**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:* A novel series of transition metal complexes of Co(II), Ni(II) and Cu(II) were synthesized from the Schiff base ligands (**L1** to **L4**) derived from 2-amino-6-nitrobenzothiazole with various aromatic aldehydes such as 4-methylbenzaldehyde, 4-ethylbenzaldehyde, 2-hydroxybenzaldehyde and 4-hydroxybenzaldehyde. The ligands (**L1** to **L4**) and their metal (II) complexes were characterized by AAS, magnetic susceptibility, molar conductance measurements, UV–Vis, FT-IR and NMR spectroscopic techniques. The spectroscopic studies reveal that complexes of **L1** to **L4**coordinate in an octahedral environment and **L4** in a square planar / tetrahedral geometry. The **L1** to **L4** 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, complexes of **L4**possess greater inhibition activity towards *Candida albicans*. The NLO activity of the ligands **L1** to **L4** was determined. These obtained results show that, ligands (**L1** and **L2**) are found to have more SHG efficiency than **L3** and **L4**.

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

RUNNING TITLE: METAL(II) COMPLEXES OF SCHIFF-BASE LIGANDS

INTRODUCTION

In the last five decades, Schiff bases emerge as the most preferred compounds in the field of coordination chemistry and medicinal chemistry. The azomethine group of Schiff base make it as a potential donor for the formation of complexes. Besides the chelating ability of Schiff bases of heterocyclic compounds containing 5 and 6 membered rings, they also find potential applications in therapeutic field1. Benzothiazole is a privileged bicyclic ring system with significant biological properties such as antimicrobial 2-5 and anticancer6. Transition metal complexes of Schiff bases of 2-amino-6-nitrobenzothiazole give us a way to study the different ligational behavior of Schiff bases. In this respect, the structure activity relationship may also be studied. In recent years organic materials have been studied for non linear optical property which is used in optical communications. A large number of organic compounds have been tested for NLO property in order to design effective communication materials7. In this context, we are interested to report synthesis of the Schiff bases of 2-amino 6-nitrobenzothiazole with various aromatic aldehydes and also Co(II), Ni(II) and Cu(II) metal complexes. The antimicrobial activity and NLO property of the synthesized compounds have been compared.

EXPERIMENTAL

All the chemicals used in the present work, viz 2-amino 6-nitrobenzothiazole 4-methylbenzaldehyde, 4-ethylbenzaldehyde, 4-hydroxybenzaldehyde, 2-hydroxybenzaldehyde, 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. Molar conductivities in DMSO (10-3 mol/dm3) at room temperature were measured on an ELICO CM-180 digital conductivity meter. Magnetic susceptibility measurements of the complexes were realized by a Gouy balance using copper sulfate pentahydrate as the calibrant. The IR spectra were recorded on 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 1H 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 suitable solvent. The SHG (Second Harmonic Generation) conversion efficiency of the ligands was determined by the modified version of powder technique in IISC, Bangalore.

*Synthesis of ligands (****L1*** *to* ***L4****)*

An ethanolic solution of 2-amino 6-nitrobenzothiazole (0.050 mol) was mixed with ethanolic solution of aldehyde (0.050 mol) (4-methyl benzaldehyde, 4-ethyl benzaldehyde, 4-hydroxy benzaldehyde, 2-hydroxy benzaldehyde) and the mixture was stirred. The completion of the reaction mixture was monitored by TLC. The precipitated yellow coloured Schiff bases were filtered, washed and dried. The scheme of the synthesis is shown in Figure. 1.


Fig.1 Scheme of the synthesis of ligands **L1 to L4**

*Synthesis of metal(II) complexes*

All the complexes were prepared from hydrated metal salts. To a solution of 20 mmol of Schiff bases (**L1** to **L4**) in 25 mL ethanol was added to 10 mmol of MCl2.nH2O (M = Co(II), Ni(II) and Cu(II); n = 6, 6 and 2). 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 studies at BSR lab, Jayaraj Annapackiam College for Women. 5 mg of the complex was dissolved in 2 ml of DMSO and the solution is made up to 50 mL with Double Distilled water. Standard solutions (1000 ppm, 100 ppm, 10 ppm and 1 ppm) 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.

*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 bacterial strains mentioned above were incubated in Nutrient Broth (NB) at 37 °C for 24 h and fungal isolates were incubated in PDA broth at 28 °C for 2 to 3 days. The well each of 5 mm in diameter was made in Muller Hinton agar using cork borer. The test solution was prepared in 10-3 moles litre-1 concentration (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 clear inhibition zone around the well. Standard drugs ampicillin and ketokonazole are used for antibacterial and antifungal testing respectively.

*NLO property of Ligands (****L1*** *to* ***L4****)*

In a nonlinear process the oscillation of electrons will become anharmonic and re-emitted light may differ in frequency and amplitude from the incident light. Inorganic materials have been dominated in the field of NLO, for example, lithium niobate (LiNbO3) has been used for electrooptic modulation9. 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 delocalised 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 delocalised orbitals may be extended over the entire molecule giving large and fast polarization10-11. In the present work the SHG (Second Harmonic Generation) efficiency of the ligands was determined by modified version of powder technique developed by Kurtz and Perry 12. The efficiency of the sample was compared with microcrystalline powder of KDP and urea. The input energy used in this particular setup was 2.2 mJ/pulse.

RESULTS AND DISCUSSION

The Schiff bases **L1** to **L4** 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 **L1** to **L4** and their metal(II) complexes together with their physical properties are given in the Table 1. 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-electrolytes13. The estimated percentage data of metal ion (II) in the complexes were in good agreement with the calculated data for the 1:2 (M:L) ratio.

TABLE 1 Physical characterization and molar conductance of the **L1** to **L4** and their metal(II) complexes

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Compounds** | **FW****g/mol-1** | **% of metal calculated****(observed)** | **Color** | **ΛM (mho cm2 mol-1)** |
| **L1** | 297 | - | Yellow | - |
| [Co(L1)2Cl2] | 723.8 | 8.14 (7.67) | Light Green | 07 |
| [Ni(L1)2Cl2] | 723.6 | 8.11 (7.62) | Dark Green | 06 |
| [Cu(L1)2Cl2] | 728.4 | 8.72 (8.06) | Brown | 07 |
| **L2** | 311 | - | Yellow | - |
| [Co(L2)2Cl2] | 751.8 | 7.83 (7.51) | Green | 04 |
| [Ni(L2)2Cl2] | 751.6 | 7.80 (7.38) | Green | 05 |
| [Cu(L2)2Cl2] | 756.4 | 8.40 (7.92) | Brown | 05 |
| **L3** | 299 | - | Yellow | - |
| [Co(L3)2Cl2] | 727.8 | 8.09 (7.81) | Green | 09 |
| [Ni(L3)2Cl2] | 727.6 | 8.06 (7.58) | Dark Green | 06 |
| [Cu(L3)2Cl2] | 732.4 | 8.67 (8.12) | Brown | 10 |
| **L4** | 299 | - | Yellow | - |
| [Co(L4)2] | 655.5 | 8.97 (8.44) | Light Green | 07 |
| [Ni(L4)2 ] | 656.6 | 8.93 (8.42) | Green | 05 |
| [Cu(L4)2] | 661.5 | 9.60 (9.11) | Brown | 07 |

*IR Spectra*

In IR spectrum of the free ligands, (**L1** to **L4**) the frequencies at 1653-1649 cm-1 are assigned to azomethine group (ν (CH=N)). The bands at 1523 -1517 cm-1 are attributed to stretching vibration of C=N group of thiazole ring (ν(C=N)). In the spectra of the metal(II) complexes of **L1** to **L3**the frequencies at 1653-1649 cm-1 and 1523-1517 cm-1 are shifted to lower values (1651 to 1504 cm-1 and 1517-1493 cm-1) confirming the coordination of the azomethine nitrogen and ring nitrogen14 of benzothiazole group respectively to the metal ion. In the spectra of metal (II) complexes **L1** to **L4** the stretching frequencies 653-516 cm-1 are assigned to M-N mode15-17. The spectrum of the ligand **L4** 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 deprotanated phenolic group to the metal(II) ion. In the spectra of metal(II) complexes of **L4**, the stretching frequencies 712-742 cm-1 are assigned to M-O vibrations 18.

NMR *spectra*

1H-NMR (300 MHz, DMSO-d6, δ/ppm) spectra of the Schiff base ligands (**L1**-**L4**) exhibited the following signals: The 1H-NMR spectrra of **L1**: 8.35 ppm (s,1H, azomethine proton), 7.46-6.93 ppm (m, 7H, aromatic protons), 1.63 ppm (s, 3H, methyl protons), **L2**:8.41 (s,1H, azomethine proton), 7.40-6.94 ppm (m, 7H, aromatic protons), 1.89 ppm (q, 2H, methylene protons), 1.63 ppm (t, 3H, methyl protons), **L3**: 8.45 ppm (s,1H, azomethine proton), 7.26-6.95 ppm (m, 7H, aromatic protons), 11.23 ppm (s, phenolic proton), **L4**: 8.40 ppm (s,1H, azomethine proton), 7.36-6.94 ppm ( m, 7H, aromatic protons), 11.34 ppm (s, phenolic proton).

The 13C-NMR (75 MHz, DMSO-d6, δ/ppm) spectra of the Schiff base ligands (**L1**-**L4**) exhibited the following signals: **L1**: δ = 22.3(-CH3), 163 (-N=CH), 175 (-S-C=N-), 121-155 (-C6H5 –S-C=N), **L2** : δ = 14.3(-CH3), 28 (-CH2CH3)  160 (-N=CH-), 129.1-146.6 (-C6H5 ), 174.3 (-S-C=N-), 121-154 (-C6H5 –S-C=N); **L3** : δ = 160 (-N=CH-), 129.1 – 160.6 (-C6H5 ), 174.6 (-S-C=N-), 121.3 – 154.8 (-C**6**H5 –S-C=N); **L4** : δ = 159.5 (-N=CH-), 130 – 160.6 (-C6H5 ), 175.5 (-S-C=N-), 120.3 – 155.0 (-C**6**H5 –S-C=N).

*Electronic absorption spectra*

The UV–Vis spectra of the complexes were recorded in DMSO solution. The copper (II) complexes of **L1**to **L3**exhibit a d–d band in the region 10000-9267 cm-1. This band may be assigned to 2B1g → 2A1g transition, characteristic for a distorted octahedral structure 19. In addition, the complexes of Co(II) and Ni(II) exhibited two bands at 14684 cm-1,16977 cm-1 and 9354 cm-1, 10405 cm-1 assigned to 4T1g(F) → 4A2g(F), 4T1g(F) → 4T2g(F) and 3A2g(F) → 3T2g(F), 3A2g(F) → 3T1g(F) transitions respectively suggesting octahedral coordination. The copper(II) complex of **L4**shows a band at 12650 cm-1 assignable to the 2B1g → 2A1g transition, characteristic for a distorted square-planar geometry20. The electronic spectra of cobalt(II) complex of **L4** shows band at 15,880 cm-1, which may be tentatively assigned to 4A2(F) → 4T1(P) transition for the tetrahedral geometry21. Nickel(II) complex exhibits absorption band at 13897 cm−1 due to 3T1(F) → 3T1(P) transition corresponding to tetrahedral geometry.

*Magnetic moments of metal(II) complexes*

Magnetic susceptibility measurements give sufficient data to characterize the structure of the metal complexes. Magnetic moment measurements of compounds were carried out at 25 °C. The magnetic moment values of copper(II) complex of **L4** is in the range 1.75 BM suggesting square planar environment22. The tetrahedral structure of nickel(II) complex of L4 is evidenced by the magnetic moment value 2.81 BM. The magnetic moment value of cobalt (II) complex of L4 is 4.35 BM suggesting the tetrahedral structure. The high spin nature and the octahedral structure of cobalt(II) complexes of **L1**to **L3** is further evidenced by the magnetic moment values 4.79 -5.40 BM. The magnetic moment values of copper (II) complexes of L1 to **L3** are in the range 1.81 – 2.08 BM indicating the octahedral coordination. The higher magnetic moment value than the spin only value (1.73 BM) might be due to orbital contribution. The octahedral structure of nickel (II) complexes of **L1**to **L3** is further supported by the magnetic moment values 3.05-3.10 BM22. The proposed structures of the complexes are shown in the Figure 2.

On the basis of above discussion the following structures are proposed for the complexes



Fig. 2. Proposed geometry of the complexes

*Antimicrobial screening*

The ligands and the complexes exhibit antifungal activity. From the zone of inhibition it is shown that the some of the ligands and complexes have very less inhibition activity towards *Escherichia coli (E. coli)*, *Staphylococcus aureus (S. aureus), Pseudomonas aeruginosa (P. aeruginosa)* and *Candida albicans (C. albicans)*. Some metal complexes are found to be more potent than the ligands against bacterial and fungal strains. The different substituents in the Schiff bases have very lesser effect in the antimicrobial activity. The metal complexes of **L2** have no antifungal activity. The data showing the zone of inhibition is given in the Table 2. It is observed that, in a 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 the whole chelating system23-24. This increases the lipophilic character of the metal chelate and favors its permeation through the lipoid layer of the bacterial membranes. So the metal complex can become more active than the free ligand. Therefore, the metal complexes show greater antifungal activities than the uncoordinated ligand and free metal ion.

The bacterial strains are resistant towards the alkyl substituted ligands **L1** and **L2** and their metal complexes. The activity may be related to the length of carbon chain25 present and they do not show a appreciable antifungal activity. The hydroxyl substituted ligands **L3** and **L4** 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 the all ligands and complexes towards most of the antibacterial strains26. Though the ligand contains the nitro group in the aromatic ring which is electron withdrawing group, the antimicrobial activity has been 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 **L3** and **L4** with the hydroxyl group have shown a better inhibition compared to metal complexes of **L1 and L2**

Some of the complexes are resistant towards *E. Coli* and it may be due to the bulkiness of the complexes2

TABLE 2 Antimicrobial activity data of the **L1** to **L4** and metal(II) complexes (Zone of inhibition in mm)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Compounds** | ***E. coli*** | ***P. aeruginosa*** | ***S. aureus*** | ***C. Albicans*** |
| **L1** | 04 | 05 | 03 | 10 |
| [Co(L1)2Cl2] | R | R | - | 11 |
| [Ni(L1)2Cl2] | R | R | 12 | R |
| [Cu(L1)2Cl2] | R | 10 | 12 | 12 |
| **L2** | R | R | R | R |
| [Co(L2)2Cl2] | R | 10 | - | R |
| [Ni(L2)2Cl2] | R | R | R | R |
| [Cu(L2)2Cl2] | R | R | R | 10 |
| **L3** | R | R | 12 | 12 |
| [Co(L3)2Cl2] | 10 | 12 | R | 11 |
| [Ni(L3)2Cl2] | 8 | R | R | 14 |
| [Cu(L3)2Cl2] | R | 12 | 10 | 14 |
| **L4** | R | R | 12 | 12 |
| [Co( L4)2] | 10 | 12 | R | 14 |
| [Ni(L4)2] | 8 | R | R | 14 |
| [Cu( L4)2] | R | 12 | 14 | 14 |
| R = Resistant towards inhibition activity |

*NLO activity*

The synthesized ligands possess NLO property. Methyl substituted ligands (**L1** and **L2**) show more SHG efficiency than the hydroxyl substituted ligands. The more pronounced electron donating nature of the alkyl groups will make the ligands more polarized and shows enhanced NLO activity28. The ligand **L3** is more NLO active than **L4**, due to the para position of hydroxyl group. The SHG efficiency was found to be less when compared with urea and KDP 29-31. The activity data is given in the Table 3.

TABLE 3. NLO property of ligands

|  |  |
| --- | --- |
| **Ligands** | **SHG Efficiency with respect to** |
| **KDP** | **Urea** |
| **L1** | 15 | 08 |
| **L2** | 20 | 10 |
| **L3** | 14 | 06 |
| **L4** | 13 | 05 |

CONCLUSION

In this work the transition metal(II) complexes of Schiff bases of 2-amino-6-nitrobenzothiazole are synthesized and characterized. The ligands and their metal complexes are studied by various physicochemical techniques such as metal estimation by AAS, UV-vis, 1HNMR and IR. All the synthesized ligands and complexes have been screened for antimicrobial activity. All the metal [Co(II), Ni(II) and Cu(II)] complexes of synthesized ligands (**L1** to **L3**) show octahedral geometry. Distorted square planar geometry is proposed for the copper complex of **L4**. The other complexes of **L4** coordinate in a tetrahedral fashion. Ligands and complexes possess lesser antimicrobial activity than the standard drugs. The synthesized compounds possess very less antibacterial activity and appreciable antifungal activity. All the ligands are found to possess NLO activity. Alkyl substituted Schiff bases **(L1** and **L2**) have more SHG efficiency than the hydroxyl substituted Schiff bases (**L3** and **L4**)

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