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Original scientific paper

Spectral, NLO and antimicrobial studies of Co(II), Ni(II) and Cu(II) complexes of Schiff base ligands of 2-amino-6-nitrobenzothiazole

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Abstract: Novel series of Co(II), Ni(II) and Cu(II) transition metal complexes were synthesized from the Schiff base ligands **HL**¹–**HL**⁴ derived from 2-amino-6-nitrobenzothiazole with various aromatic aldehydes, *i.e.*, 4-methylbenzaldehyde, 4-ethylbenzaldehyde, 2-hydroxybenzaldehyde and 4-hydroxybenzaldehyde, respectively. The ligands **HL**¹–**HL**⁴ and their metal (II) complexes were characterized by atomic absorption spectroscopy (AAS), magnetic susceptibility and molar conductance measurements, and UV–Vis, FT-IR and NMR spectroscopic techniques. The spectroscopic studies revealed that the complexes of **HL**¹–**HL**³ coordinated in an octahedral environment and **L**⁴ in square planar/tetrahedral geometry. The ligands **HL**¹–**HL**⁴ and their metal(II) complexes were screened for their antimicrobial activities against *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa* and *Candida albicans*. The results suggest that the complexes of **HL**⁴ possess greater inhibition activity towards *C. albicans*. The nonlinear optics (NLO) activities of ligands **HL**¹–**HL**⁴ were determined. The obtained results showed that ligands **HL**¹ and **HL**² have greater second harmonic generation (SHG) efficiency than **HL**³ and **HL**⁴.

Keywords: aldehydes; metal(II) complexes; spectroscopic; AAS; biological activity.

INTRODUCTION

In the last five decades, Schiff bases have emerged as the most preferred compounds in the field of coordination chemistry and medicinal chemistry. The azomethine group of Schiff bases makes it a potential donor for the formation of complexes. Besides the chelating ability of Schiff bases of heterocyclic com-

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pounds containing 5- and 6-membered rings, they also find potential applications in the field of therapeutics.¹ Benzothiazole is a privileged bicyclic ring system with significant biological properties, such as antimicrobial^{2–5} and anticancer.⁶ Transition metal complexes of Schiff bases of 2-amino-6-nitrobenzothiazole enabled a study of the different ligation behaviors of Schiff bases. In this respect, a structure activity relationship may also be studied. In recent years, organic materials have been studied for their nonlinear optical (NLO) properties, which are of use in optical communications. A large number of organic compounds have been tested for their NLO property in order to design effective communication materials.⁷ In this context, the synthesis of the Schiff bases of 2-amino 6-nitrobenzothiazole with various aromatic aldehydes and also of the corresponding Co(II), Ni(II) and Cu(II) metal complexes are reported. The antimicrobial activity and NLO property of the synthesized compounds are compared.

EXPERIMENTAL

All the chemicals used in the present work, *viz.* 2-amino-6-nitrobenzothiazole, 4-methylbenzaldehyde, 4-ethylbenzaldehyde, 4-hydroxybenzaldehyde, 2-hydroxybenzaldehyde, and cobalt(II), nickel(II) and copper(II) chlorides were of analytical reagent grade. Commercial solvents were distilled and then used for the preparation of the ligands and metal(II) complexes. Elemental analyses and ESI-MS were performed at SAIF, CSIR-CDRI-Lucknow, India. Molar conductivities in DMSO (10^{-3} mol dm⁻³) were measured at room temperature on an ELICO CM-180 digital conductivity meter. Magnetic susceptibility measurements of the complexes were realized on a Gouy balance using copper sulfate pentahydrate as the calibrant. The IR spectra were recorded on a Shimadzu FT-IR IR Affinity-1 spectrophotometer in the 4000–400 cm⁻¹ range using KBr pellets. The NMR spectra were recorded on a Bruker DRX – 300 MHz NMR spectrometer in DMSO-*d*₆ and CDCl₃ as solvents with tetramethylsilane (TMS) as the internal reference. The absorption spectra were recorded using a Shimadzu UV-1800 spectrophotometer between 200–1100 nm by using a suitable solvent. The SHG (second harmonic generation) conversion efficiency of the ligands was determined by a modified version of powder technique in IISC, Bangalore, India.

Synthesis of ligands HL¹–HL⁴

An ethanolic solution (30 mL) of 2-amino-6-nitrobenzothiazole (0.050 mol) was mixed with ethanolic solution (20 mL) of aldehyde (0.050 mol; 4-methylbenzaldehyde, 4-ethylbenzaldehyde, 4-hydroxybenzaldehyde and 2-hydroxybenzaldehyde) and the mixture was stirred. Completion of the reaction was monitored by TLC. The precipitated yellow colored Schiff bases were filtered, washed and dried. The scheme of the synthesis is shown in Fig. 1.

Synthesis of metal(II) complexes

All the complexes were prepared from hydrated metal salts. To a solution of 20 mmol of Schiff bases (**HL¹–HL⁴**) in 25 mL ethanol was added to 10 mmol of MCl₂·*n*H₂O (M = Co(II), Ni(II) or Cu(II); *n* = 6, 6 and 2, respectively). The solution was stirred for 2 h and the resulting solid product was filtered, washed with ethanol and dried under vacuum.

Estimation of percentage of metal

The percentage of metal in the complexes was estimated by atomic absorption spectroscopy at the BSR Laboratory, Jayaraj Annackiam College for Women, India. A complex (5

mg) was dissolved in 2 mL of DMSO and the solution is made up to 50 mL with double distilled (DD) water. Standard solutions (1000, 100, 10 and 1 ppm, respectively) of metal salts of cobalt, nickel and copper were prepared in DD water. Different metal filters were used for running the analysis for estimation. Comparing with the amount of metal ion present in the standard solutions, the amount of metal ion in the metal complexes was estimated graphically.

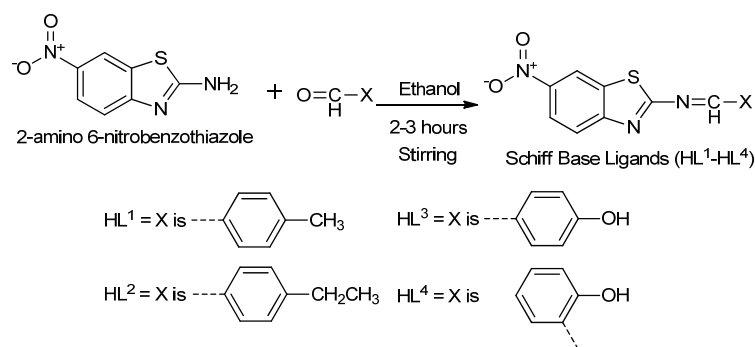


Fig. 1. Scheme of the synthesis of ligands **HL¹-HL⁴**.

Antimicrobial activity screening

Antimicrobial activity of the compounds was tested *in vitro* by the well diffusion method⁸ against the bacteria *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa* using agar nutrient as the medium. Antifungal activity was evaluated against *Candida albicans* cultured on potato dextrose agar as medium. All the mentioned bacterial strains were incubated in nutrient broth (NB) at 37 °C for 24 h and fungal isolate was incubated in PDA broth at 28 °C for 2 to 3 days. Wells each of 5 mm in diameter were made in Muller-Hinton agar using a cork borer. The test solution was prepared at 10⁻³ mol L⁻¹ concentration in DMSO and then 100 μL of the solution was transferred into each well. The plates were incubated for 24 h at 37 °C and examined for a clear inhibition zone around the well. Standard drugs ampicillin and ketoconazole were used for antibacterial and antifungal testing, respectively.

NLO properties of ligands **HL¹-HL⁴**

In a nonlinear process, the oscillation of electrons becomes inharmonic and the re-emitted light may differ in frequency and amplitude from the incident light. Inorganic materials have dominated the field of NLO, for example, lithium niobate (LiNbO₃) has been used for electro-optic modulation.⁹ In organic materials, electrons are more accessible and NLO-effects arise from the interaction between light and electrons within individual molecular units. Especially, organic structures with large delocalized π-systems have proven to be useful. The reason for this is that π-electrons are more easily affected by an external optical field as they are relatively loosely bound to the nucleus, and that the delocalized orbitals may extend over the entire molecule enabling large and fast polarization.^{10,11} In the present work, the second harmonic generation (SHG) efficiency of the ligands was determined by a modified version of the powder technique developed by Kurtz and Perry.¹² The efficiency of the sample was compared with microcrystalline powder of potassium dihydrogen phosphate (KDP) and urea. The input energy used in this particular setup was 2.2 mJ per pulse.

RESULTS AND DISCUSSION

The Schiff bases **HL**¹–**HL**⁴ were obtained as low melting solids and stored in vacuum desiccators. The ligands form stable complexes in ethanol medium. The percentage of metal in the complexes was estimated by atomic absorption spectroscopy technique. The analytical data of the **HL**¹ to **HL**⁴ and their metal(II) complexes together with their physical properties are given in the Table I. All the ligands coordinate in a bidentate fashion. The metal(II) complexes are partially soluble in ethanol, chloroform and acetonitrile but soluble in polar solvents, such as DMF and DMSO. The low values of conductance in DMSO indicate that the complexes are non-electrolytes.¹³ The estimated percentage data of metal ion (II) in the complexes were in good agreement with the calculated data for a 1:2 (M:L) ratio.

TABLE I Physical characterization and molar conductance of **HL**¹–**HL**⁴ and their metal(II) complexes

Compound	FW / g mol ⁻¹	Calculated (observed) metal content, %	Color	Λ_M / S cm ² mol ⁻¹
HL ¹	297	–	Yellow	–
[Co(HL ¹) ₂ Cl ₂]	723.8	8.14 (7.67)	Light green	07
[Ni(HL ¹) ₂ Cl ₂]	723.6	8.11 (7.62)	Dark green	06
[Cu(HL ¹) ₂ Cl ₂]	728.4	8.72 (8.06)	Brown	07
HL ²	311	–	Yellow	–
[Co(HL ²) ₂ Cl ₂]	751.8	7.83 (7.51)	Green	04
[Ni(HL ²) ₂ Cl ₂]	751.6	7.80 (7.38)	Green	05
[Cu(HL ²) ₂ Cl ₂]	756.4	8.40 (7.92)	Brown	05
HL ³	299	–	Yellow	–
[Co(HL ³) ₂ Cl ₂]	727.8	8.09 (7.81)	Green	09
[Ni(HL ³) ₂ Cl ₂]	727.6	8.06 (7.58)	Dark green	06
[Cu(HL ³) ₂ Cl ₂]	732.4	8.67 (8.12)	Brown	10
HL ⁴	299	–	Yellow	–
[Co(HL ⁴) ₂]	655.5	8.97 (8.44)	Light green	07
[Ni(HL ⁴) ₂]	656.6	8.93 (8.42)	Green	05
[Cu(HL ⁴) ₂]	661.5	9.60 (9.11)	Brown	07

IR spectra

In the IR spectrum of the free ligands (**HL**¹–**HL**⁴) the frequencies at 1653–1649 cm⁻¹ are assigned to the azomethine group ($\nu(\text{CH}=\text{N})$). The bands at 1523–517 cm⁻¹ are attributed to the stretching vibration of the C=N group of the thiazole ring ($\nu(\text{C}=\text{N})$). In the spectra of the metal(II) complexes of **HL**¹–**HL**³, the frequencies at 1653–1649 cm⁻¹ and 1523–1517 cm⁻¹ are shifted to lower values (1651–1504 cm⁻¹ and 1517–1493 cm⁻¹) confirming the coordination of the azomethine nitrogen and ring nitrogen¹⁴ of the benzothiazole group, respectively, to the metal ion. In the spectra of metal(II) complexes of **HL**¹–**HL**⁴, the frequencies at 653–516 cm⁻¹ are assigned to the M–N stretching mode.^{15–17} The

spectrum of the ligand **HL**⁴ shows a band at 3454 cm⁻¹ due to phenolic OH group. The absence of this band in the spectrum of metal(II) complexes evidences the coordination of deprotonated phenolic group to the metal(II) ion. In the spectra of the metal(II) complexes of **HL**⁴, the stretching frequencies at 712–742 cm⁻¹ are assigned to M–O vibrations.¹⁸

NMR spectra

The ¹H-NMR and ¹³C-NMR data for the Schiff base ligands **HL**¹–**HL**⁴ are given in the Supplementary material to this paper.

Electronic absorption spectra

The UV–Vis spectra of the complexes were recorded in DMSO solution. The copper(II) complexes of **HL**¹–**HL**³ exhibit a d–d band in the region 10000–9267 cm⁻¹. This band may be assigned to a ²B_{1g}→²A_{1g} transition, characteristic for a distorted octahedral structure.¹⁹ In addition, the complexes of Co(II) and Ni(II) exhibited two bands at 14684 and 16977 cm⁻¹ and at 9354 and 10405 cm⁻¹, assigned to ⁴T_{1g}(F)→⁴A_{2g}(F), ⁴T_{1g}(F)→⁴T_{2g}(F) and ³A_{2g}(F)→³T_{2g}(F), ³A_{2g}(F)→³T_{1g}(F) transitions, respectively, suggesting octahedral coordination. The copper(II) complex of **HL**⁴ shows a band at 12650 cm⁻¹, assignable to a ²B_{1g}→²A_{1g} transition, characteristic for a distorted square–planar geometry.²⁰ The electronic spectrum of cobalt(II) complex of **HL**⁴ shows band at 15,880 cm⁻¹, which may be tentatively assigned to a ⁴A₂(F)→⁴T₁(P) transition for tetrahedral geometry.²¹ The nickel(II) complex exhibits an absorption band at 13897 cm⁻¹ due to a ³T₁(F)→³T₁(P) transition, corresponding to tetrahedral geometry.

Magnetic moments of metal(II) complexes

Magnetic susceptibility measurements gave sufficient data to characterize the structure of the metal complexes. Magnetic moment measurements of compounds were performed at 25 °C. The magnetic moment values of the copper(II) complex of **HL**⁴ was 1.75 μ_B, suggesting a square planar environment.²² The tetrahedral structure of the nickel(II) complex of **HL**⁴ was evidenced by the magnetic moment value 2.81 μ_B. The magnetic moment value of cobalt(II) complex of **HL**⁴ was 4.35 μ_B, suggesting a tetrahedral structure. The high spin nature and the octahedral structure of cobalt(II) complexes of **HL**¹–**HL**³ was further evidenced by the magnetic moment values of 4.79–5.40 μ_B. The magnetic moment values of the copper(II) complexes of **HL**¹–**HL**³ were in the range 1.81–2.08 μ_B, indicating octahedral coordination. That the magnetic moment values were higher than the spin only value (1.73 μ_B) might be due to an orbital contribution. The octahedral structure of the nickel(II) complexes of **HL**¹–**HL**³ was further supported by the magnetic moment values 3.05–3.10 μ_B.²² Based on the above discussion, the proposed structures of the complexes are shown in Fig. 2.

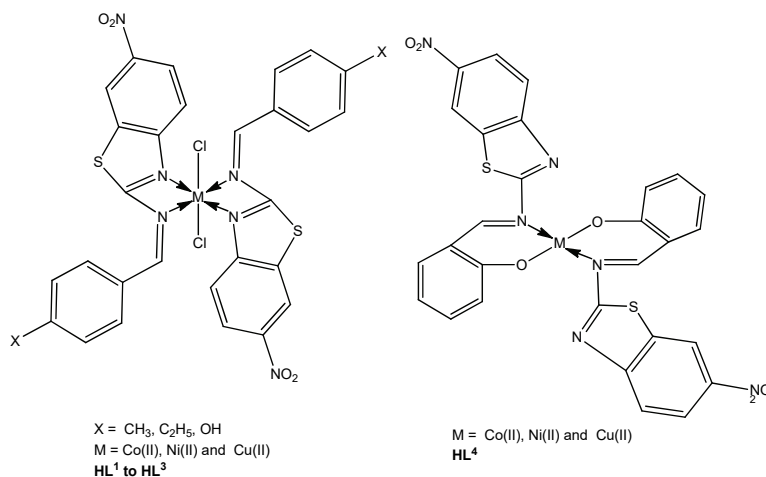


Fig. 2. Proposed geometry of the complexes.

Antimicrobial screening

The ligands and the complexes exhibited antifungal activity. From the zone of inhibition, it was shown that some of the ligands and complexes have very low inhibition activity towards *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Candida albicans*. Some of the metal complexes were found to be more potent than the ligands against bacterial and fungal strains. The different substituents in the Schiff bases had very low effects on the antimicrobial activity. The metal complexes of **HL²** exhibited no antifungal activity. The data showing the zone of inhibition are given in the Table II. It is observed that, in a

TABLE II. Antimicrobial activity data of **HL¹–HL⁴** and their metal(II) complexes (zone of inhibition in mm); R = resistant

Compound	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>S. aureus</i>	<i>C. albicans</i>
HL¹	4	5	3	10
[Co(HL¹) ₂ Cl ₂]	R	R	R	11
[Ni(HL¹) ₂ Cl ₂]	R	R	12	R
[Cu(HL¹) ₂ Cl ₂]	R	10	12	12
HL²	R	R	R	R
[Co(HL²) ₂ Cl ₂]	R	10	R	R
[Ni(HL²) ₂ Cl ₂]	R	R	R	R
[Cu(HL²) ₂ Cl ₂]	R	R	R	10
HL³	R	R	12	12
[Co(HL³) ₂ Cl ₂]	10	12	R	11
[Ni(HL³) ₂ Cl ₂]	8	R	R	14
[Cu(HL³) ₂ Cl ₂]	R	12	10	14
HL⁴	R	R	12	12
[Co(HL⁴) ₂]	10	12	R	14
[Ni(HL⁴) ₂]	8	R	R	14
[Cu(HL⁴) ₂]	R	12	14	14

complex, the positive charge of the metal is partially shared with the donor atoms present in the ligand and there may be π -electron delocalization over all the chelating system.^{23,24} This increases the lipophilic character of the metal chelate and favors its permeation through the lipid layer of the bacterial membranes. So the metal complex could become more active than the free ligand. Therefore, the metal complexes showed greater antifungal activities than the uncoordinated ligand and free metal ion.

The bacterial strains are resistant towards the alkyl substituted ligands **HL**¹ and **HL**² and their metal complexes. The activity may be related to the length of carbon chain²⁵ present and they do not show an appreciable antifungal activity. The hydroxyl-substituted ligands **HL**³ and **HL**⁴ showed a moderate antibacterial and antifungal activity. From SAR studies, it is known that electron withdrawing groups increase the antibacterial activity and this supports the resistant nature of all the ligands and complexes towards most of the antibacterial strains.²⁶ Although the ligand contains the nitro group in the aromatic ring that is electron withdrawing group, the antimicrobial activity was suppressed due to electron releasing groups, such as alkyl and hydroxyl groups. The solubility of the compound, type of the strain and the coordinating nature of the Schiff base determine the inhibition activity. The hydrogen bonding ability²⁷ of the azomethine group with the microbial strain may improve the antimicrobial activity of the synthesized compounds. In this regard, the complexes of **HL**³ and **HL**⁴ with a hydroxyl group showed better inhibition compared to the metal complexes of **HL**¹ and **HL**².

Some of the complexes were inactive against *E. coli*, which may be due to the bulkiness of the complexes.²

NLO activity

The synthesized ligands possess NLO properties. The methyl-substituted ligands (**HL**¹ and **HL**²) show greater *SHG* efficiency than the hydroxyl-substituted ligands. The more pronounced electron donating nature of alkyl groups makes ligands more polarized and show enhanced NLO activity.²⁸ The ligand **HL**³ is more NLO active than **HL**⁴, due to the *para* position of the hydroxyl group. The *SHG* efficiency was found to be lower when compared with urea and KDP.²⁹⁻³¹ The activity data is given in Table III.

TABLE III. NLO properties of the ligands

Ligand	<i>SHG</i> efficiency, %, with respect to	
	KDP	Urea
HL ¹	15	8
HL ²	20	10
HL ³	14	6
HL ⁴	13	5

CONCLUSIONS

In this work, transition metal(II) complexes of Schiff bases of 2-amino-6-nitrobenzothiazole were synthesized and characterized. The ligands and their metal complexes were studied by various physical and chemical techniques, *i.e.*, metal estimation by AAS, UV-Vis, ¹H-NMR and IR. All the synthesized ligands and complexes were screened for their antimicrobial activity. All the metal (Co(II), Ni(II) and Cu(II)) complexes of the synthesized ligands **HL**¹–**HL**³ show octahedral geometry. Distorted square planar geometry is proposed for the copper complex of **HL**⁴. The other complexes of **HL**⁴ coordinate in a tetrahedral fashion. Ligands and complexes possess lower antimicrobial activity than the standard drugs. The synthesized compounds possess very small antibacterial activity and appreciable antifungal activity. All the ligands were found to possess NLO activity. The alkyl-substituted Schiff bases (**HL**¹ and **HL**²) have greater SHG efficiency than the hydroxyl substituted Schiff bases **HL**³ and **HL**⁴.

SUPPLEMENTARY MATERIAL

Characterization data of the ligands and complexes are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/> or from the corresponding author on request.

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ИЗВОД

СПЕКТРОСКОПСКА, NLO И АНТИМИКРОБНА ИСПИТИВАЊА Co(II), Ni(II) И Cu(II)
КОМПЛЕКСА СА ШИФОВИМ БАЗАМА 2-АМИНО-6-НИТРОБЕНЗОТИАЗОЛА
КАО ЛИГАНДИМА

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Синтетисана је нова серија комплекса прелазних метала, Co(II), Ni(II) и Cu(II), са Шифовим базама као лигандима (**HL**¹–**HL**⁴) који су добијени из 2-амино-6-нитробензотиазола и различитих ароматичних алдехида, као што су 4-метилбензалдехид, 4-етилбензалдехид, 2-хидроксибензалдехид и 4-хидроксибензалдехид. Лиганди (**HL**¹–**HL**⁴) и њихови комплекси су окарактерисани помоћу AAS, мерења магнетне и моларне проводљивости, као и UV-Vis, FT-IR и NMR спектроскопских техника. На основу спектроскопских испитивања нађено је да лиганди **HL**¹–**HL**⁴ граде комплексе октаедарске геометрије, док у случају **HL**⁴ лиганда настају комплекси који имају и квадратно-планарну, односно тетраедарску геометрију. Лиганди **HL**¹–**HL**⁴ и одговарајући метал(II)-комплекси су испитивани на антимикробну активност према микроорганизмима *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa* и *Candida albicans*. Добијени резултати ових испитивања су показали да комплекси са

лигандом **HL**⁴ показују већу инхибиторску активност према *C. albicans*. Одређена је NLO активност лиганата **HL**¹–**HL**⁴. Добијени резултати су 11 показали да је у случају лиганата **HL**¹ и **HL**² SHG ефикасност већа у односу на лиганде **HL**³ и **HL**⁴.

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