



Synthesis, Structural Properties of Hydrazine Carbodithioate Schiff Base and Their Metal Complexes And Evaluation of Their Biological Activity



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Abstract

A new series of [Ni(II)L₂](**1**), [Cu(II)L₂](**2**) and [Co(II)L₂](**3**) (L = benzyl-2-((1E,4E)-1,5-diphenylpenta-1,4-dien-3-ylidene) hydrazine carbodithioate) Schiff base metal complexes have been synthesized. The ligand and its metal complexes were characterized by elemental analysis, ¹H NMR, UV-Vis, FT-IR and magnetic moment, molar conductance and thermal analysis. The electrochemical behaviors of these complexes were investigated by cyclic voltammetry in DMF. The spectroscopic analyses and magnetic moment value suggested four coordinated geometry for three metal complexes, tetrahedral structure of complex **1** and square planer structure of complex **2** and **3**. The ligand and its metal complexes were evaluated for their antibacterial (*Bacillus cereus*, *Bacillus subtilis*, *Escherichia coli*) activities. The complex **1** and Complex **2** revealed moderate activity against both gram positive bacteria (*Bacillus cereus* and *Bacillus subtilis*) with the minimum inhibitory concentration (MIC) value of 256 µg/mL.

Keywords: Hydrazine carbodithioate; Metal complexes; Spectroscopic studies; Thermal analysis; Antibacterial activities.

Introduction

Schiff base metal complexes preface a new era with multipurpose activities in the coordination chemistry and also has attracted enormous interest in the field of inorganic synthesis chemistry due to the reaction and coordination mode currently. The binding ability of Schiff base with various metal ion offers stable metal complexes with unique character and versatile application [1–3]. The Schiff base and their metal complexes extensively used for industrial purposes and reveal biological activities as well as antibacterial, antifungal, antimalarial etc. properties due to the azomethine linkage of Schiff base [4]. The evolution of bioinorganic chemistry has expand the attention in Schiff base complexes for the reason that,

understanding the biological activities [5–8]. Designing an appropriate bidentate Schiff base ligand to combine with metal ion has allowed new area of synthesizing metal complexes of specific choice. Schiff base ligand and their metal complexes have been well known for their easy synthesis, stability and various type of application. A huge number of Schiff base ligand and metal complexes are reported, and their catalytic and biological properties have been studied continuously [9,10]. The Ni(II), Cu(II) and Co(II) complexes with Schiff base are found to show enhanced biological activity with respect to their parental ligands [11]. Preparative accessibility and structural variety of metal complexes with Schiff base as ligand have played drastic change in the development of new complex design with high interest [12]. In this work, we presented the syntheses, spectroscopic characterization and

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antibacterial activities of ligand and corresponding metal complexes of Ni(II), Cu(II) and Co(II).

Experimental

Materials and methods

All chemicals and solvents were analytical grade and obtained from commercial suppliers and used without further purification. UV-Vis spectra were recorded using UVD-3200 and UV Spectrophotometer. FT-IR spectra were taken (range 4000 cm^{-1} to 400 cm^{-1} , number of scan 36) using JASCO FT-IR 4200 spectrometer with ATR unit. $^1\text{H-NMR}$ spectra were recorded on Bruker AV 500MHz. Elemental analysis measurements were performed at the Research and Analytical centre for Giant Molecules, Tohoku University. The Sherwood Scientific magnetic susceptibility balance was used to measure the magnetic moment of the solid complexes by Gouy method and the effective magnetic moment was calculated at room temperature from the following relation [13]. Effective magnetic moment,

$$\mu_{\text{eff}} = 2.828 \sqrt{\chi_m^{\text{corr}} T} B.M.$$

Where, χ_m^{corr} = Molar susceptibility corrected and T = Temperature.

The thermal properties of three metal complexes were investigated by TGA and DTA. These analyses were performed using Shimadzu DTG-60D with reference $\alpha\text{-Al}_2\text{O}_3$. All measurements were carried out from room temperature to 400 $^\circ\text{C}$ under N_2 gas flow 100 mL/min condition with sweep rate of 5 $^\circ\text{C}/\text{min}$. Electrochemistry was performed by using an ALS/HCH model 620D electrochemical analyzer. A glassy carbon (3 mm diameter) electrode was used as a working electrode, Pt wire was used as counter electrode and Ag/AgCl used as reference electrode. The supporting electrolyte was 0.1 M tetrabutyl ammonium hexafluorophosphate (TBAPF_6) in DMF at scan rate 0.10 V/s under N_2 atmosphere. The **L** and the complex **1**, complex **2** and complex **3** were screened for antibacterial activities by (MTT) assay. The prepared compounds were tested against two Gram positive (*Bacillus cereus* and *Bacillus subtilis*) and one Gram negative (*Escherichia coli*) to provide the minimum inhibitory concentration (MIC) for each complex. A stock solution of the compounds (1.024 mg/mL) in DMSO was prepared and graded quantities were incorporated in specified quantity of the corresponding sterilized liquid medium [14]. The bacterial suspension was further diluted to 1:200 in Muller- Hinton medium. The resulting suspension contained approximately 106 cfu/mL and applied to micro titration plates with serially diluted compounds in DMSO to be tested and incubated at 37 $^\circ\text{C}$ for 24h. After that, the MIC level was assessed visually.

Synthesis of L

S-benzylthiocarbamate (SBDTC) was synthesized according to the reported procedures [15,16]. SBDTC (5.94 g, 0.03 mol) was dissolved in 70 mL hot ethanol under constant stirring. The hot ethanolic solution of dibenzalacetone (7.02 g, 0.03 mol) was then added to the solution of SBDTC. The solution mixture was refluxed for 6-8 hours and then allowed to cool at room temperature. A dark red precipitate was obtained after 7 days refrigeration. After recrystallization the resultant dark red colored solid was filtered off and washed with cold ethanol. Then it was dried over silica gel.

Yield 49%, mp 75–77 $^\circ\text{C}$. IR spectrum, ν_{max} , cm^{-1} : 1650 (C=N), 1619–1596 (C=C), 1339 (C–N), 1052–1097 (C=S), 695 (C–S). UV-Vis data, CH_2Cl_2 , λ_{max} , nm: 233, 296. $^1\text{H NMR}$ spectrum, solvent DMSO, δ , ppm: 4.5 s (2H, SCH_2), 7.29–7.48 m (15H, Ar-H), 7.79 d (2H, $\text{CHC}=\text{N}$), 7.81 d (2H, ArCH). Calcd for $\text{C}_{25}\text{H}_{22}\text{S}_2\text{N}_2$ % C: 72.09, % H: 5.81, % N: 6.73. Found; % C: 71.95, % H: 5.65, % N: 6.68.

Syntheses of complex 1, 2 and 3

Complex **1**, **2** and **3** were prepared following the reported procedure [16] by the treatment of Schiff base ligand **L** and hydrated nitrate salts of Ni(II), Cu(II), Co(II) in ethanol respectively. A mixture of ligand **L** (0.84 g, 2mmol) and metal salt (1 mmol, 0.29g, 0.24g, 0.29g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, respectively) in hot ethanol was refluxed for 5-6 hours under constant stirring. The resultant mixture was kept in refrigerator and color precipitate of individual metal complex was obtained after 7 days of refrigeration. After recrystallization the precipitates were filtered off, washed with cold ethanol and dried over silica gel.

Complex **1**: Dark brown solid, yield 54%, 72–74 $^\circ\text{C}$. Calcd $\text{C}_{50}\text{H}_{44}\text{S}_4\text{N}_4\text{Ni} \cdot 0.25\text{H}_2\text{O}$ % C: 70.79, % H: 5.29, % N: 6.60. Conductivity μscm^{-1} : 9.00. μ_{eff} (B. M): 1.27.

Complex **2**: Dark green solid, yield 55%, 80–82 $^\circ\text{C}$. Calcd for $\text{C}_{50}\text{H}_{44}\text{S}_4\text{N}_4\text{Cu} \cdot 0.25\text{H}_2\text{O}$ % C: 70.69, % H: 5.28, % N: 6.59. Conductivity μscm^{-1} : 7.00. μ_{eff} (B. M): 0.99.

Complex **3**: Red solid, yield 35%, 78–80 $^\circ\text{C}$. Calcd for $\text{C}_{50}\text{H}_{44}\text{S}_4\text{N}_4\text{Co} \cdot 0.25\text{H}_2\text{O}$ % C: 70.78, % H: 5.29, % N: 6.60 Found: % C: 70.40, % H: 4.96, % N: 6.34. Conductivity μscm^{-1} : 10.00. μ_{eff} (B. M): 1.30.

Results and Discussion

Synthesis of **L** was carried out by the condensation of equimolar amount of (SBDTC) and dibenzalacetone. SBDTC was synthesized according to the reported procedures [15,16]. The metal complexes [Ni^{II}L₂] (**1**), [Cu^{II}L₂] (**2**) and [Co^{II}L₂] (**3**) were obtained by mixing **L** and corresponding metal ion sources in ethanolic solution. The structure of **L** and corresponding complexes were confirmed by ¹H NMR, IR and UV-Vis. The ¹H NMR spectrum of **L** in DMSO solvent is shown in Fig. 2. The singlet at 4.5 ppm (a) corresponds to proton for S-CH₂. The multiplet at 7.29–7.48 ppm (b) represents 15H of three phenyl rings. A doublet at 7.79 ppm (c) is assigned to the two CH=C=N protons and the doublet at 7.81 ppm (d) assigned to Ar-CH= protons.

The UV-Vis spectra of **L**, Complex **1**, **2** and **3** represents at Fig. 3. Similar types of patterns are observed in all cases. The peak ~232 nm is associated with $\pi \rightarrow \pi^*$ transition whereas peak at ~295 nm corresponds to $n \rightarrow \pi^*$ transition. The d-d transitions ~400 nm are not properly appeared in those complexes [17]. The $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{S})$ vibrations are most important in this metal complexes for determining the mode of coordination of ligand to metal ion. The IR spectra of **L** and corresponding metal complex **1**, **2** and **3** are shown in Fig. 4, 5, 6 and 7 respectively. The C=N stretching vibration occurs at 1650 cm⁻¹ in free ligand. Another important band appeared from 1052 cm⁻¹ to 1097 cm⁻¹ which are assigned to the C=S stretching vibration. The vibration of C=N groups is shifted to the lower frequency of 1589 cm⁻¹, 1556 cm⁻¹ and 1566 cm⁻¹ for complex **1**, **2** and **3** respectively. Other bands are also slightly displaced higher to lower from their previous position with respect to ligand. These shifting support the evidence of coordination of N and S atoms with the metal ions. They are further coordinated as M-N at 559 cm⁻¹, 550 cm⁻¹ and 581 cm⁻¹ for complex **1**, **2** and **3** respectively to represent the metal-nitrogen linkage. Similarly bands at 517 cm⁻¹, 494 cm⁻¹ and 513 cm⁻¹ for complex **1**, **2** and **3** respectively illustrates the diagnostic peak of metal-sulfur linkage in the Schiff base metal complexes [18–20].

The magnetic moment (μ_{eff}) measurements were carried out to get an idea about complexes structure. The observed values of effective magnetic moment of the complexes at room temperature are suggested that the **1**, **2** and **3** complexes are paramagnetic. The magnetic moment value indicate the tetrahedral structure of complex **1** and square planer structure of complex **2** and **3**.

The thermal properties of complex **1**, **2** and **3** were carried out by TGA and DTA under N₂ gas condition from room temperature to 400 °C under 5 °C/min scan rate. The thermogram of complex **1**, **2** and **3** are shown in Fig. 8, 9 and 10 respectively. In Fig. 8, the TGA curve shows a small decrease weight below 150

°C associated with the removal of moisture from the complex which reflects by the two endothermic peaks at 74 °C and 125 °C in the DTA curve. Then the large weight loss of 63% at the temperature range 175 °C to 400 °C corresponds to the removal of a ligand and =N-NH-CS-CH₂-Ph unit, which is accompanied by an endothermic peak at 280 °C and an exothermic peak at 330 °C in the DTA curve. Similar type of TGA-DTA patterns are observed for the complex **2** and **3**. In the complex **2** and **3**, there are also observed a very small weight loss of 2-3% which is attributed to the removal of adsorbed moisture from the complexes and DTA curve showed two endothermic peaks at 74 °C and 125 °C. The complex **2** and **3** show major weight loss (about 65%) in the same temperature range of 175 °C to 400 °C responsible for the removal of a ligand and =N-NH-CS-CH₂-Ph unit from the complexes. This is accorded by an endothermic peak (270 °C for complex **2** and 285 °C for complex **3**) and an exothermic peak (325 °C for complex **2** and 337 °C for complex **3**) in the DTA curves [21–24].

The electrochemical behavior of complex **1**, **2** and **3** was investigated by cyclic voltammetry analysis in DMF with 0.1 M TBAPF₆ at scan rate 0.1 Vs⁻¹ under N₂ atmosphere and shown in Fig. 11, 12 and 13 respectively. In the negative region of Fig. 11 the cyclic voltammogram of complex **1** shows quasi-reversible peak at E_{pc} = -0.69V for Ni(II) → Ni(I) with associated E_{pa} = 0.53V for Ni(II) → Ni(III). The ΔE_p value is 160 mV and the ratio of the values of I_{pc} and I_{pa} is not equal to unit value. The separation of peak potentials indicates two electron transfers in this redox system. Due to the transfer of unequal number of electron, complex **2** and **3** shows irreversible peak character in their cyclic voltammogram [16,25].

Antibacterial activity of **L** and corresponding complexes were assed against two Gram-positive (*B. Cereus* and *B. Subtilis*) and one Gram-negative (*E. Coli*) by disc agar diffusion method [25]. Kanamycin K-30 was used as reference drug. The results were assessed by zone of inhibition in mm (table-1) and measurement of MIC (table-2). The Complex **1** and Complex **2** showed significant zone of inhibition at 16mm and 12mm respectively with gram positive *B. Cereus* at the dose of 256mg/mL, whereas the standard drug Kanamycin showed zone of inhibition at 30mm at the dose of 512mg/mL. Also, in case of the bacteria *B. Subtilis* with same dose only complex **1** showed good zone of inhibition at 11mm at the dose of 256mg/mL.

But in case of the gram negative bacteria *E. Coli* the complex **3** and **L** no zone of inhibition, whereas the standard drug Kanamycin showed zone of inhibition at 30mm at the dose of 512mg/mL. According to

Table 1. Antibacterial activity of Benzyl-2-((1E,4E)-1,5-diphenylpenta-1,4-dien-3-ylidene(L), Complex 1, Complex 2 and Complex 3.

Complexes	Compounds	Zone of inhibition, mm		
		Gram (+ve) bacteria		Gram (-ve) bacteria
		<i>B. cereus</i>	<i>B. subtilis</i>	<i>E. coli</i>
	Benzyl-2-((1E,4E)-1,5-diphenylpenta-1,4-dien-3-ylidene (L)	5	6	-
Complex 1	[Ni ^{II} L ₂]	16	11	9
Complex 2	[Cu ^{II} L ₂]	12	8	6
Complex 3	[Co ^{II} L ₂]	7	6	-
	<i>Kanamycin</i> K-30 disc	30	30	30

Table 2. Minimum inhibitory concentration (MIC) of Benzyl-2-((1E,4E)-1,5-diphenylpenta-1,4-dien-3-ylidene (L), Complex 1, Complex 2 and Complex 3.

Complexes	Compounds	MIC, µg/mL		
		Gram (+ ve) bacteria		Gram (-ve) bacteria
		For <i>B. cereus</i>	For <i>B. subtilis</i>	For <i>E. coli</i>
	Benzyl-2-((1E,4E)-1,5-diphenylpenta-1,4-dien-3-ylidene(L)	512	512	512
Complex 1	[Ni ^{II} L ₂]	256	256	256
Complex 2	[Cu ^{II} L ₂]	256	256	256
Complex 3	[Co ^{II} L ₂]	256	256	256
	<i>Kanamycin</i> K-30 disc	512	512	512

accumulated data **L** and complex **3** shown poor activities against *B. Cereus* and *B. Subtilis*, while no activity against *E. Coli*. The complex **1** exhibited moderate activity against *B. cereus* and *B. Subtilis*. Complex **2** exhibited medium activity against *B. cereus*. In these experiments metal complexes were found to have prominent inhibitory property against several pathogenic microbial species related to standard drug *Kanamycin*. It is noticeable that the complexes except Complex **3** exhibited more active than the corresponding ligand for the antibacterial activities against *B. cereus*, *B. subtilis* and *E. coli*.

Conclusions

In summary, we have described synthesis, characterization and antibacterial activity of a new

Schiff base ligand and corresponding metal complexes. The spectroscopic analyses suggested, that the three metal complexes are followed four coordinated geometry. Complex **1** form tetrahedral and complex **2** and **3** are square planer structure. The antibacterial tests indicate that complex **1** is more active against *B. Cereus* and *B. Subtilis* than complex **2**, complex **3** and ligand.

Conflicts of Interest

The authors declare no conflict of interests.

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References

1. El-Shafiey Z.A., Synthesis, spectroscopic characterization, thermal investigation and antimicrobial activity of S, O and N-donor heterocyclic Schiff base ligands and their Co(II), Cd(II), Hg(II), Fe(III) and UO₂(II) metal complexes. *Egyptian Journal of Chemistry*, **53**(1), 137–162 (2010).
2. Zangrando E., Islam M. T., Al-Amin A. A., Sheikh M. C., Tarafder M. T. H., Miyatake R., Zahan R. and Hossain M. A., Synthesis, characterization and bio-activity of nickel(II) and copper(II) complexes of a bidentate NS Schiff base of S-benzyl dithiocarbamate, *Inorganica Chimica Acta*, **427**, 278–284 (2015).
3. Ghosh P., Dey S.K., Ara M.H., Karim K.M.R., Islam A.B.M.N., A review on synthesis and versatile applications of some selected Schiff bases with their transition metal complexes. *Egyptian Journal of Chemistry*, **63**(Special issue, Part 2), 523–547 (2020).
4. Sayed M. A., Gehad G. M., Zayed M. A., Mohsen S. A. El-Ela, Spectroscopic study of molecular structures of novel Schiff base derived from o-phthaldehyde and 2-aminophenol and its coordination compounds together with their biological activity. *Spectrochimica Acta part A: Molecular and Biomolecular Spectroscopy*, **73**(5), 833–840 (2009).
5. Farhan M. E., Assy M.G., Heterocyclization of Isoniazid: Synthesis and Antimicrobial Activity of Some New Pyrimidine, 1, 3-Thiazole, 1, 2, 4-Thiadiazole, and 1, 2, 4-Triazole Derivatives Derived from Isoniazid. *Egyptian Journal of Chemistry*, **62**(2), 171 - 180 (2019).
6. Yousif M.N.M., Fayed A.A., Yousif N. M., Synthesis, Reactions, and Antimicrobial Activity of N-Hydroxy-triacetonamine Derivatives. *Egyptian Journal of Chemistry*, **62**(8), 1359 - 1366 (2019).
7. Chand S., Tyagi M., Tyagi P., Chandra S., Sharma D., Synthesis, Characterization, DFT of Novel, Symmetrical, N/O-donor Tetradentate Schiff's base, Its Co(II), Ni(II), Cu(II), Zn(II) Complexes and Their in-vitro Human Pathogenic Antibacterial Activity. *Egyptian Journal of Chemistry*, **62**(2), 291 - 310 (2019).
8. Aldelfy z., Shamkani z., Assadi M., 2-Hydroxybenzylidene-4-(4-SubstitutedPhenyl)-2-amino Thiazole and Their Pt (II) Complexes: Synthesis, Characterization and Biological Study. *Egyptian Journal of Chemistry*, **62**(10), 1851 - 1867(2019).
9. Shearer J. M., Rokita S. E., Diamine preparation for synthesis of a water soluble Ni(II) salen complex. *Bioorganic & Medicinal Chemistry Letters*, **9**, 501–504 (1999).
10. Singh K., Barwa M. S., Tyagi P., Synthesis, Characterization and biological studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes with bidentate Schiff bases derived by heterocyclic ketone. *European Journal of Medicinal Chemistry*, **41**, 147–153 (2006).
11. Jin X. D., Xu C., Yin X. Y., Wang H. B., Zou Z. Y., Liu D. L., Ge C. H., Chang X. H., and Jin, Y. H., Synthesis, characterization, and antibacterial activity of two zinc(II) complexes with Schiff bases derived from rimantadine. *Russian Journal of Coordination Chemistry*, **40**(6), 371–378 (2014).
12. Xu Y., Xue L, and Wang Z. G., Synthesis, X-ray crystal structures, and antibacterial activities of Schiff base nickel(II) complexes with similar tetradentate Schiff bases. *Russian Journal of Coordination Chemistry*, **43**(5), 314–319 (2017).
13. Dalia S. A., Afsan F., Hossain S., Mannan A., Haque M. M. and Zahan K. M., Synthesis, spectral and thermal characterization of selected metal complexes containing Schiff base ligands with antimicrobial activities. *Asian Journal of Chemical Sciences*, **4**(3), 1–19 (2018).
14. Abou-Melha K. S., Transition metal complexes of isonicotinic acid (2-hydroxybenzylidene) hydrazide. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **70**(1), 162–170 (2008).
15. Ali M. A., and Tarafder M. T. H., Metal complexes of Sulphur and nitrogen-containing ligands: complexes of S-benzylidithiocarbamate and a Schiff base formed by its condensation with pyridine-2-carboxaldehyde. *Journal of Inorganic Nuclear Chemistry*, **39**, 1785–1791 (1977).
16. Jin X. D., Wang W. C., and Feng X. X., Synthesis, characterization, crystal structure, and electrochemical property of copper(II) complexes with Schiff bases derived from 5-halogenated salicylaldehyde and amantadine. *Russian Journal of Coordination Chemistry*, **43**(11), 787–794 (2017).
17. Khalil M. M. H., Ismail E. H., Mohamed G. G., Zayed E. M. and Badr A., Synthesis and Characterization of a novel Schiff base metal complexes and their application in determination of iron in different types of natural water. *Open Journal of Inorganic Chemistry*, **2**, 13–21 (2012).

18. Tarafder M. T. H., Miah M. A. J., and Bose, R. N., Metral complexes of some Schiff bases derived from S-benzylthiocarbamate. *Journal of Inorganic Nuclear Chemistry*, **43**(12) 3151–3157 (1981).
19. El-Behery M., and Ei-Twigry H., Synthesis, magnetic, spectral, and antimicrobial studies of Cu(II), Ni(II) Co(II), Fe(III), and UO₂(II) complexes of a new Schiff base hydrazone derived from 7-chloro-4-hydrazinoquinoline. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **66**(1), 28–36 (2007).
20. Chen C. L., Zhu X. F., Li M. X., Guo H. M. and Niu J. Y., Antitumor activity of manganese(II) and cobalt(III) complexes of 2-acetylpyridine schiff bases derived from S-methylthiocarbamate: Synthesis, characterization, and crystal structure of the manganese(II) complex of 2-acetylpyridine S-methylthiocarbamate. *Russian Journal of Coordination Chemistry*, **37**(6), 435–438 (2011).
21. Mohamed G. G., Omar M. M., and Hindy A. M. M., Synthesis, characterization and biological activity of some transition metals with Schiff base derived from 2-thiophene carboxaldehyde and aminobenzoic acid. *Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy*. **62**(4), 1140–1150 (2005).
22. Ei-Tabl A. S., El-Saied F. A., and Plass W., Synthesis, spectroscopic characterization and biological activity of the metal complexes of the Schiff base derived from phenylaminoacetohydrazide and dibenzoylmethane. *Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy*, **71**(1), 90–99 (2007).
23. Bera P., Kim C. H., and Seok S. I., Synthesis, spectroscopy and thermal behavior of new lead(II) complexes derived from S-methyl/benzylthiocarbamates (SMDTC/SBDTC): X-ray crystal structure of [Pb(SMDTC)(NO₃)₂]. *Inorganica Chimica Acta*, **362**(8), 2603–2608 (2009).
24. Mishra L., Prajapati R., and Pandey K. K., Mixed-ligand Ru(II) complexes with 2,2'-bipyridine and tetradentate Schiff bases auxiliary ligands: Synthesis, physico-chemical study, DFT analysis, electrochemical and Na⁺ binding properties. *Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy*, **70**(1), 79–85 (2007).
25. Raghavender M., Shankar B., Jalapathi P. and Perugu S., Synthesis, Antibacterial Activity, and Cytotoxicity of Newly Synthesized N-Substituted 5,6-Dimethoxy-1*H*-indole Derivatives. *Russian Journal of General Chemistry*, **89**(7), 1496–1501 (2019).