25%; N, 5.91%. Found: C, 47.05%; H, 3.87%; N, 5.09%. IR (cm⁻¹, KBr): v(C=N) 1620 m; v(C-N) 1220 s; v(C-H) 730 s. UV–vis, λ_{max} (nm), (ε (dm³ mol⁻¹ cm⁻¹)) in DMF: 270 (12,378), 358 (4186). ¹H NMR (DMSO-d₆, 300 MHz) δ ppm: 2.50 (–CH₂) (bs, 2H), 3.16 (–CH₂) (bs, 4H), 3.70 (–OCH₃) (s, 6H), 6.30–7.26 (Ar–H) (m, 6H), 8.30 (–CH=N) (bs, 2H).

2.2.3. Synthesis of $[Zn_2(L)_2(Na)N_3]_n$ (2)

A 2-mL aqueous methanolic solution of sodium azide (1.0 mmol, 0.065 g) was added dropwise to a methanolic suspension of **1** (1 mmol, 0.948 g). Then, the resultant reaction mixture was heated to reflux for 3 h. The solution was cooled and filtered. Yellow needle-shaped crystals resulted from slow evaporation of the methanolic solution of the complex at room temperature. Yield: 0.692 g (79%). Anal. Calcd for $C_{38}H_{40}N_7NaO_8Zn_2$: C, 52.07%; H, 4.60%; N, 11.19%. Found: C, 51.05%; H, 4.07%; N, 10.29%. IR (cm⁻¹, KBr): $v(N_3^-)$ 2075 s; v(C=N) 1625 m; v(C-N) 1217 s; v(C-H) 732 m. UV–vis, λ_{max} (nm), (ε (dm³ mol⁻¹ cm⁻¹)) in DMF: 273 (9663), 360 (4453). ¹H NMR (DMSO-d₆, 300 MHz) δ ppm: 2.48 (–CH₂) (s, 2H), 3.8 (–CH₂) (bs, 4H), 3.6 (–OCH₃) (s, 6H), 6.28–6.34 (Ar–H) (t, 9 Hz, 2H), 6.6–6. 7(Ar–H) (m, 4H), 8.28 (–CH=N) (s, 2H).

2.3. X-ray crystallography

Single-crystal X-ray data of **1** and **2** were collected on a Bruker SMART APEX-II CCD diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 298(2) K. Data processing, structure solution, and refinement were performed using Bruker Apex-II suite of programs. All available reflections in $2\theta_{max}$ range were harvested and corrected for Lorentz and polarization factors with Bruker SAINT plus [28]. Reflections were then corrected for absorption, inter-frame scaling, and other systematic errors with SADABS [29]. The structures were solved by direct methods and refined by full matrix least squares based on F^2 with the SHELX-2013 software package [30]. All non-hydrogen atoms were refined with anisotropic thermal parameters. C–H hydrogens were inserted in geometrical positions with $U_{iso} = \frac{1}{2}U_{eq}$ to those they are attached. Crystal data and details of data collection and refinement for **1** and **2** are summarized in table **1**.

2.4. Computational methods

All computations were performed using the GAUSSIAN09 (G09) [31] software. Full geometry optimizations were carried out using density functional theory at the B3LYP level [32, 33] for 1 and 2. For 1 and 2, the coordinates obtained from single-crystal X-ray diffraction data were used for optimization using the lanL2DZ effective potential (ECP) set of Hay and Wadt [34–36] for zinc and sodium and the standard 6–31 + G(d) basis set for C, H, N, O, and Cl [37, 38]. For 2, the asymmetric unit has been considered for optimization. To get local minima and only positive eigenvalues of optimized geometries, vibrational frequency calculations were carried out. Time-dependent density functional theory (TDDFT) computations [39–41] in DMF were carried out using the conductor-like polarizable continuum model (CPCM) [42–44] with the same B3LYP level and basis sets to get vertical electronic excitations. GAUSSSUM 3.0 [45] was used to calculate the percentage contributions of ligand, coligand, and metal ion to each molecular orbital.

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Table 1. Crystal parameters and selected refinement details for 1 and 2.

Complex	1	2
Empirical formula	C ₂₀ H ₄₀ Cl ₂ N ₄ O ₂ Zn ₂	C _a ,H ₄₀ N ₇ NaO ₂ Zn ₂
Formula weight	947.75	876.50
Temperature (K)	298(2)	298(2)
Crystal system	Orthorhombic	Monoclinic
Space group	F d d 2	P 21/c
a (Å)	30.7187(15)	22.4922(9)
b (Å)	8.4045(4)	9.4390(4)
<i>c</i> (Å)	30.3283(16)	20.0236(8)
α (°)	90	90.00
β (°)	90	113.767(2)
γ (°)	90	90.00
Volume (Å ³)	7830.0(7)	3890.6(3)
Ζ	8	4
D_{Caled} (g cm ⁻³)	1.608	1.496
Absorption coefficient (mm ⁻¹)	2.016	1.305
F(0 0 0)	3107	1808
heta Range for data collection (°)	0.995–27.18	0.997-25.02
Reflections collected	31,103	51,956
Independent reflections/R _{int}	4083/0.0636	6842/0.0969
Observed reflections $[l > 2\sigma(l)]$	3107	3435
Data/restraints/parameters	4083/2/251	6842/0/529
Goodness-of-fit on F ²	1.026	0.986
Final indices[$l > 2\sigma(l)$]	$R_1 = 0.0530$	$R_1 = 0.0671$
	$w\dot{R}_{2} = 0.1504$	$w\dot{R}_{2} = 0.1610$
<i>R</i> indices (all data)	$R_1 = 0.0733$	$R_1 = 0.1489$
	$w\dot{R}_{2} = 0.1672$	$w\dot{R}_{2} = 0.1929$
Largest diff. peak/hole (e Å ⁻³)	1.366/-0.717	1.003/-0.353

2.5. Hirshfeld surface analysis

Hirshfeld surface analysis has been done using Crystal Explorer version 3.1 [46]. The normalized contact distance (d_{norm}) based on d_i and d_e has been determined by the given equation where r^{vdW} is the van der Waals (vdW) radius of the appropriate atom internal or external to the surface.

$$d_{\text{norm}} = \frac{(d_{\text{i}} - r_{\text{i}}^{\text{vdW}})}{r_{\text{i}}^{\text{vdW}}} + \frac{(d_{\text{e}} - r_{\text{e}}^{\text{vdW}})}{r_{\text{e}}^{\text{vdW}}}$$

 d_{norm} becomes negative for shorter contacts than vdW separations and becomes positive for contacts greater than vdW separations and is displayed using a red–white–blue color scheme, where red high-lights shorter contacts, white is used for contacts around the vdW separation, and blue is used for longer contacts [47].

3. Results and discussion

3.1. Preparation of N,N'-bis(3-methoxysalicylidene)propylene-1,3-diamine (H₂L), $[Zn_3(L)_2Cl_2]$ (1) and $[Zn_2(L)_2(Na)N_3]_n$ (2)

H₂**L** was synthesized by condensation of 1,3-diaminopropane and *o*-vanillin in a 1 : 2 M ratio in methanol. The ligand possesses six potential donor sites: two azomethine nitrogens, two phenolic oxygens, and two oxygens of methoxy groups. Reaction of $ZnCl_2$ with **H**₂**L** in the presence of Et₃N in 3 : 2 : 4 M ratio in methanol under reflux produced the trinuclear complex $[Zn_3(L)_2Cl_2]$, **1**. Complex **1** was further subjected to react with an aqueous methanolic solution of sodium azide (1 : 1 M ratio) and produced bright yellow needle-shaped crystals of $[Zn_2(L)_2(Na)N_3]_n$, **2** (scheme 1).



Scheme 1. The route to the syntheses of 1 and 2.



Figure 1. ORTEP view of **1**. Atoms are shown as 30% thermal ellipsoids. Hydrogens are omitted for clarity (color code: green—chlorine, pink—oxygen, purple—zinc, blue—nitrogen; symmetry code: -x, -y, z).

3.2. Crystal structure description

3.2.1. Description of the crystal structure of [Zn₃(L)₂Cl₂] (1)

Complex **1** crystallized from slow evaporation of methanol. It is a neutral trinuclear molecule of formula $[Zn_3(L)_2Cl_2]$ (figure 1) with an orthorhombic space group Fdd2. Selected bond lengths and angles for **1** are presented in table 2. The core structure of **1** contains two equivalent terminal [ZnLCl] units and one central Zn(II). The molecule possesses a crystallographic 2-fold axis passing through the central Zn ion. Both terminal Zn ions are five-coordinate and located in the inner N₂O₂ cavities of the Schiff base ligands. The equatorial plane is formed by the two imine nitrogens, N(1) and N(2), with distances 2.046(8) and 2.115(8) Å and two phenoxido oxygens, O(2) and O(3), of the Schiff base with distances 2.065(6) and 2.040(5) Å, respectively. A chloride, Cl(1), coordinates to the axial position at 2.326(3) Å (figure 1). The metal atom deviates 0.592 Å from the basal plane toward Cl(1). The Addison parameter [$\tau = (\alpha - \beta)/60^\circ$ where α and β are the two largest angles around the central atom; $\tau = 0$ and 1 for perfect square pyramidal and trigonal bipyramidal geometries, respectively] is 0.42, indicating a highly distorted square pyramidal geometry [48]. The central Zn(2) is six-coordinate, encapsulated in the O_6 cavity by two phenoxido and one methoxy of each "metalloligand". A methoxy oxygen and phenoxido oxygen

	X-ray	Cal.		X-ray	Cal.
Zn1-02	2.070(4)	2.1086	Zn1–Cl1	2.321(3)	2.326
Zn1-03	2.024(4)	2.0877	Zn2-04	2.368	2.3864
Zn1–N1	2.062(6)	2.1455	Zn2-02	2.107	2.0792
Zn1–N2	2.106(6)	2.1884	Zn2-03	2.097	2.0894
Zn1–Zn2	3.303	3.2672	Zn1A–Zn2	3.303	3.2672
N1-Zn1-N2	93.7(2)	87.72	02-Zn1-Cl1	114.0(2)	120.46
03-Zn1-Cl1	114.7(1)	107.35	N1–Zn1–Cl1	113.5(2)	113.25
N2–Zn1–Cl1	113.6(2)	114.89	N1-Zn1-O2	88.8(3)	85.72
N1–Zn1–N2	93.7(2)	87.72	N2-Zn1-O3	85.8(3)	85.46
Zn1-02-Zn2	104.5	103.27	Zn1-03-Zn2	105.7	102.20
02–Zn2–O3	73.3	75.9	C9-C10-C11	122(2)	114.80

Table 2. Selected bond lengths (Å) and angles (°) for 1.

Symmetry code for 1: A = -x, -y, z.



Figure 2. 1-D supramolecular chain of **1** propagating along the *b*-axis showing C–H \cdots π and π \cdots π stacking interaction. Hydrogens of least interest are omitted for clarity.

of same ligand system coordinate axially, while the other phenoxido (symmetry operation a = -x, -y, z) and methoxy oxygens define the basal plane to complete the highly distorted octahedral geometry around Zn(2). Zn–O bond lengths are 2.096 Å (Zn(2)–O(2)), 2.102 Å (Zn(2)–O(3)), and 2.382 Å (Zn(2)–O(4)), respectively. The bridging phenoxido oxygen of the deprotonated L^{2–} connect each terminal Zn to the central Zn forming bis(µ-phenoxo)-bridged Zn(II)-Zn(II) motifs. The three Zn(II) ions deviate greatly from linearity with a Zn(1)–Zn(2)–Zn(1) angle of 148.86°. The Zn–Zn distances are the same (3.303 Å) due to the centrosymmetric nature of the crystal system (figure 1). Holmes *et al.* and Liu *et al.* reported similar zinc trinuclear molecules deploying analogous Schiff base ligands. In each case, the terminal zinc(II) ions are five-coordinate and the central zinc(II) ion is six-coordinate. Zn–N and Zn–O bond distances observed in the above cases are comparable with that of **1** [49–51].

Complex **1** further undergoes 1-D self-assembly along the *b*-axis with the support of C-H··· π interactions between the H atoms of the methoxy groups and the π -cloud of adjacent phenyl rings. These interactions are very weak (3.287 Å) (figure 2). Also, **1** exhibits weak intramolecular π ··· π interactions (centroid to centroid distance is 3.675 Å).

3.2.2. Description of the crystal structure of $[Zn_2(L)_2(Na)N_3]_n$ (2)

The asymmetric unit of **2** is presented in figure 3. Selected bond distances and angles are listed in table 2. Each asymmetric unit of **2** consists of two [ZnL] units, one sodium ion and one N₃⁻, thus balancing



Figure 3. ORTEP view of **2**. Atoms are shown as 30% thermal ellipsoids. Hydrogens are omitted for clarity (color code: pink—oxygen, purple—zinc, blue—nitrogen, orange—sodium; symmetry code: -x, 1/2 + y, $\frac{1}{2} - z$).

the charge of the unit. Terminal Zn²⁺ ions (Zn1 and Zn2) are five-coordinate through one Schiff base ligand and one azido ion as shown in figure 3. In the basal plane, each Zn^{2+} is coordinated with N₂O₂ of the Schiff base ligand. Zn–O and Zn–N bond lengths of both terminal Zn²⁺ ions are similar (Zn1– O2, Zn1-O3, Zn1-N1, Zn1-N2, Zn2-O6, Zn2-O7, Zn2-N3, and Zn2-N4 are 1.999(5), 2.019(4), 2.117(5), 2.063(7), 1.998(5), 2.003(5), 2.098(7), and 2.075(5), respectively). These Zn–N and Zn–O bond distances are comparable with those of a previously reported zinc polymer with the same ligand system [52]. To date, no zinc polymer has been reported using the same ligand system with a single µ11-azido bridging group. The Zn ions are displaced by 0.503 Å (Zn1) and 0.497 Å (Zn2) from the mean basal plane toward the azido ligand. The Addison parameter of both Zn1 and Zn2 are comparable (0.49 and 0.45, respectively), suggesting their highly distorted square pyramidal structure [48]. The central sodium ion and the two terminal zinc ions are present in an approximately linear array. The central Na⁺ core is coordinated with two ZnL units via four phenolate O and four methoxy O of L2⁻. The central Na⁺ core thus results in a relatively scarce eight-coordinate trigonal dodecahedral geometry (figure 3). The Na-O(phenolate) distances are 2.593(6), 2.557(5), 2.561(6), and 2.546(5) Å, and the Na-O(methoxy) distances are 2.464(5), 2.549(4), 2.470(7), and 2.573(8) Å, respectively; the average Na–O(methoxy) distances are shorter than the average Na–O(phenolate) distances. The two sets of salen-type Schiff base ligands are almost orthogonally arranged around the Na⁺ center; the dihedral angle between the mean planes passing through [O(1)-O(2)-O(3)-O(4)] and [O(5)-O(6)-O(7)-O(8)] is 84.71°. The intramolecular separation between $Zn(1)\cdots Zn(2)$ is 7.437 Å, whereas the $Zn(1)\cdots Na(1)$ and $Zn(2)\cdots Na(1)$ separations are 3.729 and 3.718 Å, respectively. The {Zn(1)–O(2)–Na(1)}, {Zn(1)–O(3)–Na(1)}, {Zn(2)–O(6)–Na(1)}, and {Zn(2)-O(7)-Na(1)} angles are 107.9(2), 108.6(2), 108.7(2), and 109.0(2), respectively. Each azido ion functions as a μ-1,1-bridge with similar metric parameters (2.096 Å, 2.108 Å, 132.83°). This azido bridging produces one-dimensional polymeric zig-zag chains along the b-axis (figure 4). The shortest inter-chain Zn…Zn distance is 3.853 Å.

In **2**, a 1-D chain has been generated through $\mu_{1,1}$ -azido bridging between [Zn₂Na] units. This 1-D chain is further supported by intramolecular C-H··· π interactions between aliphatic protons (ethyl) and the π -cloud of phenyl rings having an average distance of 3.168 Å. In addition, edge to edge π ··· π stacking (3.260 Å) between sp²-hybridized carbons favors this 1-D network. These 1-D networks further interact with each other by weak C-H··· π interactions (3.608 Å, between the aromatic proton and π electron cloud of phenyl ring), leading to a 2D network along the *bc* plane (figure 5).



Figure 4. Polymeric view of $\mu_{1,1}$ -azido-bridged Zn(II)-Na(I) polymer.



Figure 5. 2-D supramolecular sheet of **2** propagating along the *bc* plane showing C–H··· π and π ··· π stacking interaction. Hydrogens of least interest are omitted for clarity.

3.3. IR spectra and ¹H NMR studies

In addition to elemental analysis, all of the complexes were initially characterized by IR spectroscopy. A strong and sharp band is at 1629, 1625, and 1620 cm⁻¹, respectively, for **H₂L**, **1** and **2** due to the azomethine v(C=N). In **2**, a sharp peak at 2075 cm⁻¹ was obtained indicating $\mu_{1,1}$ -azide bridging (figures S1-S3). ¹H NMR spectra of **H₂L**, **1**, and **2** were obtained in DMSO-d₆ solvent. In **H₂L**, aromatic protons appeared at 7.03–7.00 ppm and 6.82–6.77 ppm, whereas aliphatic and azomethine protons appeared at 2.04–1.99 ppm, 3.70–3.66 ppm, and 8.56 ppm, respectively. For **1**, the aromatic protons were at 6.30–7.26 ppm. Aliphatic proton signals were near 3.16 and 2.5 ppm. The azomethine CH=N proton appeared at 8.30 ppm. In **2**, the aromatic protons were at 6.28–6.34 ppm and 6.6–6.7 ppm. Aliphatic and azomethine protons appeared near 3.8, 2.48, and 8.28 ppm, respectively (figures S4-S6).

3.4. Optical properties

Electronic spectra of the free ligand, **1**, and **2** were recorded in DMF. **H**₂**L** shows four broad absorptions around 220, 260, 295, and 420 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions (figure S7). Both complexes exhibit two sharp absorptions around 270 and 360 nm (figures S8 and S9). These absorption bands can be assigned to $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions of the Schiff base ligands. Fluorescence spectra of the free ligand, **1**, and **2** were also obtained in DMF. **H**₂**L** upon excitation gives a broad fluorescent emission band at 458 nm. Complex **1** upon excitation at 358 nm gives an intense emission peak at 490 nm and **2** upon excitation at 360 nm gives an intense emission peak at 483 nm (figure 6). The emissions of the complexes are probably based on intra-ligand ($\pi \rightarrow \pi^*$) transitions modified by metal coordination [7]. The fluorescence order follows the trend $H_2L < 1 < 2$. H_2L shows very low fluorescence intensity mainly due to photo-induced electron transfer processes (PET) where lone pairs of phenolic O delocalize within the benzene ring of o-vanillin. In the case of **1**, the rigidity of the molecule increases due to coordination of the metal ion to phenolic O of the Schiff base, resulting in inhibition of such PET processes. On the other hand, chelation-enhanced fluorescence (CHEF) is greater for **2** than for **1**, owing to $\mu_{1,1}$ -azido bridging between two Schiff base ligands within the Zn₂Na unit. As **2** is a 1-D network supported by only one $\mu_{1,1}$ -azido bridge, it is highly rigid resulting in enhancement of fluorescence intensity.

Lifetime data of **1** and **2** were studied at 298 K in DMF solution upon excitation at 358 and 360 nm, respectively. The average fluorescence decay lifetime has been measured for both of the complexes using the formula $\tau_f = a_1 \tau_1 + a_2 \tau_2$, where a_1 and a_2 are relative amplitude of decay process). The average fluorescence lifetimes of **1** and **2** are 1.42 and 0.59 ns, respectively (figure 7 and table S1). The



Figure 6. Fluorescence emission properties of H,L, 1, and 2 in DMF.



Figure 7. Time-resolved fluorescence decay curves (logarithm of normalized intensity vs time in ns) of Complexes 1 (•) and 2 (•), (•) indicates decay curve for the scattered.

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fluorescence intensity of **2** is greater than that of **1** with a slight blue shift. These values are comparable with other Zn-salen complexes [53, 54].

3.5. Computational study

3.5.1. DFT calculations

The coordinates obtained from single-crystal X-ray diffraction data of **1** and **2** were used for optimization using the DFT/B3LYP method. The DFT-optimized structures well reproduce the experimentally determined X-ray crystal structures. Calculated bond lengths and angles of both complexes show good agreement with the X-ray structures (tables 2 and 3). Mulliken charge distributions show that the positive

	X-ray	Cal.		X-ray	Cal.
Zn1–N1	2.110(5)	2.0707	Na1-01	2.467(5)	2.4556
Zn1–N2	2.074(7)	2.0633	Na1–O2	2.596(6)	2.5428
Zn1-02	1.996(5)	1.9575	Na1-03	2.568(7)	2.5755
Zn1-03	2.020(4)	1.9578	Na1-04	2.547(4)	2.7859
Zn1–N5	2.111(7)	2.0467	Na1-05	2.568(7)	2.3622
Zn2–N3	2.074(5)	2.1968	Na1-06	2.545(5)	2.4078
Zn2–N4	2.100(7)	2.1453	Na1–07	2.561(6)	2.6964
Zn2–N5	2.097(5)	2.0467	Na1-08	2.472(7)	2.6481
Zn2-06	2.003(5)	2.0547	N2-Zn1-O3	89.5(2)	93.01
Zn2–07	1.998(5)	2.0706	N3-Zn2-06	89.2(2)	85.46
Zn1–Na1	3.729	3.5007	N4-Zn2-07	88.4(2)	86.24
Zn2–Na1	3.718	3.5249	N5-N6-N7	179(1)	177.32
C9-C10-C12	118(1)	122.10	01–Na1–O2	61.3(2)	65.84
C29–C31–C32	120.72	120.9	01-Na1-03	122.49	120.17
N1-Zn1-O2	87.3(2)	92.30			

Table 3. Selected bond lengths (Å) and angles (°) for 2.

Table 4. Energy (eV) and composition (%) of selected M.O.s of 1 and 2.

	1 2				2	2		
M.O.s	Energy (eV)	% Ligand	% Metal	% Cl	Energy (eV)	% Metal	% Ligand	% Azide (N ₃)
LUMO + 5	0.35	100	0	0	-0.85	1	99	0
LUMO + 4	0.31	100	0	0	-0.95	1	99	0
LUMO + 3	-1.26	100	0	0	-1.51	1	99	0
LUMO + 2	-1.32	65	0	35	-1.96	0	100	0
LUMO + 1	-1.47	61	0	39	-2.01	1	99	0
LUMO	-1.48	99	0	1	-2.73	1	99	0
НОМО	-5.2	99	0	1	-4.69	1	33	66
HOMO-1	-5.36	41	0	59	-4.74	2	47	51
HOMO-2	-5.56	45	0	55	-4.79	1	71	28
HOMO-3	-5.6	5	0	95	-5.07	4	53	43
HOMO-4	-6.23	5	0	95	-5.3	1	99	0
HOMO-5	-6.25	4	0	96	-5.53	1	99	0

 Table 5. Electronic transitions calculated by TDDFT using B3LYP/CPCM in DMF of 1 and 2.

	$E_{\text{excitation}}$ (eV)	$\lambda_{ m excitation}$ (nm)	Osc. strength (f)	Key transition	Character
1	3.23	371.58	0.0161	HOMO → LUMO (83%)	$\pi(L) \rightarrow \pi^*(L)$
	3.29	363.98	0.0498	$HOMO \rightarrow LUMO + 1 (67\%)$	$\pi(L) \rightarrow \pi^*(L)/CI(p\pi^*)$
	3.39	353.15	0.0268	$HOMO \rightarrow LUMO + 3 (68\%)$	$\pi(L) \rightarrow \pi^*(L)$
	3.40	351.97	0.0641	HOMO-1 → LUMO + 1 (75%)	$\pi(L)/CI(p\pi) \rightarrow \pi^*(L)/CI(p\pi^*)$
2	2.17	553.22	0.0054	$HOMO \rightarrow LUMO + 1 (96\%)$	$\pi(L)/N_3^-(p\pi) \rightarrow \pi^*(L)$
	2.21	541.74	0.0054	$HOMO \rightarrow LUMO + 2 (58\%)$	$\pi(L)/N_3^{-}(p\pi) \rightarrow \pi^*(L)$
	2.73	455.23	0.0004	HOMO-1 \rightarrow LUMO (82%)	$\pi(L)/N_3^{-}(p\pi) \rightarrow \pi^*(L)$
	2.76	433.34	0.0016	$HOMO \rightarrow LUMO + 1 (85\%)$	$\pi(L)/N_3^{-}(p\pi) \rightarrow \pi^*(L)$

charges on the metal ions are 0.858687 (Zn1, 1), 1.048861 (Zn2, 1), and 1.053548 (Zn1, 2), 0.969153 (Zn2, 2), and 0.576972 (Na1, 2), respectively. Mulliken charge distributions of 1 and 2 are depicted in table S2. Energy (eV) and composition (%) of some selected M.O.s along with the key electronic transitions of 1 and 2 are presented in tables 4 and 5, respectively. Contour plots of some selected M.O.s are given in figure 8. The HOMO and LUMO energies are -5.2 (1), -4.69 (2), and -1.48 (1), -2.73 (2), respectively,



Figure 8. Contour plots of selected molecular orbitals of 1 and 2.





suggesting that the HOMO-LUMO energy gap for **2** is less than that of **1**. Table 4 clearly suggests that in **1** and **2**, the contribution of the metal center toward the respective M.O.s is almost negligible. Ligands and coligands (Cl⁻ and N₃⁻) dominate the composition of the M.O.s. In **1**, HOMO, LUMO, LUMO + 3 to LUMO + 5 are purely ligand based, whereas HOMO-3 to HOMO-5 are purely coligand based. In the cases of HOMO-1, HOMO-2, LUMO + 1, and LUMO + 2, the M.O.s are contributed to from the ligand and coligand in nearly equal proportion. In **2**, HOMO-4, HOMO-5, LUMO to LUMO + 5 are purely ligand based and HOMO to HOMO-3 have significant contributions from both ligand and coligand.

3.5.2. TDDFT calculation

For better understanding of electronic transitions within the complexes, TDDFT calculations were performed with the B3LYP/CPCM method using the same basis sets in DMF. The calculated electronic transitions along with the calculated oscillator strength (*f*) are given in table 5. Complex **1** shows intense absorption bands for ligand-based $n-\pi$ and $\pi-\pi^*$ transitions (ILCT) near 270 and 358 nm, respectively. The band at 358 nm is theoretically composed of three excitations at 3.29 eV ($\lambda = 363$ nm, f = 0.0498), 3.39 eV ($\lambda = 353$ nm, f = 0.0268), and 3.40 eV ($\lambda = 351$ nm, f = 0.0641), respectively, and is due to the contribution of HOMO \rightarrow LUMO + 1, HOMO \rightarrow LUMO + 3, and HOMO-1 \rightarrow LUMO + 1 transitions and may ascribe to a combination of $\pi(L) \rightarrow \pi^*(L)/Cl(p\pi^*)/\pi(L)/Cl(p\pi) \rightarrow \pi^*(L)$ transitions. Similarly, **2** shows intense absorptions for ligand-based $n-\pi$ and $\pi-\pi^*$ transitions (ILCT) near 272 and 360 nm. Theoretically, the band at 360 nm is a composition of two excitations at 2.76 eV ($\lambda = 433$ nm, f = 0.0016) and 2.73 eV ($\lambda = 455$ nm, f = 0.0004) and is due to the contribution of HOMO \rightarrow LUMO + 1 and HOMO-1 \rightarrow LUMO transitions and may be attributed to ILCT transitions.

3.6. Hirshfeld surface analysis

Supramolecular interactions were further studied using Hirshfeld surface analysis. Complexes **1** and **2** are mapped over d_{norm} (range of -0.1 to 1.5 Å), shape index (range of -1.0 to 1.0 Å), and curvedness (range of -4.0 to 0.4), respectively, as presented in figure S7. Surfaces are kept transparent for visualization of different supramolecular interactions. No characteristic H-bonding interactions were found during mapping. This observation was further supported from decomposed fingerprint plots. The total extent of X…H/H…X (X=O, CI) contacts were found to be only around 2.7% of the total surface. The bright red area in the Hirshfeld surfaces is mainly due to intermolecular π - π interactions (figure S10).

4. Conclusion

Herein, we have reported an easy synthetic procedure for preparation of a $\mu_{1,1}$ -azido-bridged 1-D chain of $[Zn_2(L)_2(Na)N_3]_n$ (2) from a trinuclear $[Zn_3(L)_2Cl_2]$ (1) complex. Both 1 and 2 show supramolecular architectures supported by non-covalent interactions such as CH··· π and π - π stacking. These two complexes exhibit significant fluorescence properties ("CHEF"), where 2 fluoresces more than 1 due to the presence of a more rigid coordination environment. The structure and electronic spectra of both complexes have been interpreted by DFT and TDDFT calculations.

Supplementary data

CCDC 1402663 and 1402664 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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