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Short communication

# Binuclear cobalt(II), nickel(II), copper(II) and palladium(II) complexes of a new Schiff-base as ligand: Synthesis, structural characterization, and antibacterial activity

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#### ABSTRACT

A binucleating new Schiff-base ligand with a phenylene spacer, afforded by the condensation of glycyl–glycine and *o*-phthalaldehyde has been served as an octadentate N<sub>4</sub>O<sub>4</sub> ligand in designing some binuclear complexes of cobalt(II), nickel(II), copper(II), and palladium(II). The binding manner of the ligand to the metal and the composition and geometry of the metal complexes were examined by elemental analysis, conductivity measurements, magnetic moments, IR, <sup>1</sup>H, <sup>13</sup>C NMR, ESR and electronic spectroscopies, and TGA measurements. There are two different coordination/chelation environments present around two metal centers of each binuclear complex. The composition of the complexes in the coordination sphere was found to be  $[M_2(L)(H_2O)_4]$  (where M = Co(II) and Ni(II)) and  $[M_2(L)]$  (where M = Cu(II) and Pd(II)). In the case of Cu(II) complexes, ESR spectra provided further information to confirm the binuclear structure and the presence of magnetic interactions. All the above metal complexes have shown moderate to good antibacterial activity against Gram-positive and Gram-negative bacteria.

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#### 1. Introduction

Transition metal complexes with Schiff-bases have expanded enormously and embraced wide and diversified subjects comprising vast areas of organometallic compounds [1] and various aspects of biocoordination chemistry [2]. The design and synthesis of symmetrical Schiff-bases, derived from the 1:2 stepwise condensation of carbonyl compounds, with alkyl or aryl diamines, and a wide range of aldehyde or ketone functionalities, as well as their metal(II) complexes have been of interest due to their preparative accessibility, structural variability and tunable electronic properties allowing to carry out systematic reactivity studies based on ancillary ligand modifications [3]. In recent years much effort has been put in synthesis and characterization of mono- and bi-nuclear transition-metal complexes. Schiff-base ligands that are able to form binuclear transition metal complexes are useful to study the relation between structures and magnetic exchange interactions [4], and to mimic bimetallic biosites in various proteins and enzymes [5]. The complexes thus play an important role in developing the coordination chemistry related to catalysis and enzymatic reactions, magnetism and bioinorganic modeling studies [6,7]. In

this regard, there is much current interest in designing dinucleating ligands and their transition metal complexes.

Commonly, the multidenate binucleating Schiff-bases with inbuilt spacers can take up two same or different metal ions. Various mono- and dialdehvde/ketones have been employed to condense with amines or aminoacids to explore multidentate binucleating Schiff-bases to design a variety of binuclear transition metal complexes [3-5,8-11]. Shakir and Varkey [12] have reported on the synthesis, characterization of macrocyclic binuclear Cu(II), Ni(II), Zn(II) complexes by template condensation of diethylenetrimine with dicarboxylic acids. Similarly, the binuclear Ni(II) and Pd(II) complexes have been prepared and characterized by Al-Kubaisi [13]. Recently, the authors group developed various coordination compounds including Schiff-base macrocycles derived from o-phthalaldehyde and different amines [14-24]. Further, we also disclosed the excellent catalytic and antibacterial activity of the macrocyclic Schiff-bases and their metal complexes in our recent reports [14-24]. However, to our knowledge the combination of o-phthalaldehyde and aminoacids has never been used to synthesize Schiff-base ligands. In the context of this background we are now interested to explore some multidentate binucleating Schiffbase ligands. Herein, we have noticed that glycyl-glycine with several potential donor atoms could be a good choice to condense with o-phthalaldehyde to develop binucleating Schiff-base ligands. In this connection it was interesting to synthesize and study the

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Scheme 1. Synthetic route of binuclear Co(II), Ni(II), Cu(II) and Pd(II) complexes.

transition metal complexes with Schiff-base produced from condensation reaction of *o*-phthalaldehyde with glycyl–glycine (see Scheme 1). A description on characterization data using analytical, spectroscopic, thermal and magnetic data has been systematically presented. Furthermore, the application of these metal complexes as potential antibacterial agents has also been demonstrated.

# 2. Experimental

# 2.1. Materials and methods

All the chemicals used were of analar grade. Solvents were purified and dried before use according to the standard procedures. The metal contents were determined by complexometric titration with EDTA for cobalt. Nickel and palladium were determined by gravimetric procedure using dimethylglyoxime as precipitating agent and copper was determined by iodometric procedure. Elemental analysis (C, H, N) was obtained using Perkin-Elmer elemental analyzer. The infrared spectra were recorded in KBr/CsBr/Nujoll on Perkin-Elmer-283 spectrophotometer in the range of 4000–200 cm<sup>-1</sup> and electronic spectra in MeOH were obtained using Shimadzu UV-265 Spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra in CDCl<sub>3</sub>/DMSO were recorded on a Brucker WH 300 (200 MHz) and Varian Gemini (200 MHz) spectrometers using TMS as an internal reference. Conductance measurements were carried out at room temperature on freshly prepared 10<sup>-3</sup> M EtOH solutions using a coronation digital conductivity meter. The magnetic studies were carried out at room temperature on a Gouy balance calibrated with Hg [Co(SCN)<sub>4</sub>]. All the mass spectra were recorded using MALDI Autoflex time-of-flight mass spectrometer. The ESR spectra of Cu(II) complex are recorded at room temperature and liquid nitrogen temperature. The TG–DTG thermograms of the complexes were recorded on Mettler Toledo star system. The antibacterial activity of the compounds was determined by the cup plate method and the minimum inhibitory concentration by liquid dilution method [25–28].

#### 2.2. Synthesis of Schiff-base ligand (L)

Glycyl–glycine (0.64 g, 0.02 mol) dissolved in methanol (10 mL) was added slowly with constant stirring to KOH in methanol. The solution was stirred for half an hour and then filtered. To the filtrate *o*-phthalaldehyde (1.32 g, 0.01 mol) dissolved in MeOH (20 mL) was added drop wise with constant stirring. The resulting solution was evaporated under reduced pressure and kept at room temperature for 2 h. The dirty white precipitate was washed with cold alcohol. The crystals were suction filtered washed with diethyl ether and dried in vacuum. The product was found to be TLC pure in 7:3 mixtures of methanol and chloroform (mobile phase). Our synthetic route of Schiff-base ligand is shown in Scheme 1.

# 2.2.1. 2-(2-[((E)-1-2-[(2-[(carboxymethyl)amino]-2-

oxoethylimino)methyl]phenylmethylidene)amino]acetylamino)acetic acid (L) (CMAIPA)

Yield 74%; mp 196–198 °C; IR 3318, 2918, 2842, 1720, 1643, 1632, 1570, 1128 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, DMSO)  $\delta$  in ppm 11.56

Analytical, spectral a	and physical data	of the ligand and	l complexes.

Complexes/molecular formulae	$\lambda_{max} \left( nm \right)$	$^{\Lambda}\mathrm{M}^{\mathrm{a}}$ ( $\Omega^{-1}\mathrm{cm}^{2}\mathrm{mol}^{-1}$ )	Found (Calcd.) (%)				
			С	Н	Ν	М	$\mu_{\rm eff}$ (BM)
CMAIPA C <sub>16</sub> H <sub>18</sub> N <sub>4</sub> O <sub>6</sub>	-	-	53.04 (54.84)	5.01 (4.94)	15.48 (15.46)	-	-
[Co <sub>2</sub> L(H <sub>2</sub> O) <sub>4</sub> ]·3H <sub>2</sub> O C <sub>16</sub> H <sub>30</sub> N <sub>4</sub> O <sub>13</sub> Co <sub>2</sub>	622,661	14	35.14 (35.15)	6.06 (6.05)	8.60 (8.63)	18.10 (18.15)	3.50
[Ni <sub>2</sub> L(H <sub>2</sub> O) <sub>4</sub> ]·3H <sub>2</sub> O C <sub>16</sub> H <sub>30</sub> N <sub>4</sub> O <sub>13</sub> Ni <sub>2</sub>	937, 591, 376	13	35.20 (35.17)	6.10 (6.06)	8.60 (8.63)	18.02 (18.09)	2.90
[Cu <sub>2</sub> L]·3H <sub>2</sub> O C <sub>16</sub> H <sub>24</sub> N <sub>4</sub> O <sub>9</sub> Cu <sub>2</sub>	710, 543, 432	16	36.70 (36.69)	4.58 (4.53)	10.10 (10.07)	22.80 (22.84)	1.58
[Pd <sub>2</sub> L] C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> O <sub>6</sub> Pd <sub>2</sub>	610, 520, 405	20	41.20 (41.17)	3.50 (3.46)	12.02 (12.00)	22.84 (22.80)	0.00

(s, 2H, COOH), 8.19 (s, 2H, CH=N), 7.22–7.54 (m, 4H, Ar–H), 5.83 (s, 4H, CH<sub>2</sub>), 5.60 (s, 2H, NH), 4.25 (d, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (67.93 MHz, DMSO)  $\delta$  48.5 (2C, CH<sub>2</sub>), 58.3 (2C, CH<sub>2</sub>), 130.6, 132.3, 136.4 (6C, Ar–C), 163.7(2C, CH=N), 171.2 (2C, C=O), 180.4 (2C, COOH); Anal. Found: C, 53.04; H, 5.01; N, 15.48%. Calcd. for C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>O<sub>6</sub>: C, 58.84; H, 4.94; N, 15.46%. MS: [M]<sup>+</sup> at *m*/*z* 362.

#### 2.3. Synthesis of complexes

Table 1

A solution of cobalt(II) acetate, nickel(II) acetate and copper(II) acetate (0.002–0.005 mol) in methanol (25 mL) and palladium(II) chloride (1.062 g in 40 mL 0.1 M HCl and 40 mL methanol) was added drop wise to a methanolic solution (30 mL) of Schiff-base (0.002–0.005 mol) with constant stirring at room temperature. The resulting mixture was allowed to reflux on a water bath for 2 h until a solid is separated out. The precipitates were suction filtered, purified by repeated washing with chloroform and methanol and dried in vacuum desiccators (Yield: 70–85%).

#### 3. Results and discussion

All the complexes are soluble in methanol and water. The elemental analysis data and the physical properties of the complexes are listed in Table 1. The complexes can be represented as  $[M_2L(H_2O)_4]\cdot 3H_2O$  where (M = Co(II), Ni(II)) and  $[M_2L]$ .  $3H_2O$  where (M = Cu(II)) and  $[M_2L]$  where (M = Pd(II)) and (L = ligand). The low molar conductance values of all the complexes in dichloromethane measured at  $10^{-3}$  M concentration are in the range of 13–20 indicate that all the complexes behave as non-electrolytes [29].

# 3.1. Infrared spectral analysis

The infrared (IR) spectra of all the complexes show vN–H broad bands in the 3128–3260 cm<sup>-1</sup> range. This band was shifted towards lower side about 90–110 cm<sup>-1</sup> compared to the ligand spectrum indicating the coordination of amino nitrogen to the metal ion [5]. A medium intensity band due to vC=N appeared at 1620–1630 cm<sup>-1</sup> was also found to be shifted towards lower side about 13–23 cm<sup>-1</sup> compared to ligand spectrum and supports the coordination of imino nitrogen (C=N) of ligand to the metal ion [14,15,17,18]. In addition to this, the appearance of new band in the range of 1565–1570 cm<sup>-1</sup> assignable to v(C–O) suggests the coordination of carbonyl group of glycyl–glycine moiety in the enol form through deprotonation. This situation specify the formation of binuclear

Tuble 2		
Infrared spectral data	of the ligand and com	nplexes (cm <sup>-1</sup> ).

Table 2

Co(II), Ni(II), Cu(II) and Pd(II) complexes using the coordination of nitrogens from C=N of Schiff-base and NH of amide group and the oxygens from amide and carboxyl groups [17,18,30]. Further, the bands in the range of 450–470 and 510–515 cm<sup>-1</sup> assignable to the  $\upsilon$ (M–O) and  $\upsilon$ (M–N) respectively are providing additional support to propose the M–L bonds through carboxyl oxygen and imino nitrogen in all the complexes [14,15,17,18] (Table 2). The IR spectrum of [Pd<sub>2</sub>L] binuclear complex is shown in electronic supporting information as Fig. S1.

# 3.2. <sup>1</sup>H NMR spectral analysis

In the <sup>1</sup>H NMR spectra, the integral intensities of each signal were found to agree with the number of different types of protons present in the complex. A signal appeared in the ligand <sup>1</sup>H NMR spectrum at 8.19  $\delta$  is due to CH=N protons. However, in the spectra of palladium complex the signal was moved down-field at 8.30  $\delta$  suggests the coordination of imino nitrogen to palladium ion [22,23]. The carboxyl proton of the ligand was observed at 11.56 ppm. However, this was not present in the complex spectrum due to the involvement of carboxyl oxygen in chelation through deprotonation [31]. Further, a broad signal found in the complex spectrum at 6.0 ppm of ligand give evidence to the coordination of NH group [5].

# 3.3. <sup>13</sup>C NMR spectral analysis

In the <sup>13</sup>C spectra of Pd(II) complex, a down-field shift of CH=N group was observed in at 175.4 ppm and for carboxyl carbon at 195.3 ppm. It signifies that the ligand coordinates through the nitrogen atom of CH=N [22,23] and through the oxygen of carboxyl group of the ligand [22,23,31]. Furthermore, the down-field of shifting of amide adjacent carbonyl (C–O) describes the coordination of this site to palladium ion. However, the enolic carbon peak shifted to 108.0–115.3  $\delta$  suggesting that coordination of C–O group to the metals by deprotonation. The <sup>1</sup>H and <sup>13</sup>C NMR spectrum of [Pd<sub>2</sub>L] binuclear complex is given in Supplementary Figs. S2 and S3.

# 3.4. Electronic spectral analysis

The electronic spectrum of bimolecular Co(II) complex with the ligand exhibit the d-d transition bands in the regions 622 and 661 nm assigned to the  ${}^{4}A_{2g} \leftarrow {}^{4}T_{1g}(F)(\upsilon_2)$  and  ${}^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}(F)(\upsilon_3)$  transitions respectively [14]. This indicates

Complexes	υ(C=N)	υ(N-H)	$\upsilon$ (C–O) of COOH	∪(COO-) asy/sym	U(M-H <sub>2</sub> O)	υ(M–N)	υ(M-0)
CMAIPA	1643	3318	1720, 1632	-	-	-	-
$[Co_2L(H_2O)_4]\cdot 3H_2O$	1630	3228	1570	1583, 1383	725	510	470
$[Ni_2L(H_2O)_4]\cdot 3H_2O$	1628	3206	1565	1579, 1383	725	509	470
[Cu <sub>2</sub> L]·3H <sub>2</sub> O	1620	3128	1570	1583, 1383	-	510	450
[Pd <sub>2</sub> L]	1620	3260	1570	1583, 1383	-	508	450

the octahedral geometry for Co(II) complex. Similarly, bimolecular Ni(II) complex electronic spectrum exhibits the d-d transition bands in the regions 937, 591 and 376 nm signed to the  $^3T_{\rm 2g}$  $(F) \leftarrow {}^{3}A_{2g}(F)(\upsilon_{1}), {}^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}(F)(\upsilon_{2}) \text{ and } {}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}(F)(\upsilon_{3})$ transitions respectively [17,24]. This shows the octahedral geometry and was further confirmed by  $v_2$  to  $v_1$  ratio, which was in the range of 1.50–1.63 [17,32]. The UV spectrum of the Cu(II) complex recorded in DMF showed an intensive band at about 710, 543 and 432 nm bands could be assigned to  ${}^{2}A_{1g} \leftarrow {}^{2}B_{1g}$ ,  ${}^{2}B_{2g} \leftarrow {}^{2}B_{1g}$  and  ${}^{2}E_{g} \leftarrow {}^{2}B_{1g}$  transitions respectively [33]. It indicates the square planar geometry for Cu(II) complexes. Further, Pd(II) complex shows three bands at 610, 520 and 405 nm assignable to  ${}^{1}A_{2g} \leftarrow {}^{1}A_{1g}$ ,  $^{1}B_{1g} \leftarrow ^{1}A_{1g}$  and  $^{1}E_{g} \leftarrow ^{1}A_{1g}$  transitions attributed to the square planar geometry. From the electronic spectral data, diamagnetic behavior and square planar geometry has been proposed to Pd(II) complex [22,23].

#### 3.5. Magnetic properties

The theoretical magnetic moments values of the cobalt(II), nickel(II) and copper(II) complexes were 3.87, 2.83 and 1.73 B.M respectively. Experimentally it has been found that mononuclear, octahedral cobalt(II), nickel(II) and copper(II) complexes have magnetic moments in the range 4.3-5.2, 2.9-3.3 and 1.7-2.2 B.M. However, in the present investigation, the magnetic moment observed for the binuclear, octahedral Co(II) and Ni(II) complexes were 3.50 and 2.90 B.M., respectively. These values are less than the experimental values indicate the absence of metal-metal interaction in the binuclear complex [34]. Further, the magnetic moment of Cu(II) complex lies below the 'spin only' value, i.e. 1.58 B.M. The lower value of magnetic moment at room temperature is consistent with square planar geometry around the metal ions. In general, the low magnetic moment values of binuclear copper complexes are attributed to the anti-ferromagnetic moment interaction between two central Cu(II) metal ions; this is an indication of the formation of binuclear Cu(II) complex [34]. In addition, the magnetic susceptibility measurements have also been carried out for Pd(II) complex and was found to be diamagnetic, confirmed by sharp signals in the <sup>1</sup>H NMR spectra.

# 3.6. Thermal analysis

Thermal behavior of the complexes has been studied using TGA, and DTA analysis. Based on the thermograms, decomposition stages, temperature ranges, decomposition product as well as weight loss percentages of the complexes were calculated. The complexes [Co<sub>2</sub>L(H<sub>2</sub>O)<sub>4</sub>]·3H<sub>2</sub>O and [Ni<sub>2</sub>L(H<sub>2</sub>O)4]·3H<sub>2</sub>O undergo decomposition mainly in three stages. In the first stage a peak corresponding to the loss of the water molecule in the temperature range of 70-110 °C was observed. The expulsion of water molecules in this range indicates that they are lattice held. It is further evidenced by an endothermic peak in the above temperature range in DTA curve, indicating that the water molecules are of lattice type [14,17]. The second stage corresponds to the loss of water molecules in the temperature range of 170-200 °C corresponding to the loss of coordinated water molecules. The presence of endothermic peak at 180-200 °C in DTA curve of the complex also further confirms the presence of coordinated water. The third stage corresponds to the loss of organic moiety. The final decomposition of the complexes above 500 °C corresponds to metal oxide. The thermogram of [Cu<sub>2</sub>L]·3H<sub>2</sub>O complex shows only two stages of decomposition. The first stage corresponds to dehydration of water molecules at 117 °C and second stage being the loss of organic moiety. The presence of water molecules is further evidenced by DTA curves. The expulsion of water molecules and the percentage of loss of weight in the above temperature range indicate that water

molecules are not coordinated [15]. The thermal data of  $[Pd_2L]$  complexes indicate no coordinated water molecules [22,23]. The sharp decomposition corresponding to the loss of organic moiety in complexes can be seen in the DTA curves which contain one short exothermic peak falling at 290 °C. The final product of decomposition of the complex above 680 °C corresponds to metal oxide. The analysis of the thermogram by the way of identifying the final products offers further support to the composition of the complexes of elemental and spectral analysis.

# 3.7. ESR spectral analysis

The ESR spectrum of  $[Cu_2L]$ - $3H_2O$  complex exhibits an axial signal, which can be interpreted in terms of tetrahedral species with a strong signal in the low field region, corresponding to high  $g_{\perp}$  value *viz.* 2.19, and a weak signal in the high field region due to low  $g_{\parallel}$  value *viz.* 2.06, while the  $g_{avg}$  is 2.15. Splitting of the signal in the high field region may be due to a difference in surroundings between the two Cu(II) centers suggesting a binuclear structure for this complex [35]. The *g* value is equal to 0.32, indicating that anti-ferromagnetic interaction is taking place between the Cu(II) ions [36]. The  $g_{\perp} > g_{\parallel} > 2.0023$  indicates that the unpaired electron is present in the  $d_{xy}$  ground state in a square planar geometry [37,38].

### 3.8. Mass spectral data

The formation of binuclear Co(II), Ni(II), Cu(II) and Pd(II) complexes further evidenced by mass spectral data. The proposed molecular formula of binuclear Co(II), Ni(II), Cu(II) and Pd(II) complexes was confirmed by the mass spectral analysis by comparing its molecular formula weight with m/z value. The molecular ion peaks and isotopic pattern of ligand and its binuclear Co(II), Ni(II), Cu(II) and Pd(II) complexes shows different m/z values with different intensities. The mass spectra contain molecular ion peaks at m/z (M<sup>+</sup>) 362 (ligand CMAIPA), 604 ([Co<sub>2</sub>L(H<sub>2</sub>O)<sub>4</sub>]·3H<sub>2</sub>O), 603.8 ([Ni<sub>2</sub>L(H<sub>2</sub>O)<sub>4</sub>]·3H<sub>2</sub>O), 543 ([Cu<sub>2</sub>L]·3H<sub>2</sub>O) and 572 ([Pd<sub>2</sub>L]). This data is in good agreement with the respective molecular formulae. Mass spectrum of [Pd<sub>2</sub>L] is presented in Supplementary Fig. S4.

#### 4. Antibacterial activity

Antibacterial activities of the ligand CMAIPA and its Co(II), Ni(II), Cu(II), Pd(II) complexes against two Gram-positive (*B. subtilis* and *S. aureus*) and two Gram-negative (*E. coli* and *K. pneumonia*) bacteria were studied using three existing antibacterial drugs viz., streptomycin, ampicillin and rifampicin. Preliminary screening for all the complexes was performed at the fixed concentration of

Table 3

Zone of inhibition of CMAIPA and its Co(II), Ni(II), Cu(II), Pd(II) complexes against different bacteria.

Ligand/complexes (1000 µg/mL)	Zone of inhibition (mm)				
	Gram-positive bacteria		Gram-nega	ative bacteria	
	S. aureus	B. subtilis	E. coli	K. pneumonia	
CMAIPA	11	10	08	08	
$[Co_2L(H_2O)_4] \cdot 3H_2O$	15	21	14	19	
$[Ni_2L(H_2O)_4] \cdot 3H_2O$	12	16	24	20	
[Cu <sub>2</sub> L]·3H <sub>2</sub> O	28	19	15	25	
[Pd <sub>2</sub> L]	45	42	35	40	
Streptomycin	12	10	06	06	
Ampicillin	13	11	08	07	
Rifampicin	49	51	48	45	



Fig. 1. Comparison of MIC values (in  $\mu g/mL)$  of complexes and standard drugs against different bacteria.

 $1000 \,\mu g/mL$ . Inhibition was recorded by measuring the diameter of the inhibition zone at the end of 24h for bacteria. Among the compounds tested the four metal complexes showed good inhibition towards all tested strains (Table 3). The activity of all these complexes were further confirmed by determining the minimum inhibitory concentration [25,26,39] values by liquid dilution method in which the effectiveness was observed at lower concentrations. The comparison of the MICs (in  $\mu g/mL$ ) of all complexes and standard drugs against tested strains are presented in Fig. 1 (Supplementary Table S1). It was found that Co(II), Ni(II), Cu(II) complexes have good activity against all bacterial strains with MIC value (15–35 $\mu$ g/mL). In particular, Pd(II) complex showed excellent activity (MIC range 5-10 µg/mL) against all the bacterial strains even than standard drugs streptomycin and ampicillin. The results from these studies have also shown that complexation of metals to CMAIPA serves to improve the antimicrobial of the ligand. This higher antibacterial activity of the metal complexes compared to ligand is may be due to the change in structure due to coordination and chelating tends to make metal complexes act as more powerful and potent bactereostatic agents, thus inhibiting the growth of the bacteria. Furthermore, chelation reduces the polarity of the metal ion mainly due to the partial sharing of its positive charge with the donor groups within the chelate ring system. Such chelation increases the lipophilic nature of the central metal atom, which favors its permeation more efficiently through the lipid layer of the microorganism, thus destroying them more forcefully [20,40-42]. Thus all complexes showed more increased activity than the corresponding ligand and the two antibacterial drugs. The activity of ligand, complexes and standard drugs against different bacteria were found to be  $CMAIPA(L) < streptomycin < [Ni_2L(H_2O)_4] \cdot 3H_2O = ampicillin < [Co_2]$  $L(H_2O)_4$ ]·3H<sub>2</sub>O < [Cu<sub>2</sub>L]·3H<sub>2</sub>O < [Pd<sub>2</sub>L] < rifampicin for *S. aureus*,  $CMAIPA(L) = streptomycin < ampicillin < [Ni_2L(H_2O)_4] \cdot 3H_2O < [Cu_2L] \cdot 2H_2O < [Cu_2L] \cdot 2H_2O$  $3H_2O < [Co_2L(H_2O)_4] \cdot 3H_2O < [Pd_2L] < rifampicin for$ *B. subtilis*,streptomycin<CMAIPA(L)=ampicillin<[Co<sub>2</sub>L(H<sub>2</sub>O)<sub>4</sub>]·3H<sub>2</sub>O<[Cu<sub>2</sub>L]· 3H<sub>2</sub>O [Ni<sub>2</sub>L(H<sub>2</sub>O)<sub>4</sub>]·3H<sub>2</sub>O<[Pd<sub>2</sub>L]<rifampicin for *E. coli* and streptomycin < ampicillin < CMAIPA( $\mathbf{L}$ ) < [Co<sub>2</sub>L(H<sub>2</sub>O)<sub>4</sub>]·3H<sub>2</sub>O<[Ni<sub>2</sub>L(H<sub>2</sub>O)<sub>4</sub>]·  $3H_2O < [Cu_2L] \cdot 3H_2O < [Pd_2L] < rifampicin for K. pneumonia.$ 

# 5. Conclusions

In this report the non-template synthesis of new binuclear cobalt(II), nickel(II), copper(II), and palladium(II) complexes having N<sub>4</sub>O<sub>4</sub> Schiff-base ligand obtained by condensation of glycyl–glycine with o-phthalaldehyde have been presented and all the synthesized compounds were screened for their antibacterial activity against two Gram-positive and two Gram-negative bacterial strains. In this study the most potent activity was observed in Pd(II) complex against all tested strains when compared to respective standard drugs streptomycin and ampicillin.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2010.08.004.

#### References

- [1] S. Akine, S. Sunaga, T. Taniguchi, H. Miyazaki, T. Nabeshima, Inorg. Chem. 46 (2007) 2959–2961.
- [2] J.R. Anacona, E. Bastardo, J. Camus, Transit. Met. Chem. 24 (1999) 478-480.
- [3] A. Trujillo, S. Sinbandhit, L. Toupet, D. Carrillo, C. Manzur, J.R. Hamon, J. Inorg. Organomet. Polym. 18 (2008) 81–99.
- [4] V. Lozan, C. Loose, J. Kortus, B. Kersting, Coord. Chem. Rev. 253 (2009) 2244–2260.
- [5] S.A. Sallam, Transit. Met. Chem. 31 (2006) 46-55.
- [6] J. Costamagna, J. Vargas, R. Latorre, A. Alvarado, G. Mena, Coord. Chem. Rev. 119 (1992) 67–88.
- [7] J.M. Bindlish, S.C. Bhatia, P.C. Jain, Indian J. Chem. 13 (1975) 81-82.
- [8] M.A. Ali, A.H. Mirza, M. Nazimuddin, F. Karim, P.V. Bernhardt, Inorg. Chim. Acta 358 (2005) 4548–4554.
- [9] B.J.A. Jeragh, A. El-Dissouky, J. Coord. Chem. 58 (2005) 1029–1038.
- [10] P.A. Vigato, S. Tamburini, Coord. Chem. Rev. 248 (2004) 1717-2128.
- [11] S.M.E. Khalil, K.A. Bashir, J. Coord. Chem. 55 (2002) 681-696.
- [12] M. Shakir, S.P. Varkey, Transit. Met. Chem. 19 (1994) 606-610.
- [13] A.H. Al-Kubaisi, Bull. Korean Chem. Soc. 25 (2004) 37-41.
- [14] P.M. Reddy, A.V.S.S. Prasad, K. Shanker, V. Ravinder, Spectrochim. Acta A 68 (2007) 1000–1006.
- [15] P.M. Reddy, A.V.S.S. Prasad, V. Ravinder, Transit. Met. Chem. 32 (2007) 507-513.
- [16] P.M. Reddy, K. Shanker, R. Rohini, M. Sarangapani, V. Ravinder, Spectrochim. Acta A 70 (2008) 1231–1237.
- [17] P.M. Reddy, A.V.S.S. Prasad, R. Rohini, V. Ravinder, Spectrochim. Acta A 70 (2008) 704-712.
- [18] P.M. Reddy, A.V.S.S. Prasad, Ch.K. Reddy, V. Ravinder, Transit. Met. Chem. 33 (2008) 251–258.
- [19] M. Ashok, A.V.S.S. Prasad, P.M. Reddy, V. Ravinder, Spectrochim. Acta A 72 (2009) 204–208.
- [20] K. Shanker, R. Rohini, V. Ravinder, P.M. Reddy, Y.P. Ho, Spectrochim. Acta A 73 (2009) 205–211.
- [21] P.M. Reddy, Y.P. Ho, K. Shanker, R. Rohini, V. Ravinder, Eur. J. Med. Chem. 44 (2009) 2621–2625.
- [22] K. Shanker, P.M. Reddy, R. Rohini, Y.P. Ho, V. Ravinder, J. Coord. Chem. 62 (2009) 3040–3049.
- [23] K. Shanker, R. Rohini, K. Shravankumar, P.M. Reddy, Y.P. Ho, V. Ravinder, J. Ind. Chem. Soc. 86 (2009) 153–161.
- [24] A. Prasad, P.M. Reddy, K. Shanker, R. Rohini, V. Ravinder, Color. Technol. 125 (2009) 284–287.
- [25] R. Rohini, K. Shanker, P.M. Reddy, Y.-P. Ho, V. Ravinder, Eur. J. Med. Chem. 44 (2009) 3330–3339.
- [26] R. Rohini, K. Shanker, P.M. Reddy, V.C. Sekhar, V. Ravinder, Arch. Pharm. 342 (2009) 533-540.
- [27] R. Rohini, P.M. Reddy, K. Shanker, V. Ravinder, Acta Chim. Slov. 56 (2009) 900–907.
- [28] R. Rohini, K. Shanker, P.M. Reddy, V. Ravinder, J. Braz. Chem. Soc. 21 (2010) 49-57.
- [29] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81-122.
- [30] W.R. Marson, H.B. Gray, J. Am. Chem. Soc. 90 (1968) 5721-5729.
- [31] E. Keskioglu, A.B. Gunduzalp, S. Çete, F. Hamurcu, B. Erk, Spectrochim. Acta A 70 (2008) 634–640.
- [32] S. Chandra, R. Kumara, R. Singh, Spectrochim. Acta A 65 (2006) 215-220.
- [33] J. Bjerrum, C.J. Ballhausen, C.K. Jorgensen, Acta Chem. Scand. 8 (1954) 1275-1289.
- [34] R.L. Carlin, A.J. Vandryneveledt, Magnetic Properties of Transition Metal Compounds, Springer-Verlag, New York, 1997.
- [35] S.S. Tandon, L.C. Laurence, K. Thompson, S.P. Connors, J.N. Bridson, Inorg. Chem. Acta 213 (1993) 289–300.
- [36] Z. Wang, Z. Wu, Z. Yen, Transit. Met. Chem. 19 (1994) 235-236.
- [37] A.S. El Tabl, Polish J. Chem. 71 (1997) 1213-1222.
- [38] B.A. Goodman, J.B. Raynor, Adv. Inorg. Chem. Radiochem. 13 (1970) 136–362.
   [39] R. Rohini, P.M. Reddy, K. Shanker, A. Hu, V. Ravinder, Eur. J. Med. Chem. 45
- (2010) 1200–1205. [40] B.G. Tweedy, Phytopathology 55 (1964) 910–914.
- [41] N.M.A. Atabay, B. Dulger, F. Gucin, Eur. J. Med. Chem. 40 (2005) 1096-1102.
- [42] S.A. Patil, V.H. Naik, A.D. Kulkarni, P.S. Badami, Spectrochim. Acta A 75 (2010) 347-354.