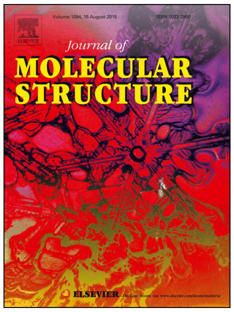

Synthesis, X-ray crystal structure, photo luminescent property, antimicrobial activities and DFT computational study of Zn(II) coordination polymer derived from multisite N,O donor Schiff base ligand (H_2L^1)

Dhrubajyoti Majumdar, M.S. Surendra Babu, Sourav Das, Jayanta Kumar Biswas, Monojit Mondal, Suman Hazra

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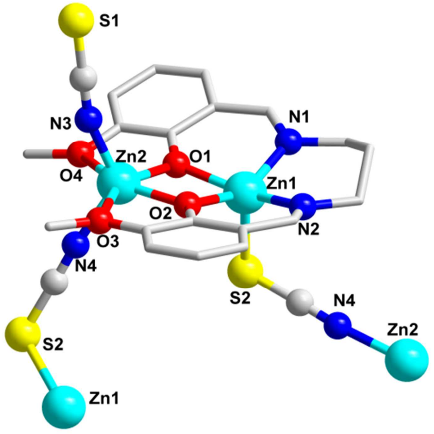
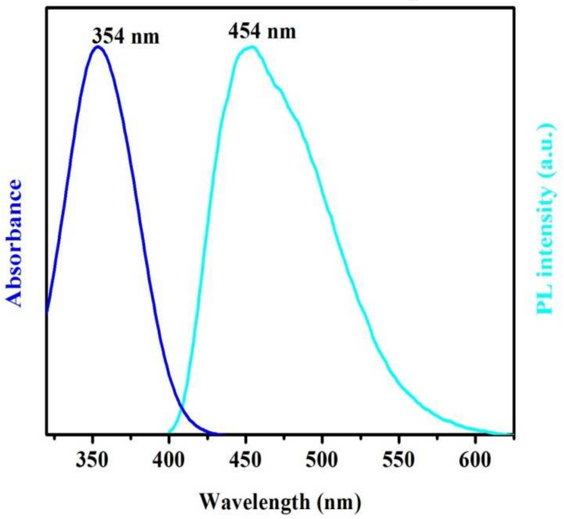
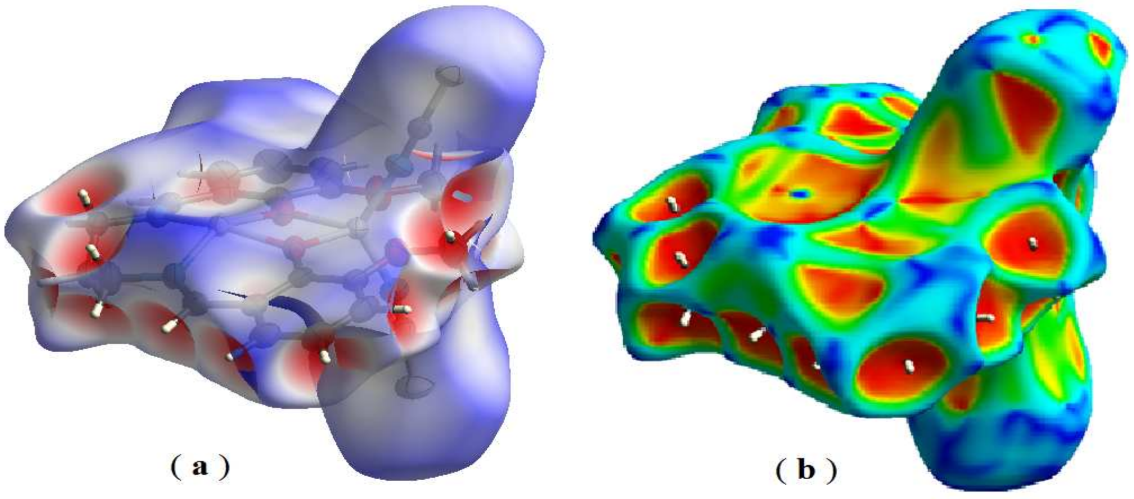
GRAPHICAL ABSTRACT






(a)
(b)

Synthesis, X-ray crystal structure, photo luminescent property, antimicrobial activities and DFT computational study of Zn(II) coordination polymer derived from multisite N,O donor Schiff base ligand (H_2L^1)

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Abstract

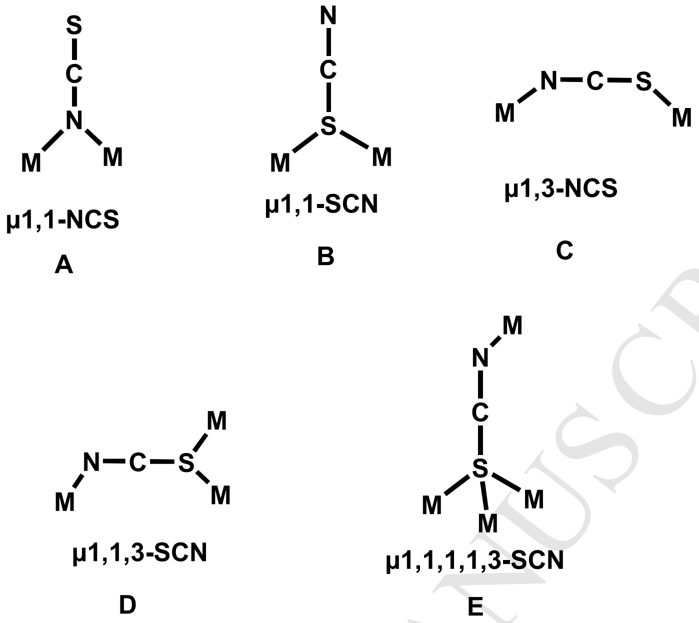
A unique thiocyanato linked 1D chain of Zn(II) coordination polymer $[Zn_2L^1(\mu_{1,3}\text{-}SCN)(\eta^1SCN)]_n$ (**1**) has been synthesized using potential multisite compartmental N,O donor Schiff base blocker ligand (L^1H_2**)** in presence of $Zn(OAc)_2$ and KSCN. The Schiff base ligand [N, N$^{'}$-bis(3-methoxysalicylidenimino)-1,3-daminopropane] (L^1H_2**)** is 2:1 molar ratio condensation product of *O*-vaniline and 1,3-diaminopropane in methanol medium. The characterization of Complex **1** was accomplished by means of different micro analytical techniques like elemental analyses, IR, UV-Vis, ^{1}H NMR, emission spectroscopy and Single X-ray crystallographic study. Complex **1** crystallizes in Orthorhombic system, space group *P*bca, with values a = 11.579(2), b = 18.538(3), and c = 22.160(4) Å; $\alpha = \beta = \gamma = 90.00^0$; V = 4756.6(14) and Z = 8. The single crystal X- ray revealed that the one dimensional chain system with the repeating unit $[Zn_2(\mu_{1,3}\text{-}SCN)(\eta^1SCN)(L^1)]_n$ bridge by a end to end $\mu_{1,3}$ thiocyanate anion. Within each repeating unit two different types of Zn(II) ions are present. One of these is five-coordinate in a square pyramidal geometry while the other is six-coordinate in an octahedral geometry. A brief but lucid comparative approach has been demonstrated in between Schiff base (L^1H_2**)** and complex **1** with respect to their photoluminescence activities. Active luminescence behavior of complex **1** in presence of ligand (L^1H_2) is due to quenching of PET process which is mediated by 'chelating effect'. Complex **1** exhibits strong antimicrobial efficacy against some important Gram +ve and Gram -ve bacteria. Apart from antimicrobial potential, a combined experimental and theoretical investigation has been performed via DFT on molecular structure of complex **1** with respect to Hirshfeld surface analysis.

Key words: Zn(II) coordination polymer, X-ray crystal structure, Photoluminescence behavior, antimicrobial activity, DFT study.

1. Introduction

The design and novel synthesis of coordination polymer (CP) and molecular framework of Group 12 metal ions (Zn, Cd and Hg) in presence of polydentate Schiff base ligand [1-6] and inclusion of a suitable linker like $[SCN]^-$, $[N_3]^-$, $[OCN]^-$ & $[N(CN)_2]^-$ have achieved an immense progress of research in the field of synthetic inorganic chemistry. Thus metal-organic coordination polymers (MOCPS) having 1-, 2- or 3-D structures are properly assembled with particular specific metal ions like Zn(II) or Cd(II). Hence current research has expanded in the fields of supramolecular chemistry and crystal engineering [7,8] because of their intriguing structural motifs and functional behaviors [9-13]. Among Group 12 metal ions, only Zn is a unique transition metal, playing important roles in different fields of Chemistry viz. enzyme catalysis [14], apoptosis [15], neurotransmission [16], luminescence, nonlinear optics, molecular sensing [17-21], biological modeling of metalloenzymes [22,23]. Since Zn(II) has no spectroscopic signature as well as d^{10} filled shell configuration, ligand field stabilization energy (LFSE) is always zero, hence the present situation permits Zn(II) with a wide range of symmetries and various coordination number fulfillment. The aforesaid conditions are considered as requisite "key criteria" for designing metal-organic coordination polymers (MOCPS). Novel pioneer Prof. Sir Hugo Schiff opened up a beautiful research gate after his novel discovery of Schiff base [24]. In the current research scenario, organic or inorganic luminescent compounds like Schiff base ligands offer a wide array of applications including emitting materials for organic light emitting diodes, photo catalysis agents and fluorescent sensors for inorganic analyses. The group 12 metal ions exhibit enhanced luminescence property owing to ligand chelation or coordination with proper donor centers [25, 26]. Thus most of the researchers find a strong intriguing relationship between Group 12 metal ions and their synthesized Schiff base in presence of suitable linker pseudo halide ions $[SCN]^-$ that it develops a totally new coordination polymer which can function as fluorescent sensors. For Zn(II) coordination polymer, the complex molecules are clipped into a very special restricted MOF work, and due to this reason we expected to gain extra conformational rigidity that helpful for strong fluorescence intensity behavior of the complex. In the present study, we have used pseudo halide $[SCN]^-$ as co-ligand which can bind with the Zn(II) ions as terminal ligand and as well as end to end bridge fashion. The studies have shown that the thiocyanate anion ligand has several different coordination modes as depicted in Scheme 1[A-E]. For bi and polynuclear complexes,,most important binding modes are identified as $\mu_{1,1}$-NCS, $\mu_{1,1}$-SCN, $\mu_{1,3}$-NCS, $\mu_{1,1,3}$-SCN and $\mu_{1,1,1,3}$-SCN [27-33]. Additionally $\mu_{1,3}$-SCN exhibits strong interaction with proper metal ions to form extended 2D, 3D , 1D network polymers in presence of suitable Schiff base ligand [34,35].

In this study, pendant $[SCN]^-$ ligand links two dinuclear units to each other through an end to end bridging fashion to accomplish the formation of 1D chain coordination polymer. This work lucidly communicated the successful synthetic details of complex **1**, spectral characterizations like IR, UV-vis, ^{1}H NMR, emission spectra and Single X-ray crystal structure analysis. The photoluminescence study reveals that complex **1** is strongly luminescence active with respect to free Schiff base ligand (H_2L^1). Accordingly, we report the first comprehensive studies involving synthesis, structure, photophysical property, antimicrobial activity, Hirshfeld surface analysis and DFT on a family of 1D chain of Zn(II) coordination polymer.



Scheme 1. Different Bridging Modes of the Thiocyanate anion.

2. Experimental

2.1 Materials

All chemicals which are used in the current research work must be reagent grade and used as received without further purification. All solvents like methanol, ethanol and other reagents used in this work were obtained from commercial sources. *O*-vaniline and 1,3-diaminopropane were purchased from Sigma Aldrich Company, USA. Zinc acetate dehydrate was purchased from Merck chemical Company. KSCN was purchased from SDFCL, India. All synthetic research reactions and work-up were done in open atmospheric condition.

2.2 Physical measurement

Elemental analyses (carbon, hydrogen and nitrogen) of both Schiff base ligand and complex **1** were determined with a Perkin–Elmer CHN analyzer 2400. FT IR spectra were recorded as KBr pellet in the range 4000–400 cm^{-1} with 16 scans at a wave number resolution of 4 cm^{-1} on a Perkin–Elmer spectrum RX 1 and FT IR detector used as DTGS (Deuterated triglycine sulphate). The UV-Vis spectra of complex **1** and ligand were recorded using DMSO solvent on a Hitachi model U-3501 Spectrophotometer. The ^{1}H NMR spectra of novel Schiff base were recorded on Bruker 300MHz FT-NMR spectrophotometer using trimethylsilane as internal standard in $CDCl_3$ solvent. All spectra were corrected for the instrumental functions. Perkin-Elmer LS50B Spectrofluorimeter model was used for the fluorescence measurements of Zn(II) coordination polymer and Schiff base ligand (H_2L^1) at room temperature (298K). The solutions of Schiff base ligand (H_2L^1) and complex **1** were prepared in DMSO solvent. The fluorescence quantum yield (Φ) has been determined using quinine sulfate as the secondary standard (Φ = 0.57 in water) [36] by employing the following equation:

$$\frac{\Phi_S}{\Phi_R} = \frac{A_S}{A_R} \times \frac{(Abs)_R}{(Abs)_S} \times \frac{n_S^2}{n_R^2} \text{----------------------------(1)}$$

Here, 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.

2.3 Antimicrobial assay

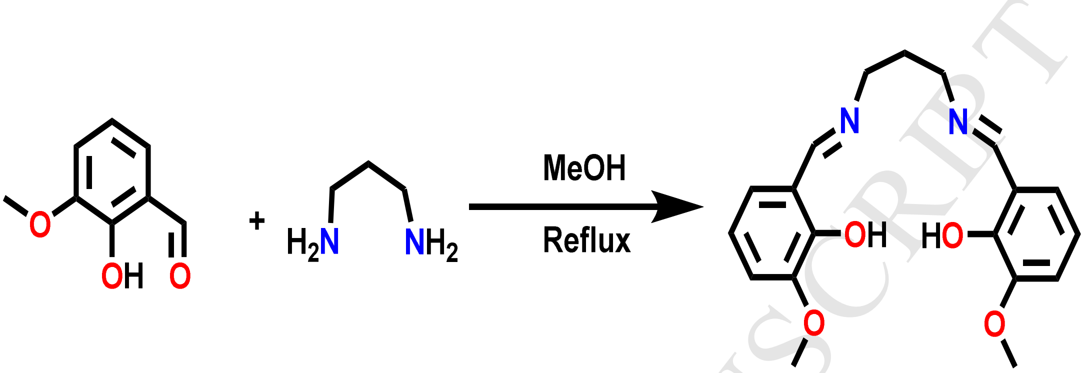
Four Gram negative bacterial strains (*Escherichia coli* K12, *Salmonella enterica ser. typhi* SRC, *Proteus vulgaris* OX19 and *Enterobacter aerogenes* 10102) and one Gram positive bacterial strain (*Bacillus subtilis* 6633) were selected for *in vitro* assessment of antibacterial properties of complex **1**. The bacterial strains were procured from Microbial Type Culture Collection and Gene Bank (MTCC), Institute of Microbial Technology, Chandigarh, India and Department of Microbiology, University of Kalyani, West Bengal, India. Primarily complex **1** was dissolved in dimethyl sulfoxide (DMSO) for antimicrobial assay while using amoxicillin, a clinically recommended antimicrobial agent as a reference [37]. Different concentrations of complex **1** were prepared in sterilized Luria-Bertani medium (Modified) and 1% over night bacterial culture was inoculated to the respective medium maintaining the final concentration of DMSO always within 1%. The media were incubated at 37°C for 24 hours. Individual bacterial growth was measured by UV-VIS spectrophotometer at 600nm and minimum inhibitory concentrations (MIC) of the complexes against the tested strains were determined as per NCCLS protocol [38]. Susceptibility of those bacterial strains to complex **1** was analyzed by agar well diffusion method and antibacterial potential was assessed on the basis of the growth inhibition zone diameter measurement (mm) [39]. Bacterial growth kinetics analyses were studied for four bacterial strains (*Bacillus subtilis* 6633, *Enterobacter aerogenes* 10102, *Proteus vulgaris* OX19 and *Salmonella enterica ser. typhi* SRC) subjected to complex **1**.

3. Synthesis

3.1 Synthesis of Schiff base (H_2L^1)

Compartmental Schiff base ligand (L^1H_2) is actually the condensation product of *O*-vaniline and 1,3-diaminopropane in a 2:1 molar ratio (Scheme 2). It was synthesized and characterized using standard method [40]**.** Yield: (90%), Anal. Calc. for $C_{19}H_{22}N_2O_4$: C, 66.65; H, 6.48; N, 8.18 Found: C, 66.71; H, 6.42; N, 8.08%. IR (KBr, ν_{max}/cm^{-1}): ν(C=N) 1641, ν(C-$O_{phenolic}$) 1254, ν(O-

H) 3449, UV-vis ($\lambda_{max/}$ nm): 258, 398 nm. ^{1}H NMR for (H_2L^1) (δ, 300MHz): 2.11(t, J=6.45, 2H^8), 3.74 (t, J=8.1, 2H^7), 3.91 (s, 3H^1), 6.79-6.95(m, 1H^2, 1H^3, 1H^4), 8.37 (s, 1H^5), 10.26 (s, 1H^6), ppm.



Scheme 2: Synthesis of Schiff base ligand (H_2L^1).

3.2 Synthesis of complex 1

Light yellow colored crystals of complex **1** was synthesized by one pot reaction after reacting Zn(II) acetatate dihydrate (0.21949g, 1mmol) and Schiff base (L^1H_2) (0.342g, 1mmol) in presence of KSCN in methanol solvent medium after constant stirring for 2.5 hrs. The light yellow colored solution was additionally refluxed for 15 min at 70^{0}C and the resulting filtrate was kept in a refrigerator for crystallization by slow evaporation. After 5 days light yellow colored plate-shaped single crystal suitable for X-ray crystallography was obtained. Yellow crystal was isolated by filtration and air dried (Yield: 0.325 g: 60%). Anal. Calcd. for $C_{21}H_{20}Zn_2N_4O_4S_2$: C, 42.91; H, 3.40; N, 9.52. Found: C, 42.92; H, 3.40; N, 9.50 %. IR (KBr pellet, cm^{-1}): ν(C≡N) 1627, ν(C-O$_{phenolic}$) 1251-1249, ν(Zn-N) 454 , ν_{SCN} 2146-2086, ν(O-H)3467-2936 , λ_{max}(CH_3OH) 230.5, 269.2 & 354 nm.

3.3. X-ray crystallographic study

Diffraction quality single crystal data of Zn(II) coordination polymer was collected at 293(2) K. Data collections were made using a AXS SMART APEX-II CCD area detector equipped with a graphite monochromatic MO-K_α radiation (K = 0.71073Å) source in the ω scan mode at 293(2) K. The molecular structure of complex **1** has been solved by direct methods and refinement by full-matrix least squares on F^2 using the SHELXS-2014 package [41, 42]. Non-hydrogens atoms in complex **1** crystal were refined with anisotropic thermal parameters. Hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. Absorption correction were applied to the collected data of reference complex **1** using the program SADABS [43,44]. For Crystal structure refinement purpose we have used different programs like SHELXS-2014, ORTEP-3, DIAMOND-3.1v [45] and MERCURY-3.8. Different crystallographic figures were generated using Diamond-4.2 software. A summary of the crystallographic data and structure refinement parameters of complex **1** is given in Table 1**.** Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1501365. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.: http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, e-mail: data request@ccdc.cam.ac.uk or fax: +44 1223 336033.

Table1 Crystal Data and Structure Refinement Parameters of Complex **1**

Formula	$C_{21}H_{20}N_4O_4S_2Zn_2$
M/g	587.27
Crystal system	orthorhombic
Space group	P b c a
a/Å	11.579(2)
b/Å	18.538(3)
c/Å	22.160(4)
β (°)	90.00
V/Å^3	4756.6(14)
Z	8
ρ_c/g cm^{-3}	1.640
μ/mm^{-1}	2.228
F(000)	2384
Cryst size (mm^3)	0.042 × 0.028 × 0.014
θ range (deg)	25.242 to 26.594
Limiting indices	$-14 \leq h \leq 14$ $-23 \leq k \leq 23$ $-22 \leq l \leq 27$
Reflns collected	57230
Ind reflns	4918 [R_{int} = 0.0445, R_{sigma} = 0.0230]
Completeness to θ (%)	99
Refinement method	Full-matrix-block least-squares on F^2
Data/restraints/ parameters	4918/0/300
Goodness-of-fit on F^2	1.128
Final R indices [$I > 2\theta(I)$]	R_1 = 0.0368 wR_2 = 0.0872
R indices (all data)	R_1 = 0.0606 wR_2 = 0.1058
Largest diff. peak and hole(e ·Å^{-3})	0.661 and -0.339

3.4 X-ray crystal structure of complex 1

Single crystal x-ray diffraction was used unambiguously to establish the identifiable structure of complex **1.** The perspective view of complex **1** with numbering scheme is depicted in Figure 1a. The single X-ray crystallographic analysis of complex **1** reveals that it crystallizes in orthorhombic system with space group *P*bca. Selected bond parameters of **1** are summarized in the Table S1 (See Supplementary material)**.**

The asymmetric unit of **1** (Fig. 1b) consists of dinuclear moieties which are assembled together by the coordination action of one fully deprotonated equatorial $[L^1]^{2-}$ and two axial $[SCN]^-$ ligands. In complex **1**, H_2L^1 acts as a hexadentate (N_2O_4) dianionic ligand $[L^1]^{2-}$. Two unidentate imine N atoms bind Zn1 centre, two unidentate oxygen atoms of methoxy groups coordinate with Zn2 centre, two bridging deprotonated phenoxide O atoms bride between two Zn(II) ions (Zn1 and Zn2) into a dinuclear unit . In each dinuclear unit, Zn2 atom unites to its neighboring unit by means of one end-to-end (EE μ-1,3) $[SCN]^-$ coligands to Zn1 centers forming a one dimensional zigzag chain polymeric chain running along the *b*-axis (Fig 2).

The stereochemistry at Zn1 centers can be described as a distorted square pyramidal with two phenoxido O, two imine N atoms in equatorial plane and one thiocyanato S atom in the the axial plane. In addition, geometry distortion information can be obtained from structural index or Addison parameter tau (ꞇ) which represents the relative amount of distortion in the crystal structures (for square pyramid, ꞇ = 0; trigonal bipyramid, ꞇ =1; ꞇ = (α-β)/60º, where α and β are the two largest angles around the central metal) [46].The Addison parameter ꞇ =0.133 of Zn1 center is also supportive for distorted square pyramidal geometry (Fig 3a). Here it is important to mention that in order to satisfy the charge and coordination requirements, apart from the bridging thiocyanate anion another thiocyanate anion coordinate the Zn2 through its N-coordinating site in a momodentate fashion generating ZnO_4N_2 coordinating environment in a distorted octahedral geometry where two oxygen atoms are coming from phenolate oxygen and other two are from oxygen atoms are from methoxy groups (Fig 3b).

Here, we would like to add further details on the molecular structure of complex **1** as follows: $[SCN]^-$ is an active potential ambidentate ligand which prefers to bind with Zn2 centre through electronegative hard centre (N-donation). On the other hand, Zn1 center has shown affinity for relatively softer S-coordination of $[SCN]^-$ ions. The coordination preference of different binding atoms towards metal can be explained in terms of symbiosis concept. The Zn2 center are relatively harder compared to Zn1 as former is attached to four oxygen atoms. So, hard centre dontion i.e. N-donation of $[SCN]^-$ ion is preferable towards Zn2. Complex **1** displays strong intramolecular C-H…….S [3.848 (Å)] interactions which also propagates along *b*-axis where two neighboring dinuclear subunits are interacting with each other (Fig 2).

An examination of the metric parameters reveals that $Zn-O_{phenolato}$ bond lengths are in the range of 2.02-2014 Å which is relatively shorter than $Zn-O_{OMe}$ bond lengths (2.48-2.60 Å). Two different type nitrogens are coordinated to each Zn(II) ions. Bond lengths of coordinated imino nitrogens are in the range of 2.03−2.04 Å, which are slightly longer than those of coordinated nitrogen of thiocyanate anion nitrogen [$Zn- N_{Thiocyanate}$ = 1.94-1.97 Å]. The bond distance of Zn-S is 2.468 (1) Å. These data are similar to those found in the literature [47-49].

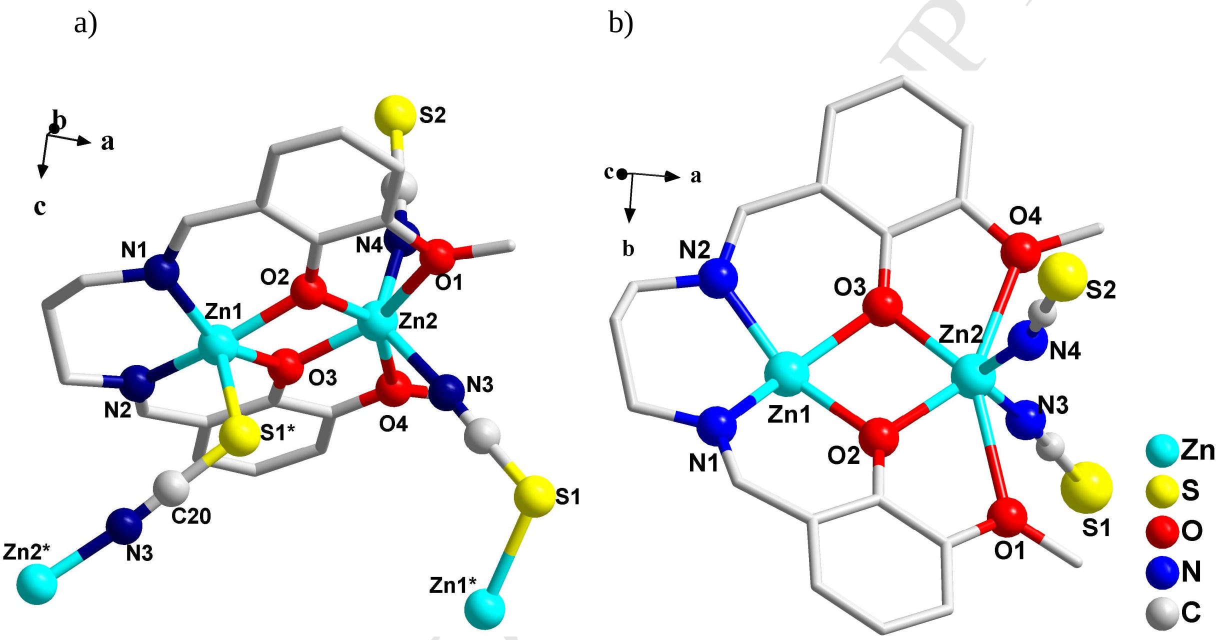


Figure 1. (a) Molecular structure of **1**(hydrogen atoms have been omitted for clarity).The numbering is also shown in the picture for the dinuclear unit in the 1D single chain of 1. (b) Asymmetric unit of complex **1**(hydrogen atoms have been omitted for clarity).

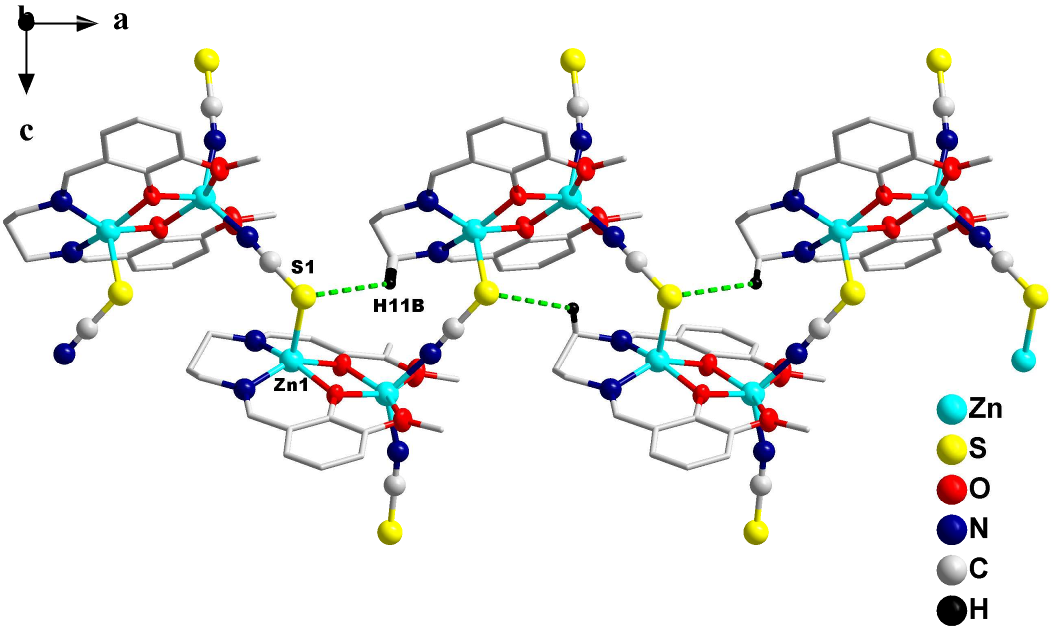


Figure 2. Perspective view of the crystal packing of **1** with extended H-bonding feature along the *b* axis.

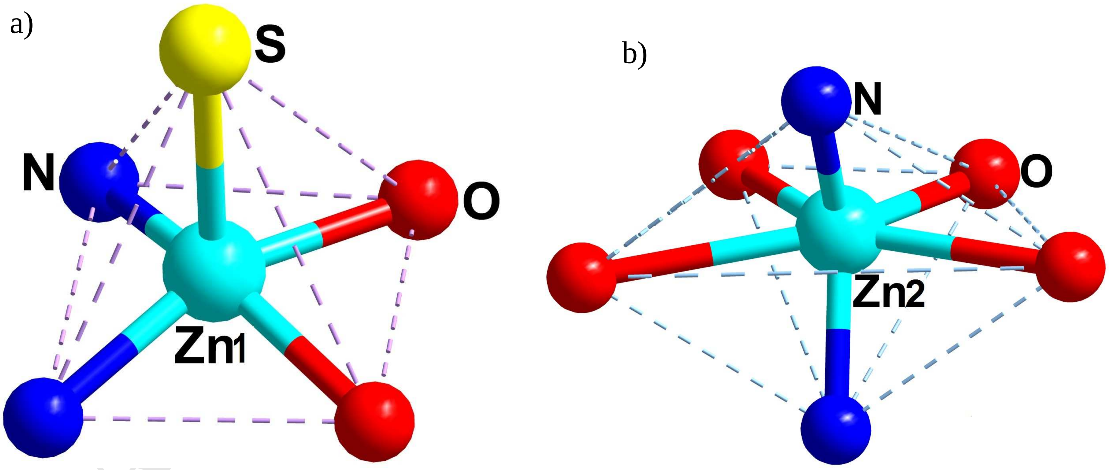


Figure 3. (a) Distorted square pyramidal and (b) distorted octahedral geometry around Zn(II) ion.

4. Results and discussion

4.1 Synthesis and characterization of Complex 1

We have unambiguously used one-pot synthetic methodology to obtain complex **1** where 1:1:1 molar ratio of the respective Zinc(II) acetate dehydrate, di-compartmental Schiff base (H_2L^1) and KSCN has been used in methanol solvent medium at room temperature to yield light yellow colored plate shaped Zn(II) coordination polymer. The synthesized complex **1** has been characterized by different micro analytical techniques ^1H NMR, FT IR and UV-Vis spectroscopic study. Our synthesized light yellow complex **1** is stable over long period of time in powdered form as well as crystalline states and readily soluble in organic solvent like DMSO, DMF, CH_3CN, but insoluble in water. Several weak bands in the range 2960-2870 cm^{-1} are clearly observed in complex **1,** which is attributed to the aliphatic C-H stretching vibration [50]**.** An intense strong band at 1627 cm^{-1} for complex **1** is shifted considerably towards lower frequencies compared to that of the free Schiff base ligand (H_2L^1) indicating coordination of the imino nitrogen atom with the Zn(II) metal centers [51]. Complex **1** exhibits sharp ν_{SCN} 2146-2086 cm^{-1} bands suggesting $[SCN]^{-1}$ coordinating mode towards Zn(II) metal ions [Figure S1-S2]. Further ν_{SCN} 2146-2086 bands have become bifurcated indicating two different coordinating mode during Zn(II) coordination polymer formation **(**Figure S1). Complex **1** exhibits ligand–based broad transition at 354 nm presumably due to $n\rightarrow\pi$ or $\pi\rightarrow\pi^*$ transitions in DMSO solution at room temperature [52, 53] **[**Figure S3].

4.2 Active Photoluminescence behavior of complex 1

We have studied photoluminescence properties individually for Schiff base ligand (H_2L^1) and complex **1** to find out the silent or active nature of fluorescence since fluorescence active property of complex **1** opens up the new possibility for photochemical applications [54-60]. On this ground fluorescence properties of Schiff base ligand and its respective 1D chain CP of complex **1** were studied at room temperature (298 K) in DMSO solvent. Generally a metal ion enhances or quenches fluorescence emission in presence of Schiff base ligand containing aromatic ring structure. Since Zn(II) ion has no optical spectroscopic signature due to its closed–shell $3d^{10}$ configuration, Zn(II) ion is very difficult to oxidize or reduce. Therefore, it is expected that complex **1** shows no emission emanating mainly from metal-centered MLCT/LMCT excited states. Here the emission may be assigned to the intraligand ($\pi \rightarrow \pi^*$) fluorescence. The above fluorescence can be elucidated on the basis of '*chelation mediated fluorescence intensity*'. Normally Zn(II) metal ion enhances or quenches fluorescence emission in presence Schiff base ligand that contains aromatic π cloud ring system and ligand potential donor centers (nitrogen and oxygen) are selectively bonded with respective metal ion . Quenching of metal ions in presence of Schiff base ligand during complex formation via different donor center (N, O) is a rather common fact which is explained by a process like magnetic perturbation, redox activity and electronic energy transfer. In the absence of suitable metal ions fluorescence property of the ligand is probably quenched by the occurrence of photoinduced electron transfer (PET) process due to presence of ligand donor atoms like N, O nonbonding electrons pairs. Such PET process is prevented by the Schiff base ligands when its nonbonding electron pairs gets stable being complexed with Zn(II) metal center. Fluorescence graphical plot reveals that Schiff base ligand exhibits emission at 390 nm (Fig 4a) while complex **1** shows emission at 454 nm upon excitation at 354 nm (Fig. 4b). The red shift as well as greater intensity of complex **1** is presumably due to the conformational rigidity of the ligand upon complexation or strong ligand donor centers (N,O) binding with Zn(II) metal. The overall process is referred as ‘*chelation enhancement fluorescence*’ [CHEF] [61-65]. From emission spectral curve Figure 4(a) of Schiff base ligand (H_2L^1), we observed that an emission maximum is bathochromically shifted as compared to Schiff base ligand (H_2L^1). This is mainly due to the methoxy group incorporation on the salen structural skeleton of the ligand. A similar absorption and emission maxima have been observed for tridentate Schiff base ligand with a methoxy group in ortho position of the phenol moiety [66]. Reported Schiff base ligand quantum yield is very low and this is identical with Schiff base (H_2L^0) N,N’-bis(salicylidene)-1,3-diaminopentane [67]. However, the introduction of methoxy substituent in the ortho position of the phenol ring is also responsible for red shift emission maxima of Schiff base. Beside for bromine or chlorine substituted salicylidene structural skeleton Schiff base ligands induce a noticeable decrease of the quantum yields in comparison with ligand (H_2L^1) [67]. The luminescence spectral nature depicted in [Figure 4b] are typically common for Salen-type Schiff-base Zn(II) complexes where only intraligand $\pi \rightarrow \pi^*$ transition can be positively assigned [68,69]. We have calculated Fluorescence quantum yield for complex **1** by employing equation (1) using quinine sulfate as the secondary standard (Φ = 0.57 in water) and thus quantum yield value for complex 1was found to be 0.01635. Again with reference to highly luminescent Zn(salen) complexes [67], the reason for weak luminescent of complex **1** is due to the additional non-radiative deactivation pathways. Apart from, one additional possibility in this respect through electron transfer takes place in presence isothiocyanate anions [70, 71].

Table 2. Photo-physical parameters of Schiff base ligand (H_2L^1**)** and complex **1** in DMSO solvent at room temperature 298 K.

Compound	**Abssorption (λ_{max}), nm**	**Excitation (λ_{max}), nm**	**Emission (λ_{max}), nm**
Schiff base(H_2L^1)	258 & 398 nm	332 nm	390 nm
Complex **1**	230, 265 & 345 nm	354 nm	454 nm

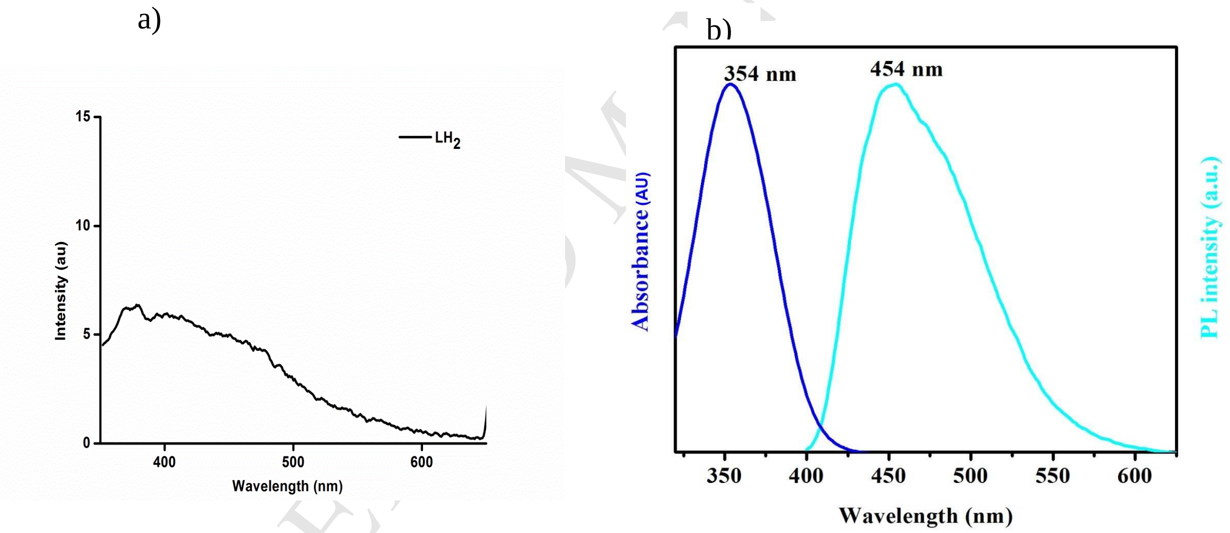


Figure 4. (a) Emission spectra of Schiff base ligand (H_2L^1**)** in DMSO solution at 298 K. (b) Absorption and emission spectra of complex **1** in DMSO solution.

5. Antimicrobial screening of complex 1

Complex **1** exhibited antibacterial potency against all five bacterial strains. The MIC values and growth inhibition zone diameter for the complexes against the tested bacterial strains are shown in Figure 5 and 6 respectively. Complex **1** had encouraging potentiality to inhibit the growth of *B. subtilis* 6633 and *P. vulgaris* OX19 in contrast to *E. aerogenes* 10102 and *S. Typhi* SRC that showed less susceptibility to them. *In vitro* growth curve of four bacterial strains (*Bacillus subtilis* 6633, *Enterobacter aerogenes* 10102, *Proteus vulgaris* OX19 and *Salmonella enterica ser. typhi* SRC) in presence of complex **1** are shown in Figure 7. It reflected distinct treatment differences (LSD test; $p < 0.05$) in the inhibition pattern of bacterial growth subject to selected complex **1** excepting *S. typhi*. Complex 1 showed reasonable efficacy as potential antimicrobial agent in rendering bacterial growth inhibition. The results showed that complex **1** had a wide spectrum of antibacterial activity. Moreover both Gram positive and Gram negative bacteria were similarly susceptible to this complex **1**. The growth kinetics study subjected to antimicrobial candidates proved that the tested complex 1 had encouraging efficiency to hinder the bacterial growth as a bacteriostatic agent. Hence, it can be concluded that complex **1** can be promoted as potential broad spectrum antimicrobial agents.

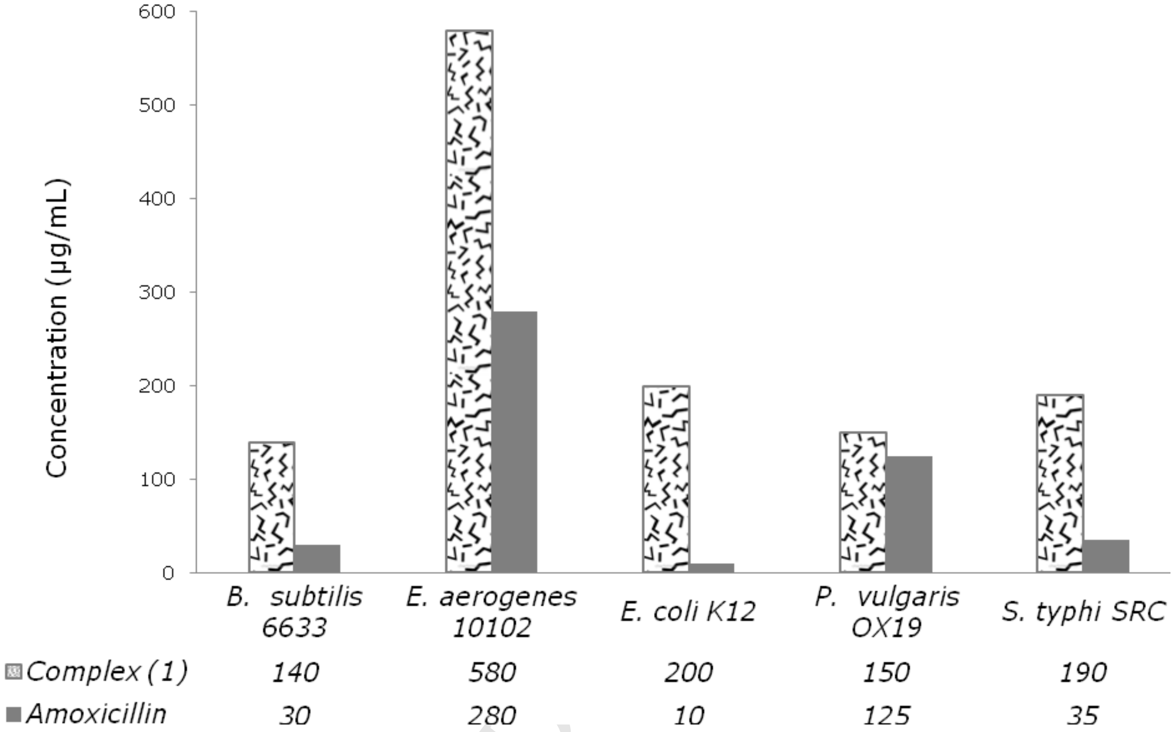


Figure 5. MIC values (µg/mL) and bacterial growth inhibition zone diameter (mm) of the complex **1** and amoxicillin (the reference antimicrobial agent) to the tested bacterial strains. All data were taken in triplicate.

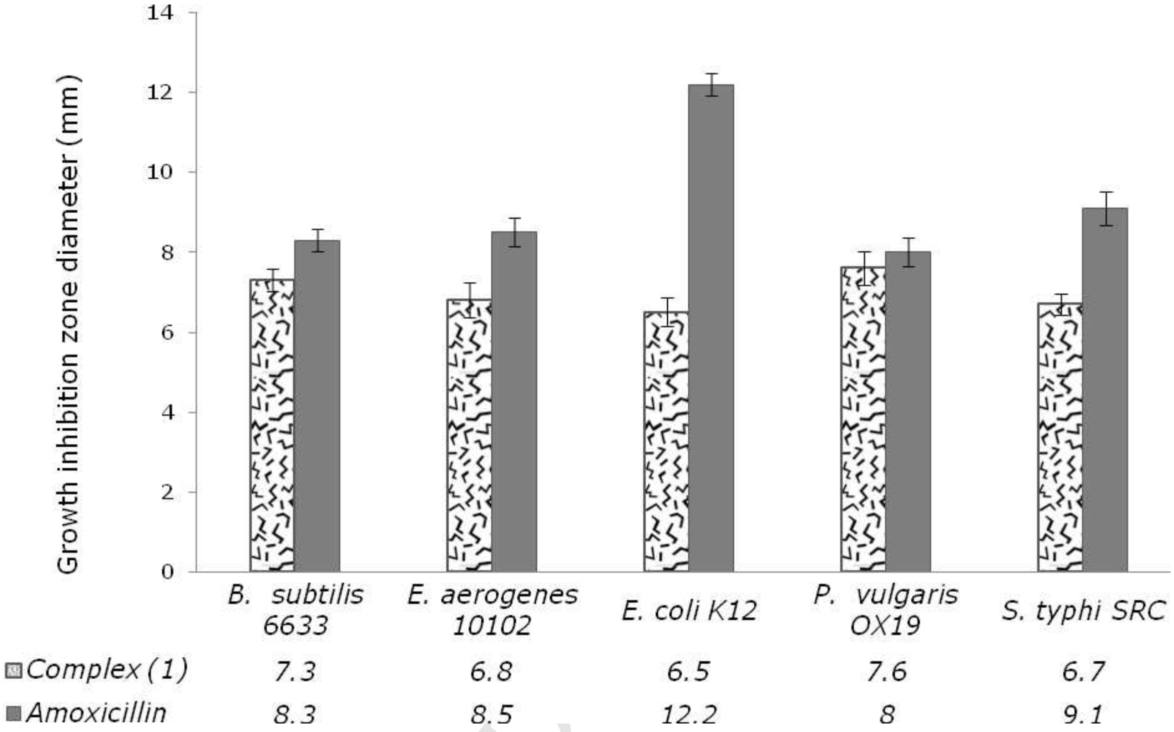
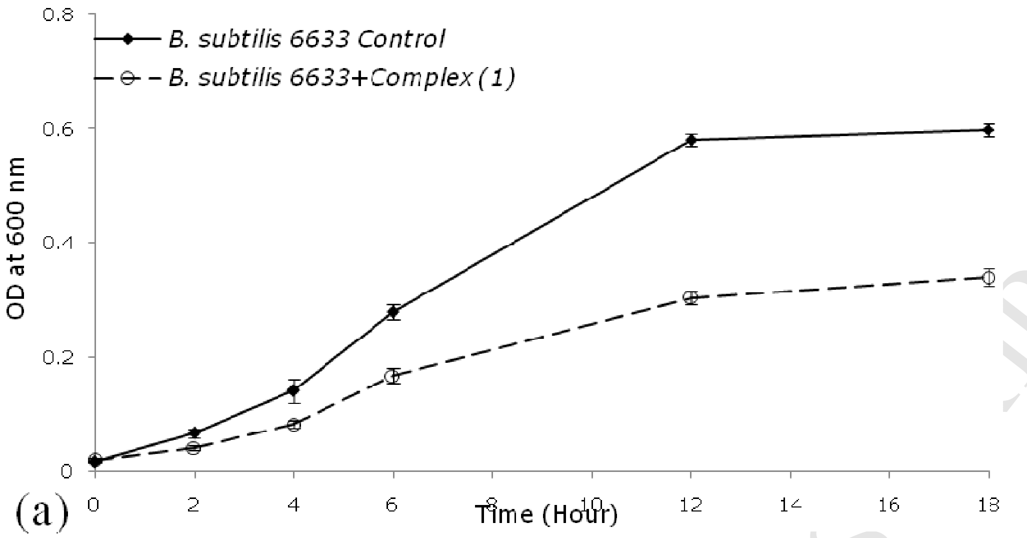
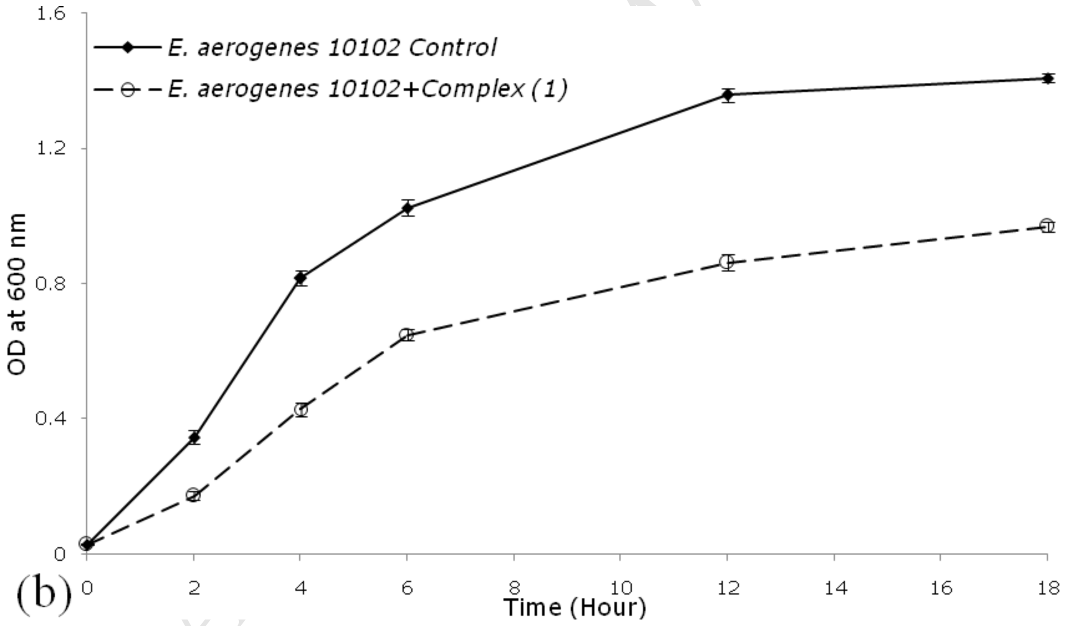


Figure 6. Bacterial growth inhibition zone diameter (mm) of the complex**1**and amoxicillin (the reference antimicrobial agent) to the tested bacterial strains. All data were taken in triplicate and error bars shows standard deviation.


0.8
0.6
0.4
0.2
0
OD at 600 nm
B. subtilis 6633 Control
B. subtilis 6633+Complex (1)
0
2
4
6
8
10
12
14
16
18
Time (Hour)
(a)


1.6
1.2
0.8
0.4
0
OD at 600 nm
E. aerogenes 10102 Control
E. aerogenes 10102+Complex (1)
0
2
4
6
8
10
12
14
16
18
Time (Hour)
(b)

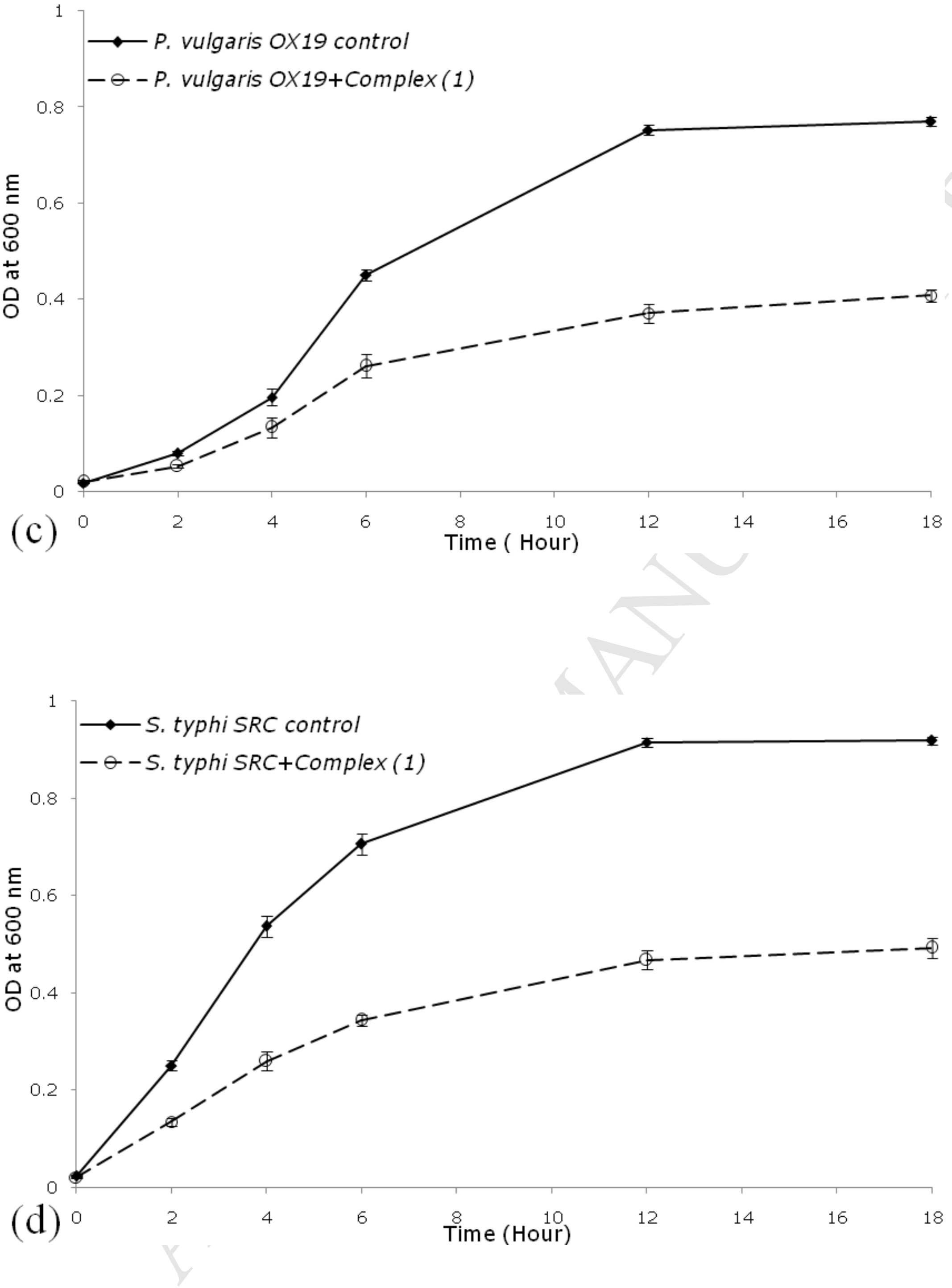


Figure 7. *In vitro* growth curves of (a) *Bacillus subtilis* 6633, (b) *Enterobacter aerogenes* 10102, (c) *Proteus vulgaris* OX19 and (d) *Salmonella enterica ser. typhi* SRC against complex 1, all data were taken in triplicate and error bars show standard deviation.

6. DFT analysis

Geometry optimization of complex **1** was carried out on basis set 6-31G(d) at the B3LYP level[72] in ground state using density functional theory (DFT) calculations[73]. The frontier orbital's of HOMO and LUMO of Zn(II) coordination polymer complex **1** is shown in Figure 8.

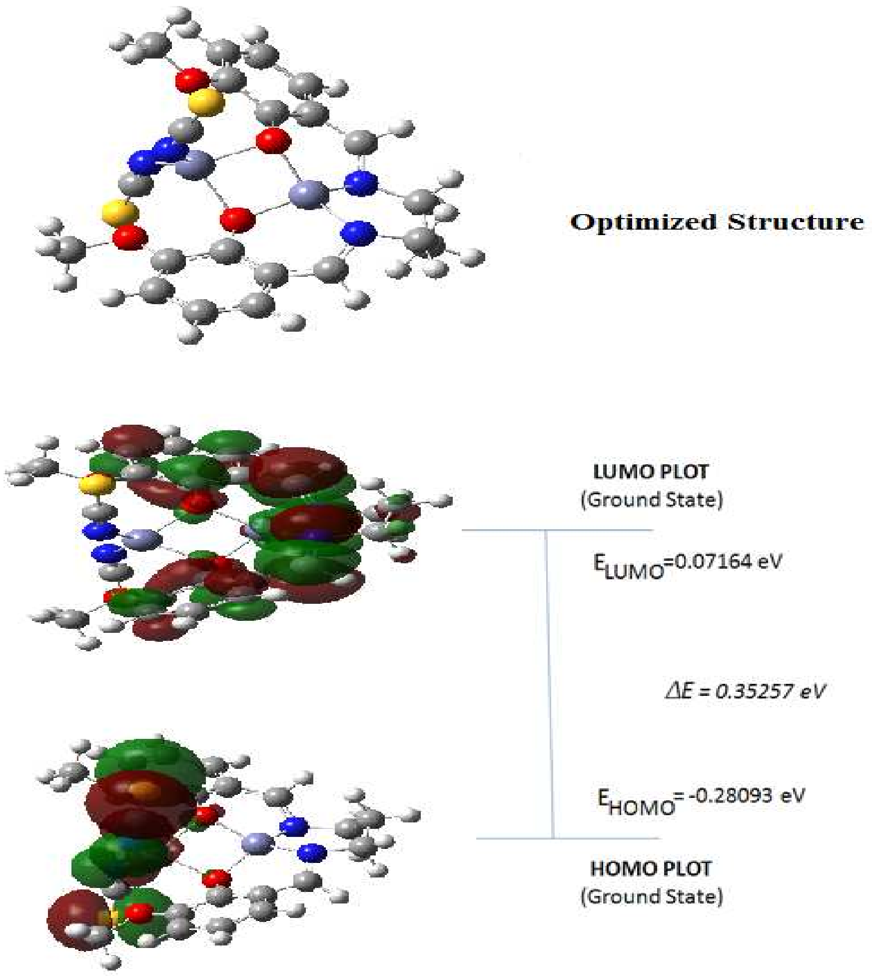


Figure 8. The optimized structure, HOMO and LUMO orbital of complex **1**.

From optimized structure of complex **1** the bond lengths of Zn–S_1 and Zn-S_2 atoms are 1.97Å and 1.94Å and bond angle S-Zn_2-S of 124°, while N-Zn-N is 101°. The bond lengths of Zn_1-N and Zn_1-O atoms are 2.04Å and 2.03Å respectively. From Figure 8 it is apparent that electron densities in HOMO plot of complex **1** has largely localized on o-vaniline aromatic ring section and in LUMO plot electrons density are localized on di-amine propane chain and partly on o-vaniline ring moiety. The HOMO-LUMO energy gap in the ground state of complex **1** has been predicted to be 0.35257 eV. The electronic cloud distribution of HOMO and LUMO in singlet excited state localizes largely on Schiff base ligand. Suggesting the absorption transition is mainly due to the intraligand charge transfer (ILCT or $\pi \rightarrow \pi^*$) and partly by ligand-to-metal charger transfer (LMCT), metal-to-ligand charger transfer (MLCT) and metal centered (MC) transitions which is also supported by UV-Vis absorption spectra.

7. Hirshfeld Surface analysis

Hirshfeld surface and 2D fingerprint plot generated from crystal data of complex **1** using crystal explorer v. 3.1[74] are shown in Figure.9a and 9b. The colour mapping and the shape of the three dimensional Hirshfeld surfaces of complex **1** show the different intermolecular interactions present in the crystal packing. The red spots on the surfaces indicate the close-contact interactions, which are mainly responsible for the molecular packing in the crystals. Apart by hydrogen bonding, the crystal packing of complex **1** is controlled by dominant interactions involving S···H, N···H and O···H contacts, which are observed as red spots on the Hirshfeld surfaces shown in Figure 10 (a-d). The % of H-bonding interaction data with S, N and O atoms are given in Table 3. From table 3, it is clear that S···H interaction dominates with 15.9% contributing highest % for the molecular packing stability.

Table 3. Percentage interactions of H-bonding with S, N and O atoms in complex **1.**

S.No	Interaction	%
1.	S....H	15.9
2.	N....H	5.9
3.	O....H	3.9

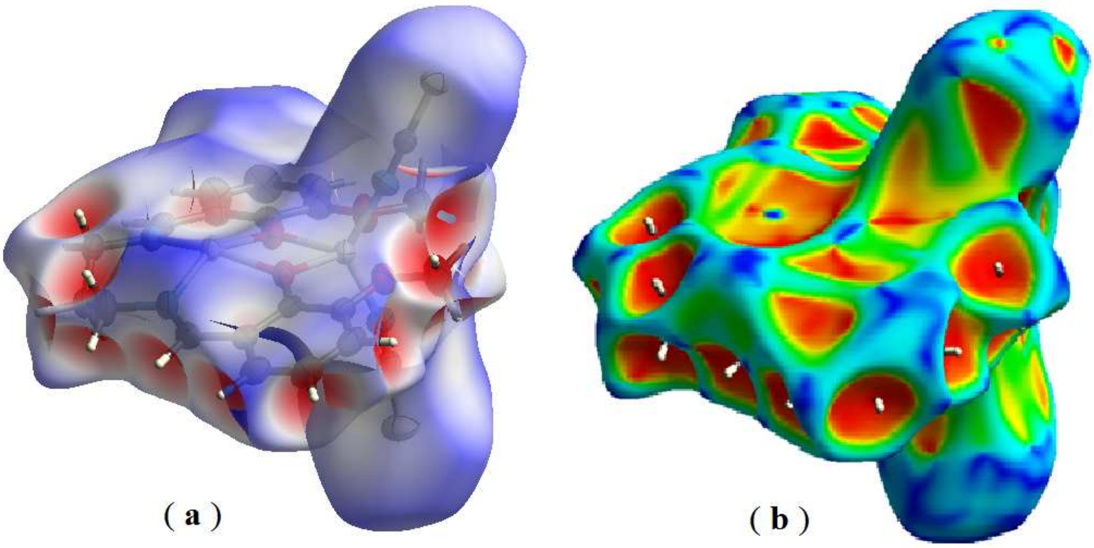
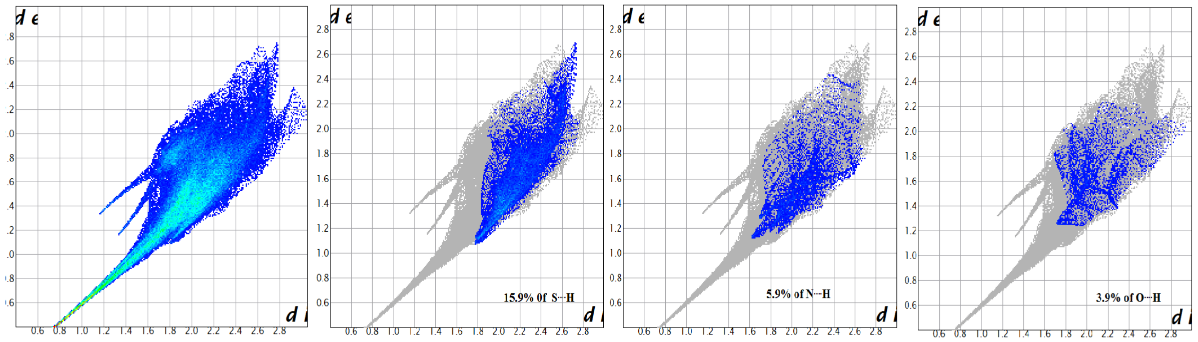


Figure 9. Hirshfeld surfaces of complex 1 mapped with (a) d_{norm} property, the molecules in tube/licorice representation within the transparent surface maps and (b) Shape Index



(a) (b) (c) (d)

Figure 10. (a-d) Hirshfeld 2D fingerprint plots of intermolecular contacts with di and de-ranging from 0.3 to 2.8 Å (a) all interactions (b) S···H with 15.9% (c) N···H with 5.9% (d) O···H with 3.9% interaction

8. Conclusion

In this work, we have reported the synthesis of a a one-dimensional polynuclear zinc(II) complex using a one-step self-assembly process from zinc acetate, ptassium thiocyanate, Schiff base (L^1H_2**)** in methanol medium. The investigation shows that *in situ* formation of building blocks yielded the polymer of $[Zn_2L^1(\mu_{1,3}\text{-SCN})(\eta^1SCN)]_n$ (**1**) where two different environment of Zn(II) ions are present. Apart from that $[SCN]^-$ ion acts as end to end bridging fashion to accomplish the formation of 1D chain as well as terminal ligand to satisfy the charge and coordination. Photoluminescent study revealed that enhanced red shift fluorescence intensities of complex **1** compared to that of Schiff base ligand (H_2L^1) in presence of $[SCN]^{-1}$ pseudohalide ion confirmed its credential as a potential photoactive candidate. Besides, complex **1** exhibited a strong antimicrobial activity towards some important Gram +ve and Gram–ve bacteria. As a complementary revelation Hirshfeld surface analysis via DFT has been investigated for our synthesized complex **1**.

8. Supplementary data

Certain selected crystal metrical parameters related to Complex **1** are shown in Table S1 and Figure S1-S2 as supplementary materials. Figure S2 shows ligand IR spectra as supplementary material. CCDC 1501365 contains the supplementary crystallographic data (excluding structure factors) in CIF format for the structure reported of complex **1.** The 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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HIGHLIGHTS

- 1D chain of Zn(II) coordination polymer
- Single X-ray crystallography
- The photoluminescence behavior
- The antimicrobial agent
- DFT and Hirshfeld surface analysis