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# **Graphical Abstract**



# Synthesis, structure, fluorescent property, and antibacterial activity of new Cd(II) metal complex based on multidentate Schiff base ligand N,N'-Bis(3methoxysalicylidenimino)-1,3-diaminopropane

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#### Abstract

The sequential reaction of a multisite coordinating compartmental ligand N,N'-Bis(3methoxysalicylidenimino)-1,3-diaminopropane  $(H_2L^1)$  with Cd(OAc)<sub>2</sub> followed by the addition of NaCl in a 2:3:2 stoichiometric ratio affords homometallic trinuclear Cd(II) coordination compound  $[Cd_3(L^1)_2(Cl)_2]$  (1). The complex 1 has been thoroughly characterized by common elemental analysis (CHN), FT-IR and UV-Vis spectroscopy. Single crystal X-ray diffraction was also performed to determine the complete structure of complex 1. X-ray diffraction studies reveal that the molecular complex comprises a linear tri-nuclear ensemble of cadmium metal ions, which is further supported by the concerted coordination action of two dianionic  $[L^1]^{2-}$  ligands along with two monodentate Cl<sup>-</sup> ligands. The central Cd(II) ion is attached to the terminal Cd(II) ions through two phenoxide bridging groups of the fully deprotonated ligands  $[L^1]^{2-}$ . This arrangement leads to two neighboring four membered Cd<sub>2</sub>O<sub>2</sub> rings. The terminal Cd(II) ions are penta-coordinated (2N, 2O, Cl) in a distorted square pyramidal geometry and central Cd(II) ion attained distorted trigonal prismatic geometry through six oxygen atoms coordination from ligands. Tri-nuclear Cd(II) complex 1 display intraligand  $(\pi - \pi^*)$  fluorescence in DMSO solution at room temperature. The fluorescence properties of complex 1 as well as the respective di-compartmental Schiff base ligand (H<sub>2</sub>L<sup>1</sup>) have been investigated in DMSO solvent at room temperature with a comparative approach. Result confirmed that complex 1 is highly fluorescence active mediated due to "chelation enhanced fluorescence" [CHEF] but Schiff base ligand  $(H_2L^1)$  is fluorescence silent. The antibacterial efficacy of complex 1 was further investigated against some important Gram-positive and Gram-negative bacteria.

**Keywords:** Cd(II) trinuclear complex, X-ray crystal structure, fluorescence properties, week supramolecular interaction, Antimicrobial activity.

#### **1. Introduction**

Over the past few decades, the complexation behavior of group 12 metal ions (Zn, Hg or Cd) in presence multidentate Schiff base ligands have rigorously studied vital research area in the field of coordination chemistry [1-5]. The molecular metal ensembles derived from Schiff base ligands and group 12 metal ions are of substantial contemporary interest considering versatile functional behaviors, intriguing structural motifs [6-10] and optoclectronics properties [11-13].However, from the synthetic point of view the major confront is to design suitable ligands which can assemble metal ions together. Multi-metal assemblies of varying nuclearity are often synthesized and crystallized from common one-pot reaction from a pool of ingredients like appropriate molar ratios of metal salts, suitable multi-compartmental Schiff base ligands, in one step which affords many diverse structural topologies [14,15]. Hence Schiff base on account of its endearing popularity and versatility towards wide range of complex formations, many inquisitive chemists got interested to their complex formation. In the 19<sup>th</sup> century [1864] Prof. Sir Hugo Schiff opened the beautiful research gate in the field of coordination chemistry after his novel discovery of Schiff base [16]. Recently many inquisitive inorganic chemists carry out their research work by using Schiff base because of their easily preparation, wide structural varieties, varied denticities and ease of tunability in ligand steric or electronic properties. Hence in the current research scenario, Schiff base complex formation have been extensively studied on account of their different mode of applications, e.g. catalysis[17-19], magnetism [20,21], synthons for crystal engineering and most popular materials chemistry[22-24]. Group 12 metal ions Cd and its congeners metal Zn, Hg are always biologically harmful, yet recently it has been found that Cd(II) ion can potentially serve catalytic center in a newly discovered carbonic anhydrase [25]. In Cd(II) complexes, the metal centre always enable a diverse range of coordination geometries and coordination numbers due to lack of crystal field stabilization energy as well as imposed ligands steric demands from the Schiff base ligands. Thus a balance between bonding energies and repulsion created by inserted Schiff base ligands determine the overall flexibility in coordination numbers [26-28]. Since Cd(II) ion has no optical spectroscopic signature due to its closed–shell  $3d^{10}$  configuration, luminescence behavior of Cd(II) metal is enhanced due to 'chelation concept' developed by metal and ligand donor centers strong binding ability. Additionally  $d^{10}$  metal ions like Zn(II) & Cd(II) when associated with Schiff base ligands that already conjugated with aromatic  $\pi$  rings favour the development of sensitive fluorescent active property[29-33]. A complete literature survey reveals that di-compartmental Schiff base ligand, N,N'-bis(2-hydroxyacetophenone)-1,3-diaminopropane where only one phenoxo-bridged tri-nuclear copper(II) complex has been reported so far [34,35]. A plenty of examples of tri-nuclear Cd(II) thiocyanato or azido bridging complexes [36,37] are well known but on contrary Cd-Cl terminal linking tri-nuclear complexes are scare. This Literature survey work stems from our interest to investigate the coordination behaviors of endeaviour Schiff base towards Cd(II) metal ion in concert with Cl ion as monodentate ligating fashion.

In the present research study, we have synthesized  $N_2O_4$  donor di-compartmental Schiff base ligand ( $H_2L^1$ ) by the condensation of one equivalent 1,3-diamines and two equivalent 3methoxysalicylaldehyde (Scheme1). Using the Schiff base ligand we have successfully synthesized a new tri-nuclear ensemble Cd(II) complex [Cd<sub>3</sub>( $L^1$ )<sub>2</sub>(Cl)<sub>2</sub>] (**1**). Our research interest in the current work is to observe Cd(II) metal ions coordination behavior towards the respective Schiff base ligand using NaCl as Cl<sup>-</sup> spacer. The synthetic details of Schiff base ligand, its respective complex **1**, their spectral characterization, X-ray crystal structure, details fluorescence and antibacterial study have been reported in this work.



**Scheme 1:** Synthesis of the ligand  $(H_2L^1)$ 

#### 2. Experimental

#### 2.1. General remarks and physical measurement

#### 2.1.1. Materials

All chemicals were of reagent grade, purchased from commercial sources and used as received without further purification. High purity 3-methoxysalicylaldehyde was purchased from Sigma Aldrich Company, USA. 1,3-Diaminopropane was also purchased from the same company. Cadmium(II) acetate and Sodium chloride were purchased from E. Merck, India. The Schiff base ( $H_2L^1 = N,N'$ -Bis(3-methoxysalicylidenimino)-1,3-diaminopropane) has been prepared by condensation of a 1:2 M ratio of 1,3-diaminopropane and 3-methoxysalicylaldehyde following a reported method [38]. All other chemicals and solvent methanol used were AR grade. The total synthetic reactions for research purpose and work-up were done in open air condition.

## 2.1.2. Instrumentation

Elemental analyses (carbon, hydrogen and nitrogen) of the Scihff base  $(H_2L^1)$  and the metal Cd(II) complex **1** were determined with a Perkin–Elmer CHN analyzer 2400. IR spectra (KBr pellet, 400–4000 cm<sup>-1</sup>) were recorded on a Perkin–Elmer model 883 infrared spectrophotometer. The electronic UV-Vis spectra of the Cd(II) complex **1** and respective Schiff base ligand in organic solvent DMSO were recorded on a Hitachi model U-3501 spectrophometer. The <sup>1</sup>H NMR spectra of novel Schiff base  $(H_2L^1)$  were recorded on Bruker 300MHz FT-NMR

spectrophotometer using trimethylsilane as internal standard in CDCl<sub>3</sub> solvent. All spectra were corrected for the instrumental functions. Perkin-Elmer LS50B spectrofluorimeter model was used for the fluorescence measurements of tri-nuclear Cd(II) complex **1** and Schiff base ligand  $(H_2L^1)$  at room temperature(298K). The solutions of Schiff base ligand  $(H_2L^1)$  and Cd(II) complex **1** were prepared in DMSO solvent.

#### 2.3. X-ray Crystallography

The crystal data for the compounds have been collected on a Bruker SMART CCD diffractometer (MoK<sub>a</sub> radiation,  $\lambda = 0.71073$  Å). The program SMART[39] was used for collecting frames of data, indexing reflections, and determining lattice parameters, SAINT [39] for integration of the intensity of reflections and scaling, SADABS [40] for absorption correction, and SHELXTL [41,42] for space group and structure determination and least-squares refinements on  $F^2$ . The crystal structures were solved and refined by full-matrix least-squares methods against  $F^2$  by using the program SHELXL-2014 [43] using Olex-2 software [44]. All the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen positions were fixed at calculated positions and refined isotropically. Different crystallographic figures were generated using Diamond-3.1 software [45]. A summary of the crystallographic data and structure refinement parameters of tri-nuclear Cd(II) 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 1495264. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, 1EZ, U.K.: e-mail: data request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

Formula	$C_{38}H_{40}Cd_3Cl_2N_4O_8$		
M/g	1088.84		
Crystal system	monoclinic		
Space group	$P2_1/c$		
a/Å	19.433(4)		
b/Å	8.9050(18)		
$c/{ m \AA}$	23.357(5)		
β(°)	100.61(3)		
V/Å <sup>3</sup>	3972.8(14)		
Z	4		
$ ho_{ m c}/ m g\  m cm^{-3}$	1.820		
$\mu/\mathrm{mm}^{-1}$	1.782		
F(000)	2152		
Cryst size (mm <sup>3</sup> )	0.054  imes 0.038  imes 0.012		
$\theta$ range (deg)	4.464 to 58.26		
Limiting indices	$-26 \le h \le 26$		
-	$-12 \le k \le 12$		
	$-31 \le 1 \le 31$		
Reflns collected	65644		
Ind reflns	10584 [ $R_{\rm int} = 0.1061, R_{\rm sigma} = 0.0766$ ]		
Completeness to $\theta$ (%)	99		
Refinement method	Full-matrix-block least-squares on F <sup>2</sup>		
Data/restraints/ parameters	10584/0/500		
Goodness-of-fit on $F^2$	1.034		
Final <i>R</i> indices	$R_1 = 0.0505$		
$[I > 2\theta(I)]$	$wR_2 = 0.1028$		
R indices (all data)	$R_1 = 0.0777$		
	$wR_2 = 0.1133$		
Largest diff. peak and hole( $e \cdot A^{-3}$ )	1.07 and -0.92		

Table 1. Crystal Data and Structure Refinement Parameters of Complex 1

# 2.1.3. Experimental of antimicrobial activity

*In vitro* antimicrobial potentiality of complex **1** was analyzed against four Gram negative bacterial strains viz. *Escherichia coli* K12, *Salmonella enterica ser. typhi* SRC, *Proteus vulgaris* OX19 and *Enterobacter aerogenes* 10102, and one Gram positive bacterial strain viz. *Bacillus subtilis* 6633, which were obtained from Microbial Type Culture Collection and Gene Bank (MTCC), Institute of Microbial Technology, Chandigarh, India and Department of

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Microbiology, University of Kalyani, West Bengal, India. Initially complex **1** was dissolved in dimethyl sulfoxide (DMSO) and the final concentration of DMSO was always maintained below 1%. As the reference material Amoxicillin was used (Saha et al., 2014) [46]. Luria-Bertani (LB) medium (Modified) was used for antimicrobial analysis and minimum inhibitory concentrations (MIC) of complex **1** against the tested strains were determined as per NCCLS protocol (NCCLS, 1993) [47]. Different concentrations of complex **1** were prepared and administered in the sterilized LB broth. Following inoculation (1%) of the overnight culture the tubes were incubated at 37°C for 24 hours. Turbidity in the broth was measured by UV-VIS spectrophotometer at 600 nm to identify the MIC. Bacterial susceptibility of the complex was experimented using agar well diffusion method and the potentiality was determined by measuring the growth inhibition zone diameter (mm) (Bauer et al., 1966) [48]. Bacterial growth kinetics in presence of complex **1** was examined against four bacterial strains (*Bacillus subtilis* 6633, *Enterobacter aerogenes* 10102, *Proteus vulgaris* OX19 and *Salmonella enterica ser. typhi* SRC).

#### 2.2. Synthesis

## 2.2.1. Synthesis of Schiff base (H<sub>2</sub>L<sup>1</sup>)

The Schiff base ligand  $(H_2L^1)$  has been synthesized and characterized using literature method [38]. Yield: (90%), Anal. Calc. for  $C_{19}H_{22}N_2O_4$ : C, 66.65; H, 6.48; N, 8.18 Found: C, 6.71; H, 6.42; N, 8.08%. IR (KBr,  $v_{max}/cm^{-1}$ ): v(C=N) 1641,  $v(C-O_{phenolic})$  1254, v(O-H) 3449, UV-vis  $(\lambda_{max}/nm)$ : 258, 398 nm. <sup>1</sup>H NMR for  $H_2L^1$  ( $\delta$ , 300MHz): 2.11(t, J=6.45, 2H<sup>8</sup>), 3.74 (t, J=8.1, 2H<sup>7</sup>), 3.91 (s, 3H<sup>1</sup>), 6.79-6.95(m, 1H<sup>2</sup>, 1H<sup>3</sup>, 1H<sup>4</sup>), 8.37 (s, 1H<sup>5</sup>), 13.94 (s, 1H<sup>6</sup>).

# 2.2.2. Synthesis of complex 1 $[Cd_3(L^1)_2(Cl)_2]$

Schiff base (H<sub>2</sub>L<sup>1</sup>) (0.342 g, 1 mmol) in methanol (15mL) was added dropwise to a solution of Cadmium acetate dihydrate (0.345 g, 1.5 mmol) of the same solvent (25mL) and stirred for 10 minutes. To the resulting deep yellow solution, aqueous solution (5mL) of NaCl (0.05844 g, 1mmol) was added slowly with constant stirring for 4 hr. The yellow coloured solution was additionally refluxed for 15 min at 70<sup>o</sup>C and the resulting yellow filtrate was kept in refrigerator for crystallization by slow evaporation. After 10 days yellow coloured single crystal suitable for X-ray crystallography was obtained. Deep yellow crystal was isolated by filtration and air dried. Yield: 0.382 g (70%) Anal. Calc. for  $C_{38}H_{40}Cd_3Cl_2N_4O_8$ : C, 41.92; H, 3.70; N, 5.15 Found: C, 41.90; H, 3.70; N, 5.14 %. IR (KBr,  $v_{max}/cm^{-1}$ ): v(C=N) 1627, v(O-H) 3442, v(C-H) 2931-2849 , v(Cd-N) 457, v(Cd-O) 400, UV-vis ( $\lambda_{max}/mm$ ): 266 nm & 348 nm.

#### 3. Results and discussion

# 3.1. Tri-nuclear Cd(II) complex (1) synthesis and characterization

We have unambiguously used one-pot synthetic methodology to obtain tri-nuclear Cd(II) complex **1**, where 3:2:2 M ratio of the respective Cadmium(II) acetate dehydrate, dicompartmental Schiff base ( $H_2L^1$ ) and Sodium chloride(self-assembly) from methanolic solvent medium at room temperature yield the Cd(II) yellow colored complex **1**. The synthetic reaction for yellow coloured complex **1** is depicted in scheme 2.



Scheme 2: Synthetic scheme for the preparation of metal complex 1

The synthesized new Cd(II) complex 1 has been characterized by different well known microanalytical (C, H and N), spectroscopic and other well known physicochemical results. Different microanalytical data are in good conformity with the Cd(II) complex formulation. Our synthesized yellow Cd(II) 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<sub>3</sub>CN, but insoluble in water. Several week bands in the range 2931-2849 cm<sup>-1</sup> are strongly observed in complex 1, this is mainly assignable to the aliphatic C-H stretching vibration [49]. The infrared spectra of complex 1 is consistent with the structural data given in Figure S1 (see Supplementary material). An intense strong band at 1630  $\text{cm}^{-1}$  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 Cd(II) metal centers [50]. Schiff base ligand coordination to Cd(II) metal center is substantiated by prominent bands appearing at 457 and 400 cm<sup>-1</sup> which can be attributed to v(Cd-N) and v(Cd-O) respectively in complex 1. Yellow coloured DMSO solution at room temperature of tri-nuclear Cd(II) complex exhibit ligand-based transition at 266 nm and 348 nm presumably due to  $n \rightarrow \pi^*$  or  $\pi \rightarrow \pi^*$  transitions [51,52]. The UV-visible absorption spectrum is depicted in Figure S2 (see Supplementary material).

# **3.2.** X-ray Crystal Structure of $[Cd_3(L^1)_2(Cl)_2](1)$

Single-crystal X-ray diffraction studies reveal that **1** is neutral complex that crystallize in the the monoclinc system in  $P2_1/c$  space group with Z = 4. A perspective view of the complex **1** is depicted in Figure 1. Selected bond parameters of **1** are summarized in the Table S1 (See Supplementary material).



**Scheme 3.** Binding mode of the ligand  $([L]^{2^{-}})$ 

The homometallic complex possesses a trinuclear  $[Cd_3(\mu_2-O)_4]^{3+}$ core (Figure 1 and 3) which is assembled as a result of the cumulative coordination action of two doubly deprotonated  $[L]^{2-}$ ligands. The fully deprotonated ligand has six potential coordination site but its uses its five potential coordination site to hold together two Cd(II) ions in a  $\mu_2 - \eta^1$ :  $\eta^2$ :  $\eta^1$ :  $\eta^1$ :  $\eta^2$  fashion (Scheme 3). Each  $[L]^{2-}$  uses two  $\mu$ -phenolate oxygen, two imino nitrogen, and the one oxygen atoms of the methoxy (-OMe) groups. Interestingly, one -OMe group of the ligand remains noncoordinating (Scheme 2 and 3). In the trinuclear ensemble, each of the two terminal Cd(II) centers is surrounded by a  $[L]^{2-}$  ligand and is bound by two phenolate oxygen atoms (O2 and O3), two imino nitrogen atoms (N2 and N1). Apart from these in order to satisfy the charge and coordination requirements, a chloride anion coordinate the terminal Cd(II) ion in a monodentate fashion generating a CdO<sub>2</sub>N<sub>2</sub>Cl coordinating environment. So, the terminal Cd(II) center display

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distorted square pyramidal coordination sphere (Figure 2). The geometry distortion information in favor of complex **1** can be obtained from structural index or addison parameter **r**[53] which represents the relative amount of trigonally in the crystal structures and for square pyramid,  $\mathbf{r} =$ 0; trigonal bipyramid,  $\mathbf{r} = 1$ ;  $\mathbf{r} = (\alpha - \beta)/60^\circ$ , where  $\alpha$  and  $\beta$  are the two largest angles around the metalions Cd1 & Cd3 .The calculated Addison parameter **r** are 0.0635 & 0.175 for Cd1, Cd3 that confirmed distorted square pyramidal geometry around the metal centers Cd1 & Cd3.



**Figure 1.** ORTEP diagram of **1** with the atom numbering scheme (non-hydrogen atoms have been shown at 50% ellipsoid probability).



**Figure 2.** (a) Distorted square pyramidal and (b) distorted trigonal prismatic geometry around Cd(II) ion.

An *all-oxygen* coordination sphere is achieved around the central Cd(II) ion which has an overall 6O coordination environment in a distorted trigonal prismatic geometry (Figure 2). Interestingly, here it is important to mention that the non-coordinating -OMe group of the ligand display strong of van der waals interaction with the central Cd(II) ion with a average bond distance around 2.721(3) Å (Figure 1). All the two  $[L]^{2-}$  ligands present in the complex are involved in binding of central Cd(II) centre. In addition to the four phenolate oxygen atoms (O2, O3, O6 and O7) two oxygen atoms from the methoxy group (O1 and O5) are also involved in coordination. Each of

the terminal Cd(II) and the central Cd(II) centers are bridged by two phenolate oxygen atoms generating two 4-membered slightly non-planar  $Cd_2(O)_2$  rings which bisect each other with an angle of 82.36(9)° with respect to each other (Figure 3). Also, as result of the bridging phenolate coordination the three metal ions are placed in a almost linear arrangement with a Cd1-Cd2-Cd3 bond angle of 174.31(2)°. The average inter Cd<sup>II</sup>-Cd<sup>II</sup> distance is 3.58(1) Å.



Figure 3. The trinuclear core of 1 showing two four-membered  $Cd_2(O)_2$  rings at an angle of ~  $82^{\circ}$ .

An inspection of metric parameter reveals that the Cd– $O_{phenolate}$  bond lengths are in the range of ~2.220–2.279 Å. On the other hand, Cd– $O_{methoxy}$  and Cd-Cl bond lengths are moderately larger than previous one and falls in the range of 2.458-2.489Å and 2.419-2.428 Å respectively. The imino-nitrogen of the ligand binds with Cd<sup>II</sup> ion with a distance of 2.250–2.285 Å. The Cd–O–Cd angles lie in narrow ranges: 104.92–106.26° (See Supplementary material).



**Figure 4.** Neighbouring [Cd]<sub>3</sub> trinuclear array are connected by 2D-hydrogen bonding network along the *ac* plane.

Complex **1** is involved extensive with intermolecular C–H.....Cl interactions. A two-dimensional hydrogen bonding network is seen along the *ac* plane where each trinuclear unit inteacts with five neighbouring molecules through two coordinating  $Cl^{-}$  ions with terminal metal ions (Figure 4). The bond parameters associated with the intermolecular hydrogen bonding are given in Table S2 (See Supplementary material).

#### 3.3. Luminescence behavior of complex 1

We have studied fluorescence properties individually for Schiff base ligand  $(H_2L^1)$  and complex 1 to find out the fluorescence silent or active nature since fluorescence active property of complex 1 opens up the new possibility of opportunity for photochemical applications [54-60]. Hence for this reason fluorescence properties of Schiff base ligand and its respective Cd(II) complex 1 were studied at room temperature (298 K) in DMSO solvent. A Complete Analysis reveals that Schiff base ligand exhibit emission at 390 nm while complex 1 shows emission at 462 nm upon excitation at 349 nm (Figure 5 and Table 2). Since Cd(II) ion has no optical spectroscopic signature due to its closed-shell 3d<sup>10</sup> configuration, hence Cd(II) is very difficult to oxidize or reduce. Therefore fluorescence emission originating mainly from metal-centered MLCT/LMCT excited states is not expected for complex 1. Thus for complex 1 emission is tentatively assigned due to intraligand  $(\pi \rightarrow \pi^*)$  fluorescence. From Figure 5, we observed that complex 1 fluorescence intensity is higher than that of free Schiff base ligand. 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 coordination with Schiff base (N,O) donor ligand [61-64]. The question comes out our minds that why complex1 fluorescence intensity is higher than that of free Schiff base ligand. It is best way to explain such fact that on the basis of "chelation mediated fluorescence intensity". Normally Zn(II), Cd(II) metal ions enhance or quench fluorescence emission in presence Schiff base ligand that contains aromatic  $\pi$  cloud ring system and ligand donor centers nitrogen, oxygen are selectively bonded with respective metals. 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 in a lucid manner 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 photo induced electron transfer (PET) process due to presence of ligand donor atoms N, O nonbonding electrons pairs. Such PET process is prevented by the Schiff base ligands when its nonbonding electron pairs of donor centers N, O gets stable complexed with Cd(II) metal center. The overall process is referred as "chelation enhanced fluorescence intensity". Due to the chelation effect of Cd(II) metal ion with Schiff base ligand ( $H_2L^1$ ) donor centers nitrogen or oxygen increases the rigidity of the ligand and thus reduces the loss of energy by thermal vibrational decay[65].

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

Compound	Abssorption ( $\lambda_{max}$ ), nm	Excitation ( $\lambda_{max}$ ), nm	Emission ( $\lambda_{max}$ ), nm
Schiff base ligand	258 & 398 nm	332 nm	390 nm
$(H_2L^1)$	<b>N</b>		
Complex 1	266 & 348 nm	348 nm	462 nm



**Figure 5.** Fluoresecence spectra of Schiff base ligand  $(H_2L^1)$  & complex 1 in DMSO solution at 298 K.

#### 3.4. Antimicrobial screening of complex 1

This study exhibited that the synthesized complex **1** has the potentiality to inhibit bacterial growth. MIC values and growth inhibition zone diameters of the tested bacterial strains for the complex are presented in Table 3. The complex **1** showed a wide range of antibacterial activity and it had the similar antibacterial potentiality against both Gram positive and Gram negative bacteria. Among the tested strains *B. subtilis* 6633 and *P. vulgaris* OX19 were most susceptible to MIC value of  $60\mu g/mL$ , where as *E. aerogenes* 10102 was less susceptible to MIC value of  $200\mu g/mL$  against the complex. The MIC values of the complex **1** were lower than the MIC values of Amoxicillin in case of *P. vulgaris* OX19 and *E. aerogenes* 10102. From this study it can be concluded that the complex **1** has broad spectrum of antibacterial activity. The growth kinetics analysis showed that the complex has promising potentiality to restrict bacterial growth

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as a bacteriostatic agent, which is illustrated in the *in vitro* growth curve (Figure 6) of four bacterial strains (*Bacillus subtilis* 6633, *Enterobacter aerogenes* 10102, *Proteus vulgaris* OX19 and *Salmonella enterica ser. typhi* SRC).

Table 3. MIC ( $\mu$ g/mL) and corresponding growth inhibition zone diameter (mm) of complex 1 and Amoxicillin against the tested bacterial strains. Amoxicillin was used as standard antimicrobial agent. All data were taken in triplicate.

	Complex 1		Amoxicillin	
Organisms	MIC	Zone of	міс	Zone of
	(µg/mL)	Inhibition (mm)	(µg/mL)	Inhibition (mm)
B. subtilis 6633	60	$8.5 \pm 0.5$	30	$8.4\pm0.3$
E. aerogenes 10102	200	$6.2 \pm 0.3$	280	$8.5 \pm 0.4$
E. coli K12	140	$5.7 \pm 0.2$	10	$12.3 \pm 0.2$
P. vulgaris OX19	60	$9.7 \pm 0.3$	125	$8.0 \pm 0.3$
S. typhi SRC	130	$5.5 \pm 0.5$	35	9.1 ± 0.3



**Figure 6.** Time dependent *in vitro* growth curves of (a) *Bacillus subtilis* 6633, (b) *Enterobacter aerogenes* 10102, (c) *Proteus vulgaris* OX19 and (d) *Salmonella enterica ser. typhi* SRC subjected to complex **1**. (All data were taken in triplicate and error bars show standard deviations).

#### 4. Concluding remarks

The synthesis and structural characterization of homometallic trinuclear linear complex  $[Cd_3(L^1)_2(Cl)_2]$  (1) was described. The homometallic complex consists a trinuclear  $[Cd_3(\mu_2 - O)_4]^{3+}$  core which is assembled as a result of the cumulative coordination action of two doubly deprotonated  $[L]^{2-}$  ligands. The central cadmium attached by  $\mu$ -phenolato-oxygen & methoxy

group oxygen atoms. Terminal Cd(II) metal bonded with  $\mu$ -phenolato-oxygen & imino-nitrogen atoms in addition with monodentate Cl<sup>-</sup> ions. Thus central Cd(II) attained distorted trigonal prismatic geometry but other two terminal Cd(II) metal ions are distorted square pyramidal. Complex **1** exhibits extensive 2D intermolecular hydrogen bonding with respect to C–H.....Cl along crystallographic *ac*-plane. The enhanced fluorescence intensities of the tri-nuclear cadmium(II) complex **1** compared to that of di-compartmental hexadentate Schiff base ligand (H<sub>2</sub>L<sup>1</sup>) confirmed its potentiality to be a photoactive material. Complex **1** revealed better antibacterial activity towards some important gram positive and gram negative bacteria.

**Supplementary material:** Selected some bond distances, angles values and H-bonding associated interactions. Figure S1-S3 shows complex **1** IR, UV spectral curve and complex 1 as well as ligand excitation spectrum as supplementary information. Figure S4 as supplementary information for complex 1 and ligand solid state fluorescence spectra.

CCDC 1495264 contains the supplementary crystallographic data (excluding structure factors) in CIF format for the structure reported of Cd(II) tri-nuclear complex **1**. The data can be obtained free of charge via <u>http://www.ccdc.cam.ac.uk/</u> 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: <u>deposit@ccdc.cam.ac.uk</u>.

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# HIGHLIGHTS

- Trinuclear linear Cd(II) Schiff base complex 1 has been synthesized
- Complex 1 highly fluorescence behavior
- Shows antimicrobial activity against some important Gram +ve and Gr –ve bacteria

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