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Dicyanamide-interlaced assembly of Zn(II)-Schiff-base complexes derived from salicylaldimino type compartmental ligands: syntheses, crystal structures, FMO, ESP,TD-

DFT, fluorescence lifetime, in vitro antibacterial and anti-biofilm properties

Dhrubajyoti Majumdar^{a,b}, Dhiraj Das^c, S. S. Sreejith^d, Sourav Das^e, Jayanta Kumar Biswas^f, Monojit Mondal^f, Debarati Ghosh^f, Kalipada Bankura ^a, Dipankar Mishra ^{a,*}

^aDepartment of Chemistry, Tamralipta Mahavidyalaya, Tamluk-721636, West Bengal, India

^bDepartment of Applied Chemistry, Indian Institute of Technology (Indian School of Mines),

Dhanbad, Jharkhand 826004, India

^cDepartment of Chemical Sciences, IISER, Mohali, Manauli, PO 140306, India

^dDepartment of Applied Chemistry, Cochin University of Science and Technology, Kochi,

682022, Kerala, India

^eDepartment of Chemistry; Institute of Infrastructure Technology Research and Management; Near Khokhara Circle, Maninagar East, Ahmedabad-380026, Gujarat, India ^fDepartment of Ecological Studies & International Centre for Ecological Engineering, University of Kalyani, Kalyani 741235, West Bengal, India

AUTHOR EMAIL ADDRESS: <u>dmishra.ic@gmail.com</u>

ABSTRACT

Two new dicyanamide-interlaced tetranuclear Zn(II)-Schiff-base complexes $[Zn_2(L^{OMe})(\mu_{edca})]$ $\kappa N^1 \kappa N^5 (\mu - dca - \kappa N^1)_2$ (1) and $[Zn_2(L^{OEt})(\mu - dca - \kappa N^1 \kappa N^5)(\mu - dca - \kappa N^1)_2$ (2) were synthesized by using salicylaldimino type Schiff bases (H_2L^{OMe}) and (H_2L^{OEt}) respectively. Schiff base ligands and the complexes were characterized by elemental analyses, powder X-ray diffraction, FT-IR, FT-Raman, ¹H NMR, ¹³C NMR, UV-Vis, TGA and fluorescence spectroscopy. Dicyanamide modulated complexes were structurally characterized by single crystal X-ray diffraction studies. X-ray crystal structure divulges that the two complexes are iso-structural. In both the complexes, the Zn1 metal centers fulfill 5-coordinated distorted square pyramidal geometry having ZnN₃O₂ chromospheres where Schiff bases are mainly trapped in their complete deprotonated dianionic forms[L]²⁻, whereas Zn2 metal center attained distorted octahedral geometry. In both complexes two asymmetric units are connected by double $\mu_{1,5}$ -dicyanamide ion thus forming Zn₄-nuclear metal complex. B3LYP/def2-TZVP level of theory (DFT) successfully applied in both complexes. The complexes (1-2) exhibit intraligand $(\pi \rightarrow \pi^*)$ fluorescence in DMSO solvent with lifetimes in the range 0.66-0.82 ns. In vitro antibacterial, membrane damage assay and antibiofilm properties of both complexes are evaluated against some important Gram-positive and Gram-negative bacterial strains. Finally, the UV-Vis experimental spectral findings are well rationalized with the electronic distribution of HOMO-LUMO through TD-DFT level of calculations.

Keywords: Schiff base, Dicyanamide, tetranuclear Zn(II), TD-DFT, Antibacterial, Fluorescence

1. Introduction

The coordination chemistry is largely explored to design and synthesis of polynuclear and supramolecular structure in last few decades [1a-b]. Proper selection of ligands in conjunction with different ancillary co-ligands, like pseudo-halide (SCN⁻/N₃⁻/NCO⁻/CN⁻), dicyanamide $[N(CN)_2]$ anion is the key factors for construction of coordination compounds of such architectures and topologies [1c-4]. The flexible dicyanamide pseudo-halide anion exhibit diverse coordination motifs through amide and nitrile nitrogen atoms when coordinated with particular transition metal ions [5] to extend varieties of molecular architectures from discrete, di-nuclear to multi-dimensional etc. [6-9]. Till date different dimensional network structures of dicyanamide ligand involving complexes have emerged in literature [10-25] but terminal monodentate coordination mode of dicyanamide (µ1-M) is truly rare owing to its long chain structure and negative (-ve) charge delocalization over the symmetrical molecule [26]. The design and syntheses of such Zn(II) metal template complexes involving dicyanamide pseudo-halide ligands are drawing much more aesthetic attention not only due to different structural varieties observed in the metal-organic frameworks or porous coordination polymers but also their important emerging applications like catalysis [27], magnetism [28], light emission, electron-transport processes [29], material science, optoelectronic devices etc. viz. Zn(II) salen-type Schiff base complexes are always excellent electroluminescent materials [30] and in supramolecular chemistry such Zn(II) complexes have been widely used in sensors and in host-guest chemistry. Thus significant number of research works was imposed on supramolecular Zn(II)-Schiff-base complexes [31a-n]. From biological standpoint, zinc is the most important second abundant trace metal after iron and play several important roles in enzyme catalysis, apoptosis, neurotransmission [32a-c]. Further, Zn(II) metal ion, a d¹⁰ electronic system may adopt

versatile coordination number with different type of molecular architectures and topologies that may be produced in presence of suitable ligands framework .

In the last few years, we have explored photoluminescent, DFT, TD-DFT, thermal, *in vitro* antibacterial, membrane damage assay and anti-biofilm properties of Zn(II)/Cd(II) metal ion complexes in presence of $[N_2O_4]$ donor-type salicylaldimino ligands (H_2L^{OMe}/H_2L^{OEt}) $[H_2L^{OMe}=N,N^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{OEt}=N,N^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{OEt}=N,N^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{OEt}=N,N^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{OEt}=N,N^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{OEt}=N,N^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{OEt}=N,N^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{OEt}=N,N^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{OEt}=N,N^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{OEt}=N,N^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{OEt}=N,N^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{OEt}=N,N^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{OEt}=N,N^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{OEt}=N,N^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{OEt}=N,N^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{2}-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{2}-bis(3-methoxysalicylidenimino)-1,3-bis(3-methoxysalicylidenimino)-1,3-diaminopropane,H_2L^{2}-bis(3-methoxysalicylidenimino)-1,3-bis(3-methoxysalicylidenimino)-1,3-bis(3-methoxysalicylidenimino)-1,3-bis(3-methoxysalicylidenimino)-1,3-bis(3-methoxysalicylidenimino)-1,3-bis(3-methoxysalicylidenimino)-1,3-bis(3-methoxysalicylidenimino)-1,3-bis(3-methoxysalicylidenimino)-1,3-bis(3-methoxysalicylidenimino)-1,3-bis(3-methoxysalicylidenimino)-1,3-bis(3-methoxysalicylidenimino)-1,3-bis(3-methoxysalicylidenimino)-1,3-bis(3-methoxysalicylidenimino)-1,3-bis(3-methoxysalicylidenimino)-1,3-bis(3-methoxysali$

ethoxysalicylidenimino)-1,3-diaminopropane] and potential pseudo-halide anions [SCN]⁻, $[N_3]^-$ or anions like Cl⁻, NO₃⁻ etc. Therefore, the only outcome of previous works is that pseudo-halides [SCN]⁻/[N₃]⁻ linked metal complexes exhibit strong photoluminescence, antimicrobial and anti-biofilm properties [33a-g]. In search of new luminescent Zn(II)-Schiff-base complexes, we have been motivated to frame another two closely resembling less explored salen-type ligands (H₂L^{OMe}/H₂L^{OEt}). Thus a target oriented complexing reaction was carried out in presence of Zn(II) metal template, Schiff-base ligands and dicyanamide pseudo-halide leading to the formation of complexes (**1-2**).

In this work, we report the syntheses, characterizations, crystal structures, FMO, ESP, TD-DFT, fluorescence life-time, thermal, *in vitro* antibacterial and anti-biofilm properties of tetranuclear Zn(II) dicyanamide modulated Schiff base complexes.

4

2.1. Materials and physical measurements

All the reagents were of analytical grade and used as purchased without further purification. Elemental analyses were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were recorded as KBr pellets within the range 4000–400 cm⁻¹on a Perkin–Elmer spectrum RX 1. Raman spectra were analyzed by using BRUKER RFS 27 between 4000-50 cm⁻¹. UV-Visible spectra (200-1100nm) in DMSO were performed with a Hitachi model U-3501 spectrophotometer. Fluorescence spectra in DMSO were measured by using Perkin-Elmer LS50B Spectrofluorimeter model at room temperature (298K). Fluorescence lifetime measurements were recorded by using JOBIN-VYON M/S Fluorimeter. Thermogravimetric analyses (TGA) of both complexes were carried out on a TGA-5OH analyzer from ambient temperature to 700°C at a temperature rate of 10°C/min in a flowing 30ml/min under environment of nitrogen atmosphere using a platinum cell. X-ray powder diffraction measurements were carried out using BRUKER AXS, GERMANY X-ray diffractometer model using radiation Cu K-alpha-1. Quantum yield (Φ) have been determined using popular equation (1) where quinine sulfate is used as the secondary standard ($\Phi = 0.57$ in water) [34]

$$\frac{\Phi_s}{\Phi_R} = \frac{A_s}{A_R} \times \frac{(Abs)_R}{(Abs)_S} \times \frac{n_s^2}{n_R^2} - \dots$$
(1)

According to equation (1), A terms denote the fluorescence area under the curve; Abs denotes absorbance; n is the refractive index of the medium; Φ is the fluorescence quantum yield; and subscripts S and R denote parameters for the studied sample and reference respectively.

2.2. X-ray crystallography

The good quality crystal data of complexes (1-2) were collected on a Bruker SMART CCD [35] diffractometer using MoK_a radiation at $\lambda = 0.71073$ Å. Different common programs were operated for collection of crystal data of complex 1, 2 e.g. SMART program used for collecting frames of data, indexing reflections, and determining lattice parameters, SAINT [36] for integration of the intensity of reflections and scaling, SADAB[37] for absorption correction, and popular SHELXTL for space group and structure determination and least-squares refinements on F^2 . The crystal structure of complex 1, 2 was fully solved and refined by full-matrix leastsquares methods against F^2 by using the program SHELXL-2014[38] and Olex-2 software [39]. For that reason all the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen positions were fixed at calculated positions and refined isotropically. Crystallographic diagrams of different molecules were constructed for 1, 2 with the aid of latest Diamond software [40]. In this context a detailed summary of the crystallographic data and full crystal structure refinement parameters for complexes (1-2) are clearly presented in Table 1. Crystallographic data (excluding structure factors) for both complexes have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1876204-1876205. Copies of the data can be obtained, free of charge, on application to CCDC, 12 UnionRoad, Cambridge U.K.:http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, CB2 1EZ, email:data_request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

Formula	$C_{46}H_{40}N_{16}O_8Zn_4$ (1)	$C_{50}H_{48}N_{16}O_8Zn_4(2)$
M/g	1206.52	1262.52
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a/Å	9.5908(14)	9.4196(19)
b/Å	11.3039(17)	11.815(2)
c/Å	12.838(2)	13.394(3)
β (°)	94.164(8)	93.183(11)
$V/\text{\AA}^3$	1277.3(3)	1360.8(5)
Ζ	1	1
$ ho_{ m c}/{ m g~cm^{-3}}$	1.5684	1.541
μ/mm^{-1}	1.924	1.809
F(000)	613.4464	644
Cryst size (mm ³)	$0.2 \times 0.2 \times 0.1$	$0.2 \times 0.2 \times 0.1$
θ range (deg)	0.9817	0.998
Limiting indices	$-12 \le h \le 12$	-11 ≤ h ≤ 11
	$-15 \le k \le 13$	$-14 \le k \le 14$
	$0 \le l \le 17$	$-14 \le 1 \le 15$
Reflns collected	18562	11007
Ind reflns	$6319[R_{int} = 0.1242, R_{sigma} =$	4774 [$R_{int} = 0.0291$, $R_{sigma} =$
	0.0831]	0.0435]
Completeness to θ (%)	98.17	99.8
Refinement method	Full-matrix-block least-	Full-matrix-block least-squares on
	squares on F ²	F ²
Data/restraints/ parameters	6319/0/295	4774/0/301
Goodness-of-fit on F^2	1.0314	1.049
Final <i>R</i> indices	$R_1 = 0.0854$	$R_1 = 0.0727$
$[I > 2\theta(I)]$	$wR_2 = 0.2546$	$wR_2 = 0.1886$
R indices (all data)	$R_1 = 0.1254$	$R_1 = 0.1057$
	$wR_2 = 0.3011$	$wR_2 = 0.2120$
Largest diff. peak and hole($e \cdot Å^{-3}$)	1.8426 and -1.1660	0.981 and -0.970

Table 1 Crystal data and full structure refinement parameters of ${\bf 1}$ and ${\bf 2}$

CCDC	1876204	1876205

2.3. Computational methodologies

DFT calculations were done using Becke's three-parameter hybrid exchange functional including [41] the Lee-Yange-Parr [42] nonlocal correlation functional (B3LYP) by employing ORCA 3.0.3 software package [43-44]. The triple zeta valence basis set with one set of polarization function TZVP basis sets [42] was used. To accelerate the calculations, we utilized the resolution of identity (RI) approximation with the decontracted auxiliary def2eTZV/J Coulomb fitting basis sets and the chain-of-spheres (RIJCOSX) approximation to exact exchange as implemented in ORCA [45]. The orbital composition were found out using Mulliken method by using multiwfn program [46]. The graphics of the results were plotted using Avogadro software [47a]. The choice of the TZVP basis set was made on the known fact that it reduces the basis set superposition error (BSSE) to negligible in the calculation of systems with noncovalent interactions. The Time Dependent-Density Functional Theory (TD-DFT) calculation were performed for complexes (1-2) by using Gaussian 09 [47b] at DFT/B3LYP level using 6-31G* basis set for C, H, O and N atoms and common LANL2DZ [47c-d] basis set and an effective core potential was used for Zn atoms. The effect of the solvent was modeled with the polarized continuum model (PCM) [47e]. The crystallographic coordinates have been considered for the DFT calculation. All the generated molecular orbitals (MOs) at the time of TD-DFT calculations were commonly visualized using software Gauss view 5.0.

2.4. Antibacterial screening

The antibacterial potentials of the selected two tetranuclear Zn(II) dicyanamide complexes were tested *in vitro* against bacterial strains belonging to Gram-positive (*Enterococcus gallinarum*

MTCC 7049 and *Staphylococcus haemolyticus* MTCC 3383) and Gram-negative (*Enterobacter aerogenes* MTCC 111 and *Proteus vulgaris* MTCC 744) categories, which were obtained from Microbial Type Culture Collection and Gene Bank (MTCC), Institute of Microbial Technology, Chandigarh, India.

The assessments of antibacterial potential and minimum inhibitory concentrations (MIC) of the complexes were performed against the selected strains following standard protocol recommended by Clinical and Laboratory Standards Institute (CLSI) [48]. The susceptibility of the bacterial strains to those complexes was ascertained by agar well diffusion method and the potentiality was expressed by growth inhibition zone diameter (mm) measurement [49]. At mid log phase the representative Gram-positive (*E. gallinarum*) and Gram-negative (*P. vulgaris*) bacterial strains were subjected to the complexes at their respective MICs, and respective time-kill curves were drawn [49]. The biofilm removal efficiencies of (1-2) were assessed against Gram-positive (*E. gallinarum*) and Gram-negative (*P. vulgaris*) bacterial strains following standard protocol [50a-b].

Membrane damage assay was performed on a Gram-positive (*E. gallinarum*) and a Gramnegative (*P. vulgaris*) bacterial strain to test one of the plausible modes of antimicrobial action of the complexes tested on affecting bacterial cell membrane disintegration. Membrane damage was evaluated by estimating the amount of nucleic acids released out of the bacterial cells [51, 52a]. Overnight cultures of the both bacterial strains were subjected to centrifugation at 8000 rpm for 5 min. The cell pellet was washed three times by phosphate buffer saline (PBS, pH 7.4) and resuspended in the liquid media. The specific optical density (0.7) of the selected bacterial suspension was fixed at 600 nm, and disseminated into different conical flasks. The individual concentration of the tested complexes was set at their respective MIC relevant against the

bacterial strains. The set devoid of any complexes was maintained as control. On 30 min interval sample (2 mL) was taken and filtered with 0.2 μ m syringe filter. The filtrate was measured on a UV-Vis spectrophotometer at 260 nm, and the amount of released nucleic acids was quantified.

2.5. Synthesis of the ligands

Two Schiff base ligands (H_2L^{OMe} and H_2L^{OEt}) were synthesized by the common condensation process of 1 mmol (0.152g) 3-methoxysalicylaldehyde or (0.1662g) 3-ethoxysalicylaldehyde with 0.5 mmol (0.0371g) 1,2-propanediamine (*Pn*) in (50 mL) of methanol for ca. 1 h (Scheme 1).The dark orange yellow solution was directly used for tetranuclear Zn(II) dicyanamide complex formation.



Scheme1. Syntheses of Schiff base ligands

2.6. Synthesis of $[Zn_2(L^{OMe})(\mu - dca - \kappa N^1 \kappa N^5)(\mu - dca - \kappa N^1)]_2$ (1)

To the methanolic solution (25 mL) of zinc acetate dihydrate (0.2195g, 1 mmol), dark orange yellow solution of Schiff base (H_2L^{OMe}) was added directly followed by mixing a methanolic solution (5 mL) of sodium dicyanamide (0.0891g, 1 mmol) and the overall solution mixture was

refluxed for 1 hour at 60 °C. Acetonitrile (CH₃CN) (5 mL) was then added into this refluxed solution. Yellowsolution was immediately cooled at room temperature and constant stirringcontinued for 1 h. Finally, the light-yellow filtrate was kept for crystallization by slow evaporation at normal room temperature. After 4 days yellow colored single crystal suitable for X-ray crystallography was obtained. Crystals were isolated by filtration and air dried. Yield: 0.365 g (68%), Anal. Calc. for C₄₆H₄₀N₁₆O₈Zn₄: C, 45.79; H, 3.34; N, 18.58.Found: C, 44.9; H, 3.5; N, 18.35 %. IR (KBr cm⁻¹) selected bands: v(C=N), 1634 vs, v(C=N), 2284 m, 2221 m, 2176 vs, FT-Raman (cm⁻¹) selected bands: v(C=N), 1644 vs, v(C=N), 2280 vs, 2228 s, 2173 w.

2.7. Synthesis of $[Zn_2(L^{OEt})(\mu-dca-\kappa N^1\kappa N^5)(\mu-dca-\kappa N^1)]_2$ (2)

Complex **2** was prepared by the identical procedure as **1** except Schiff base solution used is (H_2L^{OEt}) . Yield: 0.368 g (68.75%), Anal. Calc. for $C_{50}H_{48}N_{16}O_8Zn_4$: C, 47.64; H, 3.68; N, 17.78. Found: C, 47.35; H, 3.45; N, 17.58%. IR (KBr cm⁻¹) selected bands: v(C=N) 1633 vs, v(C=N) 2282 m, 2223 s, 2175 vs, FT-Raman (cm⁻¹) selected bands: v(C=N) 1631 vs, v(C=N) 2283 w, 2240 m, 2129 m.

3. Results and discussion

3.1. Synthetic methodology

The tetradentate Schiff-base ligands were synthesized using the literature method [52b]. The tetra nuclear Zn(II) metal complexes (**1** and **2**) were synthesized by stirring $Zn(OAc)_2.2H_2O$ with Schiff base ligands in methanol followed by slow addition of methanolic solution of $[N(CN)_2]^{-}$ in 1:1:1 molar ratio (Scheme 2). Complexes were successfully isolated in crystalline form from slow evaporation of CH₃OH-CH₃CN mixture. Metal assisted (M⁺²) versatile binding ability of Schiff base ligands and dicyanamide anions are presented in Scheme S1 and S2. The

obtained complexes were air stable, yellow colored, soluble in common organic solvents. Complexes are characterized by elemental analyses, UV-Vis, IR, Raman, powder X-ray diffraction, thermal, fluorescence and X-ray crystallography. Schiff base ligands are tetradentate in nature but in context of our synthesis they are well behaved as 'pendant ligands'. A large number of 'pendant ligands' are used in a variety of different chemical applications [53a-e]. Till date, using identical ligands and dicyanamide anions four zinc metal complexes have emerged in literature [54]. Hence, at least to the best of our knowledge this specific type of Schiff-base ligands has never been used to synthesize zinc dicyanamide-interlaced assembly.



Scheme2. Synthetic scheme for complexes (1-2)

3.2. Spectral characterizations

The characteristic imines (C=N) stretching vibration of Schiff base ligands are found to be 1628, 1631 cm^{-1} respectively [55a-b] (Fig.S1, Fig.S3, Fig.S5A). The above stretching vibration bands are shifted to 1634, 1633 cm⁻¹ in complexes (1-2) [55c]. The dicyanamide anion [N(CN)₂]⁻ showed three sharp strong characteristic band preferably in the region 2300-2170 cm⁻¹[56]. Two medium intensity bands (at 2284, 2221 cm⁻¹ in **1** and 2282, 2223 cm⁻¹ in **2**) and a strong intensity

band (at 2176 cm⁻¹ in **1** and 2175 cm⁻¹ in **2**) are indicative of the presence of dicyanamide in these two complexes. FT-IR spectra with other reported Zn(II) dicyanamide complexes were compared in TableS2.FT-Raman spectral data of some reported Zn(II) dicyanamide complexes were further consider to established the bridging mode of $[N(CN)_2]^-$ anions shown in Table S3.In addition, aliphatic C-H stretching resonances for Zn(II) dicyanamide complexes were observed within the range 2934-2835 cm⁻¹and 2924-2873 cm⁻¹[57a]. Ar-O stretching frequencies in **1-2** observed near at 1250-1222 cm⁻¹and 1244-1218 cm⁻¹ which is similar to the other reported salentype ligands [57b].

3.3. UV-Vis spectra

UV–Visible spectral bands near at 283 and 334 nm of Schiff base ligands are assigned due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions (Fig.S2). Both complexes in DMSO solvent exhibits ligand–based transition near at 286, 368 nm and 282, 368 nm presumably due to $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ type of transitions [58, 59]. Since Zn(II) metal have filled d¹⁰ configuration hence no metal centric d-d transition band was observed in the complex spectrums.

3.4 X-ray powder diffraction

The phase purity of complexes (1-2) was ensured by X-ray powder diffraction pattern. The X-ray powder diffraction pattern for both tetranuclear complexes was recorded experimentally after considering effectively 2θ scan from 4^0 to 50^0 . The experimental powder X-ray diffraction pattern of two complexes agree very well with the patterns simulated from single-crystal diffraction data (cif file) obtained from Mercury software (Fig. S4). Hence the study of X-ray powder diffraction is further established the phase purity of the bulk crystal samples of Zn₄-nuclear metal complexes. Thus, powder X-ray diffraction patterns of (1-2) positively confirmed that dicyanamide modulated complexes are completely isostructural.

4. Description of the X-ray crystal structures

4.1. $[\operatorname{Zn}_2(\operatorname{L}^{\operatorname{OMe}})(\mu - \operatorname{dca} - \kappa N^1 \kappa N^5)(\mu - \operatorname{dca} - \kappa N^1)]_2$ (1) and $[\operatorname{Zn}_2(\operatorname{L}^{\operatorname{OEt}})(\mu - \operatorname{dca} - \kappa N^1 \kappa N^5)(\mu - \operatorname{dca} - \kappa N^1)]_2$ (2) The solid-state structures of the complexes have been confirmed by single-crystal X-ray diffraction and both the complexes crystallize in triclinic space group $P\overline{1}$. The complexes are tetranuclear homometallic in nature and isostructural. Full crystallometric parameters for complexes (1-2) are summarized in Table S1. In connection of the structural aspects of homometallic tetranuclear complexes, herein we have only described in details the structure of complex 1 as a representative example to show the common structural features of two complexes. The asymmetric unit (Fig.1) contains two Zinc metal ions, one Schiff base ligand fully deprotonic forms [L^{OMe}]²⁻or [L^{OEt}]²⁻and two dicyanamide ions that is equivalent to basic structural core $[Zn_2(\mu_2-O)_2]^{2+}$. The ligand has two binding sites, which is chelated with the two zinc ions. The crystal structure analysis of 1 divulges that Zn1 center in ZnN₃O₂chromophoric environment adopted distorted square pyramidal geometry (Fig.2) and Addition tau (τ) parameter [60] is 0.04 (ideal value of tau for square pyramidal geometry is 0). The equatorial positions are occupied by two imine nitrogens (N1 and N2) and two phenolic oxygens. The apical position is occupied by the nitrogen atom (N8) of dicyanamide ion. Zn1 is displaced towards axial N8/N7 atom by 0.623 and 0.641 Å, respectively in 1 and 2 from their respective mean equatorial planes. The Zn2 center is hexa-coordinated (Fig.2) and adopted distorted octahedral geometry. The equatorial plane is occupied by two phenolic oxygens (O1 and O3) and two methoxy oxygens (O2 and O4). The axial positions are occupied by nitrogen atoms (N3 and N6) of two dicyanamide ions. Selected some major important bond lengths and angles of 1-2 are given in Table 2. The above bond distances are totally comparable to other reported Zn(II) dicyanamide complexes (Table S4). The bond distances between Zn2 and oxygen atoms of

alkoxy groups are quite longer $\{Zn2-O2 = 2.631\text{ Å}, Zn2-O4 = 2.781\text{ Å} \text{ in } 1, Zn2-O3 = 2.798\text{ Å}, Zn2-O4 = 2.781\text{ Å} \text{ in } 1, Zn2-O4 = 2.781\text{ Å} \text{ in } 1,$ Zn2-O4 = 2.722 Å in 2, as this site is open in nature causing steric hindrance by methyl groups [61]. The Zn1 and Zn2 are bridged by phenolic oxygens (O1/O1 and O3/O2) and the distances are 3.085 Å and 3.068 Å in 1 and 2, respectively. The distance between Zn 1 and Zn 2 metal centers is 3.085 Åthat is comparable to other Zn—Zn separation of double phenoxo bridged Zn₂ complexes[62a-b]. One dicyanamide ion act as a monodentate ligand via μ_1 -dca bridging mode and coordinated to the Zn2, whereas the other one connects Zn1 and Zn2 centers via $\mu_{1.5}$ -dca bridging and the distance between two centers is 7.973 Å and 8.111 Å in 1 and 2, respectively. Thus, two asymmetric units are connected by double $\mu_{1.5}$ -dicyanamide ion, [Zn1(NC-N-CN) $Zn2]_2$ and formed a discrete dimeric Zn_4 -nuclear metal complex 1 (Fig.2) and for complex 2 (Fig.4). In the solid-state, they exhibit hydrogen bonding interactions and developed network structure. The N5 atom of dicyanamide ion is hydrogen bonded in a bifurcated way with imine hydrogen and methine hydrogen and N4 is hydrogen bonded with hydrogen of the methoxy group and generated a 2-dimensional network (2D) (Fig.3). Packing diagram of complex 1 is clearly shown in Fig.S5B. In complex 2, the solid-state structure shows C-H $\cdots\pi$ interactions and generated a 1-dimensional network (1D) (Fig.5). The effective strong steric effect by ethyl side chain in complex 2 as compared to 1 prevents further association of the molecules through dicyanamide co-ligand resulting 1D dimensional network [61]. In the structural aspect, architectures and bridging propensity of dicyanamide anion of complex 1 and 2 has been compared with different complexes coordinated to identical salen-type ligands (Table S5).

Bond lengths (Å)	Bond lengths (Å) Value (Å)		Value (°)
1			
Zn1-N1	2.032(1)	N1-Zn1-N2	81.90(3)
Zn1-N2	2.049(8)	O1-Zn1-O3	78.20(2)
Zn1-N8	1.999(7)	O3-Zn1-N2	142.8(2)
Zn1-O1	2001(6)	01-Zn1-O3	78.20(2)
Zn1-O3	2.022(6)	N2-Zn1-N8	108.4(2)
Zn2-N6	1.957(6)	N2-Zn2-N6	115.9(2)
Zn2-N3	1.942(8)	N1-Zn1-N8	113.2(2)
2		4	
Zn1-N1	2.09(1)	N1-Zn1-N2	80.50(4)
Zn1-N2	2.049(8)	O1-Zn1-O2	78.90(2)
Zn1-N7	1.991(7)	O2-Zn2-N6	112.2(3)
Zn1-O1	2.016(6)	O2-Zn2-N3	114.10(3)
Zn1-O2	2.026(6)	O1-Zn2-N3	113.10(3)
Zn2-N3	1.948(9)	N2-Zn1-N7	114.7(3)
0]
V			



Fig.1. ORTEP view of asymmetric unit for complex 1(a) and for complex 2(b)



Fig.2.Dimeric unit of complex 1



Fig.3.2D hydrogen bonded network of complex 1



1

Fig.4.Dimeric unit of complex 2



Fig.5.1D hydrogen bonded network of complex 2

4.2. Frontier molecular orbital (FMO) analysis

The two complexes were optimised in the gaseous phase at B3LYP/TZVP level of theory. The optimised geometry was found to be of minimum energy *via* carrying out frequency calculations of the optimised structures which returned no imaginary frequency. The value of HOMO (highest occupied molecular orbital) dictates the ability of a molecule to donate electron while the electron accepting nature is decided by LUMO (lowest unoccupied molecular orbital) value and from the computed values suggest that complex **1** is more kinetically stable and chemically inert than complex **2** (Fig.6). From the plot itself it is clear that the HOMO of **1** is mainly concentrated on methoxy oxygen (15.64%, *p* type) and the two phenyl rings on either side (58.49%, π -type) while in the case of LUMO, methoxy group is not at all involved and it is concentrated on chelate rings and phenyl rings (91.32%, π *type). In the case of **2**, the HOMO is fully on theN(CN)₂ coligand and LUMO is having heavy contribution from both metallocycles and phenyl rings (67.63%, π * type). The global chemical reactivity descriptors associated with **1** and **2** are given in Table S6.



Fig.6.FMO with the associated energies computed at B3LYP/TZVP level of theory

4.3. Electrostatic Potentials (ESP) analysis

Electrostatic potential maps were mapped on electron density iso-surface between +50 kcal/mol to-50 kcal/mol reveals a positive charge on metal centre on both the complexes. With complex 2, has a relatively high positive charge compared to complex 1 (Fig.7). It is worth noting that, in both the complexes the higher positive charge is near the area in the proximity of azomethine hydrogen (+43.1kcal/mol and+44.6 kcal/mol for 1 and 2) respectively which is common in these classes of compounds [63]. Phenyl rings in the two compounds have a value *ca.*-23 kcal/mol while the donor oxygen atoms in both the compounds have comparatively high value with an average of about -36 kcal/mol. The highest negative potential is near the coligand (dca) in both the complexes with the highest value for 1. This different but opposite potentials between coligand (dicyanamide) and metal centre (Zn) results in the formation of dimeric structures in the

+43.6 +43.6 +13.8 +13.8 1 1 2 +10 kcal/mol

packing diagrams of both the structures of the complexes and account for the stability of their solid structures.

Fig.7. ESP mapped over the electron density isosurface of **1** and **2** computed at B3LYP/TZVP depicting the nucleophilic and electrophilic regions

4.4. TD-DFT analysis

The computational TD-DFT study of both tetranuclear Zn(II) dicyanamide complexes exhibits electronic transitions that are mainly due to intra-ligand charge transfer transition. The calculated absorption maxima for complex **1** arises at 357.90 nm (Experimental ~368 nm) with oscillator strength, f = 0.0161. In case of complex **2**, it shows calculated peak at 368.88 nm (Experimental ~368 nm) that arises mainly due to intra-ligand transitions with oscillator strength, f = 0.0595. All the HOMOs in both tetranuclear Zn(II) dicyanamide complexes are mainly consist of π orbitals only and the LUMOs are consist of ligand π *-orbitals only.TD-DFT related all possible orbital electronic transitions are clearly submitted in Table S7. Further, TD-DFT generated all possible MOs are lucidly presented in Fig.S6.

4.5. Fluorescence and lifetime studies

Metal complexes fluorescence behaviors are extremely important due to their plenty of application such as chemical sensors, in photochemistry and also in electroluminescent displays [64a]. The fluorescence behavior of Schiff base ligands $(H_2L^{OMe})/(H_2L^{OEt})$ and the complexes were recorded in DMSO solvent at room temperature (Table 3). The comparable fluorescence spectra are presented in Fig.8 revealing strongly that each Schiff base ligand is practically weak fluorescence with respect to either complex 1 or 2 but both complexes are highly fluorescent active. Upon photo excitation at 333 nm, both Schiff bases exhibits a fluorescent emission maximum centered at 441nm and 445 nm. Complexes 1, 2 upon photo excitation at wavelength 370 nm shows fluorescence maxima with the emission peak near at 483 nm and 485 nm. Emission spectra of Zn₄ dicyanamide complexes and ligands are similar with other reported Schiff bases e.g. L⁰H₂, L¹H₂, L²H₂, L³H₂, L⁴H₂ etc. [64b] and Zn(II) dicyanamide complexes (Table S7). C. E. Burrow et. al, has reported an emission spectrum of mixed metal [Zn₂Tb₃] complex of salen type ligand [65]. Apart from, quantum yield (ϕ) value of Schiff base ligands and complexes have been determined (Table3). Schiff bases quantum yield (ϕ)values are comparable with other reported salen-type ligands L¹H₂, L²H₂, L⁰H₂, L³H₂, L⁴H₂etc [66a-b].The strong fluorescence behavior of Zn(II)-Schiff-base complexes compared to ligands may be due to the reason that d¹⁰ candid metal is difficult or hard to oxidize or reduce. Hence the enhance of fluorescence behavior in both complexes may presumably attributed due to the increased in conformation rigidity of the Schiff base ligands impartedvia chelation effect with Zn(II) metal ion. Therefore, the fluorescence may be assigned mainly due to the intraligand $(\pi \rightarrow \pi^*)$ transition or L \rightarrow M charge transfer. Such type of fluorescence emission is called CHEF [67-70] but in case of quenching of fluorescence concept this is referred as 'Chelation enhancement of Quenching

effect'(CHEQ) [71]. The individual decay profiles of Schiff base ligands and the complexes have been lucidly generated in Fig.S7. The average fluorescence decay life times $\langle \tau_{av} \rangle$ have been determined for ligands and the complexes using the following the literature method in Equation S1. The nature of decay profile of Schiff base ligands can be best fitted to tri-exponential manner [72] (Fig.S7) whereas for tetranuclear Zn(II) complexes it will be best fitted to bi-exponential nature (with acceptable comparable χ^2 values). Decay profile are comparable to other reported Zn(II)-salen complexes [73a-c]. According to Table **3**, it reveals that the average fluorescence lifetime for Zn₄-nuclear metal complexes are smaller than free salen-type ligands. Therefore, fluorescence lifetime analysis further divulges that excited states of both complexes are unstable with respect to Schiff base ligands. The bi-exponential decay profiles for both complexes are best explained as due to competition of different excited states that is $\pi \rightarrow \pi^*$ excited states involved in the emission features for both complexes and the preferably CT character that quenches the fluorescence [74a].

 Table 3 Photoluminescence and time resolved photoluminescence decay of Schiff base ligands and complexes (1-2)

Compounds	λ_{ex} (nm)	λ_{em} (nm)	(φ)	$\tau_1[ns]$	$\tau_2[ns]$	$\tau_3[ns]$	<\cap\$\tag{ns}\$	χ^2
(H_2L^{OMe})	333	441	0.00353	2.78	0.73	9.44	2.35	1.21
		r		(17.4%)	(81.5%)	(1.1%)		
(H_2L^{OEt})	333	445	0.00351	2.77	0.75	9.41	2.34	1.20
6				(17.4%)	(81.5%)	(1.1%)		
1	370	483	0.00209	0.58	5.54	-		1.24
				(99.8%)	(0.2%)		0.66	
2	370	489	0.01445	0.61	4.93	-	0.82	1.23
				(99.4%)	(0.6%)			



Fig.8.Ligand centered emission spectra of Schiff bases and complexes (1-2)

4.6. Thermogravimetric analysis

Thermal characteristics of the complexes were studied using TG-DTG techniques under nitrogen atmosphere. In complex **1**, an initial disintegration within the $\mu_{1,5}$ -dicyanamide linker unit occurs in the temperature range 225-385°C which corresponds to a mass loss of about 4.98 % and is in good agreement with the calculated value (5.06 %) Fig.S8 (a). The powder sample obtained after this run was investigated with IR spectral study which clearly shows the disappearance of common dicyanamide FT-IR spectral peaks but Schiff base ligand stretching frequencies are still present [74b]. This is followed by almost complete decomposition of the dimeric complex (95.21 %) in the narrow temperature range 397-404°C. Unlike complex **1**, complex **2** undergoes well-defined thermal multi-decomposition pattern Fig.S8 (b). In the temperature range 100-287 °C,

there is a mass loss of about 6.84 % (calculated value 6.57 %) which may be due to the loss of the two $\mu_{1,5}$ -dicyanamide linker units linking the dimeric complex. This is further proved by a major weight loss of about 21.24 % (calculated value 21.61 %) between 285-528 °C which marks the initiation of the thermal disintegration of the complex after the removal of dicyanamide linking units. This may be due to the decomposition of the Schiff base ligand units in one of the complexes of the dimer. The thermal decomposition of the complex continues at higher temperatures. Even though the thermal disintegration pattern is different for the two complexes, they have similar thermal stability up to temperatures around 400 °C (except dicyanamide unit).

4.7. Analysis of in vitro antibacterial, membrane damage assay and anti-biofilm properties

Complexes and respective Schiff base ligands (H_2L^{OMe}/H_2L^{OEt}) exhibited antibacterial potency against the four selected bacterial strains. The selected both complexes showed high antibacterial activity against both Gram-positive and Gram-negative bacterial strains which is evident from their respective MIC values and growth inhibition zone diameters whereas Zn₄ dicyanamide complexes had the lower MIC (μ g/mL) values compared to their respective salen-type ligands implying greater antimicrobial efficiencies shown in Table 4. In our previous paper [52a]. it has been shown that both complexes have higher growth inhibition zone diameter (mm) than the free Schiff-base ligands (H_2L^{OMe}/H_2L^{OEt}) (Table 4). With the lowest MIC (μ g mL⁻¹) and highest growth inhibition zone diameter (mm) both the complexes were found to be most effective against *P. vulgaris* among the tested strains. In contrary, the complexes had the maximum MIC (μ g mL⁻¹) and minimum growth inhibition zone diameter (mm) against *E. gallinarum* among tested bacterial strains showing their least efficacy against the bacterial strain.

Subjected to the challenge of complexes (1-2) at MIC levels both bacterial growths suffered an inhibition. The time-kill curves (Fig.9) of the bacterial strains (*E. gallinarum* and *P. vulgaris*) showed distinct treatment differences in the bacterial growth inhibition pattern in the following order: complex 2 > complex 1 (LSD test; p < 0.05). Biofilm removal study undertaken against *E. gallinarum* and *P. vulgaris* (Fig.10) showed that both the complexes were more effective in removing biofilm produced by Gram-negative bacteria (*P. vulgaris*) compared to that of Grampositive bacteria (*E. gallinarum*) (Fig.11). The complex 2 had better biofilm removal efficiency for the tested bacterial strains.

Membrane damage assay with the complexes against Gram-positive (*E. gallinarum*) and a Gram negative (*P. vulgaris*) bacterial strain (Fig.11) presented promising potential for damaging bacterial cell membrane. Both complexes showed higher efficacy against Gram-negative (*P. vulgaris*) bacteria than the Gram-positive (*E. gallinarum*) one. The quantum of nucleic acids released differed significantly ((LSD test; p < 0.05) between the complexes (complex 2 > complex 1). Based on this signature of bacterial membrane disintegration of complex 2 was proved more powerful than complex 1.

Table 4 Minimum inhibitory concentration (MIC; μ g/mL) and bacterial growth inhibition zone diameter (mm) of Schiff base ligands (H₂L^{OMe/} H₂L^{OEt}) against the selected Gram-positive and Gram-negative bacterial strains [52a]

Bacteria	(H ₂ L ^{OMe})		$(H_2 L^{OEt})$	
-	MIC (µg/ML)	Growth Inhibition Zone (mm)	MIC (µg/ML)	Growth inhibition zone (mm)
B. subtilis	550	4.13±0.28	500	4.35±0.51

E. gallinarum	500	5.89±0.31	450	5.13±0.62
P. vulgaris	350	7.94±0.22	300	8.29±0.42
E. aerogenes	450	6.67±0.41	400	7.68±0.19

Table 4 Minimum inhibitory concentration (MIC; μ g/mL) and bacterial growth inhibition zone diameter (mm) of complex **1** and **2** against the selected Gram-positive and Gram-negative bacterial strains. All values of growth inhibition zone diameters have been expressed as mean ± standard deviation

Bacterial strains	Complex 1 (X)	6	Complex 2 (Y)	
	MIC (µg/mL)	Growth inhibition zone (mm)	MIC (µg/ML)	Growth inhibition zone (mm)
S. haemolyticus	270	7.80 ± 0.49	240	9.2 ± 0.97
E. gallinarum	300	7.20 ± 0.40	250	8.4 ± 0.49
P. vulgaris	240	13.60 ± 0.80	200	14.4 ± 0.49
E. aerogenes	250	13.20 ± 0.75	230	14.00 ± 0.63



Fig.9.Time-kill curves of the selected bacterial strains as challenged by the tested chemical complex **1** and complex **2**, (a) *E. gallinarum*, (b) *P. vulgaris*. All data were taken in triplicate, and error bars represent standard deviation



Fig.10.Biofilm removal efficiency of the tested complexes **1** & **2** against *E. gallinarum* and *P. vulgaris*. All data were taken in triplicate and error bars represent standard deviation



Fig.11. Membrane damage potential of the complexes against selected bacterial strains: (a) Gram-positive (*E. gallinarum*); (b) Gram-negative (*P. vulgaris*). All data were taken in triplicate and error bars shows standard deviation

5. Conclusion

This paper primarily describes the syntheses and molecular architectures of Zn(II) dicyanamide complexes utilizing (N₂O₂) donor type Schiff base ligands. Schiff bases are potentially trapped by Zn(II) metal after strong deprotonic actions $[L]^{-2}$. In both complexes, dicyanamide pseudohalide linker plays crucial role showing fascinating $\mu_{1,5}$ and μ_1 dual bridging modes to form polymeric metal-organic frameworks and thus to attain metal-organic framework thermal stability. The photophysical properties of zinc metal complexes and that of the ligands have been determined in DMSO solvent with a comparative approach to search mainly the origin of emission spectra. The fluorescence behaviors of both complexes are predominantly ligand centered. Fluorescence lifetime study further confirmed that the importance of excited state stabilities of Schiff base ligands is greater than Zn₄-nuclear metal complexes. Both complexes exhibited *in vitro* antibacterial and anti-biofilm properties against some important Gram-positive

and Gram-negative bacterial strains that strongly implying their prospective use as bacteriostatic or anti-biofilm agents.

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Appendix A. Supplementary material

Details supplementary data related to this article can be associated in ESM.CCDC number 1876204-1876205 contains the supplementary crystallographic data (excluding structure factors) in CIF format for the structure reported of tetranuclear Cd(II) complexes.Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.: <u>http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi</u>, e-mail: data_request@ccdc.cam.ac.uk, or fax: +44 1223 336033

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Accelertero

The MANUSCRIP

- Two new tetranuclear Zn(II) dicyanamide complexes were synthesized
- Complexes are characterized by different spectroscopic techniques

- Crystal structure discloses Zn₄ molecular ensembles reflecting $\mu_{1,5}$ & μ_1 -dicyanamide • bridging propensity
- FMO, ESP and TD-DFT methods were employed to substantiate the experimental results •
- In vitro antibacterial and anti-biofilm properties were evaluated

Acception

