

Thermal and Antimicrobial studies of Synthesized and Characterized Rhodium, Platinum and Gold Metal Complexes Derived from (2E) N- (naphthalen-2yl)-3 phenyl prop-2en-1 imine Schiff Base

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Abstract: The derived schiff base (2E) N- (naphthalen-2yl)-3 phenyl prop-2en-1 imine synthesized by condensing (2E)-3-Phenylprop-2-enal and 2-Naphthylamine. The above synthesized Schiff base forms stable coordinated metal complexes, using salts of Rhodium, Platinum and Gold. The synthesized Schiff base and metal complexes were characterized by U.V, FTIR, ¹H-NMR and the percentage of elemental detections were determined by CHNS analyser. The thermal stability of metal complexes were studied using TGA indicating the synthesized metal complexes upto 350-650°C. The characterization study confirms the formation of stable octahedral Rh (III) complex whereas Pt (II) and Au (III) complexes show square planar structures. Further the comparative antimicrobial activities of the Schiff base and corresponding metal complexes have been studied.

Index Terms: Antimicrobial activity, Metal complexes, Schiff bases, Spectral studies and Thermal studies

INTRODUCTION

A large number of study have been published on Schiff base and their metal complexes. In general Schiff bases show very good coordinating ability with the transition metal ions (Singh, J., & Gupta, S. P., 1976), (Acharyya, R., Basuli, F., Rosair, G., & Bhattacharya, S. 2004), (Çukurovali, A., Yilmaz, I., Özmen, H., & Ahmedzade, M. 2002). The variety of studies on transition metal complexes of Schiff bases show interesting properties such as chemical, antimicrobial, analytical as well as physiochemical effects (Singh, N. K., & Singh, S. B., 2001), (Leovac, V. M., Divjakovič, V., Petrovič, D., Argay, G., &

Kālmān, A. 1983). We tried to synthesize, characterized the Rh(III), Pt(II) and Au(III) complexes of Schiff base derived from (2E)-3-Phenylprop-2-enal and 2-Naphthylamine and also studied their biological activities of corresponding metal Schiff base complexes.

EXPERIMENTAL

A. Materials and methods

1) Chemicals

All the chemicals used were of Analytical reagent grade. (2E)-3-Phenylprop-2-enal, 2-Naphthylamine and metal salts were obtained from S.D. fine-Chem. Ltd. Distilled solvents were used throughout the experiments. Purity of the synthesized schiff base and metal complexes were checked by TLC using Merck silica gel plates. The melting points of all the Schiff base compounds were obtained on a VMP-D /DS melting point apparatus. The percentages of C, H & N in Schiff base metal complexes were determined using a Thermo finnigan FLASH EA 1112 series CHN analyzer. The IR spectra were recorded in KBr pellets on Shimadzu IR Prestige 21. UV Visible spectra were recorded with Shimadzu UV1800A spectrophotometer. ECZR Series 600 MHz NMR spectrometer was used for ¹H NMR. Thermal analysis was done using Perkin Elmer 4000. The antimicrobial activity of the Schiff base and their complexes are determined by the zone inhibition method against bacterial strains of Staphylacoccus aureus, Staphylacoccus pyogenes, Escherichia coli and Klebsiella Pneumonia.

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2) *Synthesis of Ligand (HL): (2E) N- (naphthalen-2yl)-3 phenyl prop-2-en-1-imine*

The Schiff base was prepared by condensing equimolar quantities of (2E)-3-Phenylprop-2-enal (1.26 ml) and 2-Naphthylamine (1.43 g). Using two-neck round bottom flask, 25 ml hot alcoholic solution of (2E)-3-Phenylprop-2-enal was slowly added to 25 ml hot alcoholic solution of 2-Naphthylamine. The reaction mixture was then refluxed for five hours in water bath then hot reaction mixture was poured in ice-cold water. The precipitate obtained was filtered, washed with cold water, recrystallized from ethanol and air dried. Its physical

and analytical data is given in (TABLE 1). Graphical abstract of synthesis and structure of Schiff base is given in Fig.1.

3) *Synthesis of Metal Complexes*

a) *Synthesis of Rhodium complex*

Procedure: The metal complex was synthesized by reflux-precipitation method in a two necked round bottom flask. The hot alcoholic solution of Schiff base (HL) (0.001 mol) was mixed with alcoholic solution of with constant stirring. The Rh (III) complex Rh (III) was precipitated at pH =

Table I. Physical, Analytical and Conductivity data of Schiff base and its metal complexes

| Ligand/ Complexes | Colour | M.P. °C | Mol. Wt. gms. | Elemental analysis % Calculated (Found) | | | | | Molar Cond. (Scm ² mol ⁻¹) |
|--|----------------|---------|------------------|--|----------------|----------------|------------------|------------------|---|
| | | | | C | H | N | Cl | Metal | |
| HL | Green | 140°C | 257.12 | 80.69 (79.57) | 5.87 (5.54) | 6.27 (6.32) | - | - | - |
| [Rh(HL)Cl ₃ 2H ₂ O] | Brown | 177°C | 501.62 | 45.45 (45.10) | 3.78 (3.86) | 2.79 (2.92) | 21.03 (21.48) | 20.53 (20.32) | 0.032 |
| [Pt (HL) Cl ₂ H ₂ O] | Brown | 169°C | 540.52 | 42.22 (42.10) | 3.14 (2.98) | 2.59 (2.92) | 12.83 (12.48) | 36.11 (36.32) | 0.020 |
| [Au(HL)Cl ₂ H ₂ O].Cl.H ₂ O | Light Brown | 172°C | 594.51 | 38.25 (32.61) | 3.19 (3.28) | 2.25 (2.29) | 17.83 (17.10) | 32.90 (32.41) | 0.088 |

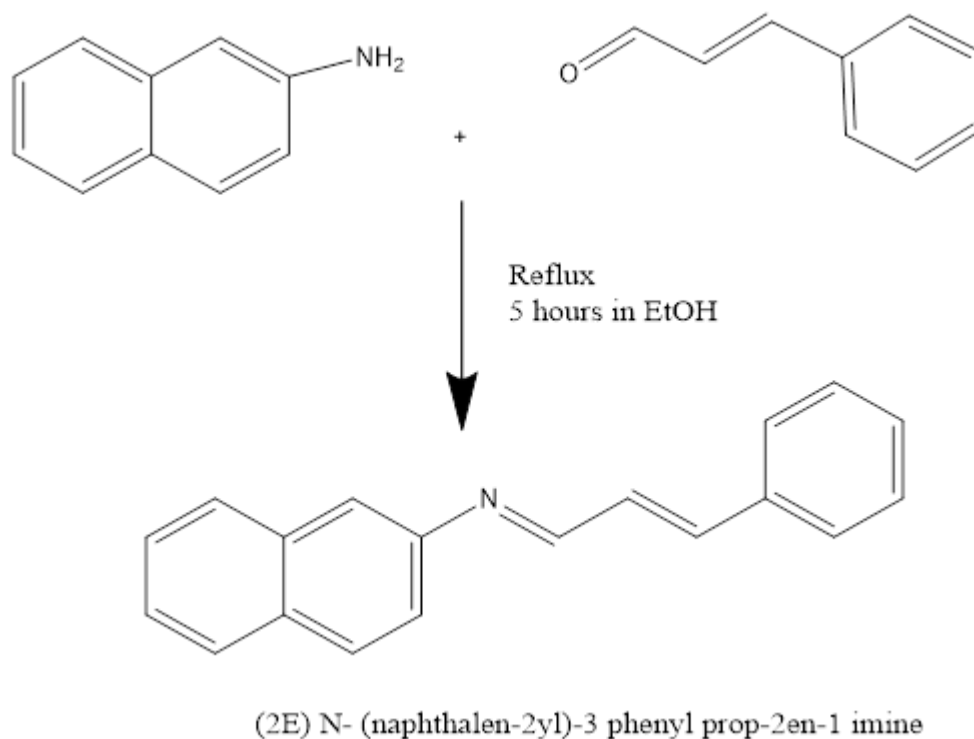


Fig. 1. Graphical Abstract of Synthesis and structure of Schiff Base

8.50 by refluxing an alcoholic solution of Schiff base (0.001 mol) with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.001 mol) for about 6-8 hours. The buff coloured metal complexes separated were filtered, washed with hot water and then with 5% hot ethanol, air dried and melting point recorded.

b) Synthesis of Platinum complex

Procedure: The Pt (II) metal complex was synthesized by reflux-precipitation method in a two necked round bottom flask. The hot alcoholic solution of Schiff base (HL) (0.001 mol) was mixed with an alcoholic solution of K_2PtCl_4 (0.001 mol) with constant stirring. The pH of reaction mixture was adjusted to 3.26. The red coloured precipitate Pt (II) metal complex separated was filtered washed with hot water and then with 5% hot ethanol air dried and melting point was recorded.

c) Synthesis of Gold complex

Procedure: The Gold metal complex was synthesized by reflux-precipitation method in a two necked round bottom flask. The hot alcoholic solution of Schiff base (HL) (0.001 mol) was mixed with an alcoholic solution of $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ (0.001 mol) with constant stirring. The pH of reaction mixture was adjusted to 3.26. The reddish brown coloured Au (III) metal complex precipitated was separated, filtered, washed with hot water and then with 5% hot ethanol, air dried and melting point was recorded.

The physical and analytical data of metal complexes are given in (Table I).

4) Physical Measurements

The melting point of the Schiff base and all metal complexes were determined by open capillary method. Elemental analysis was carried out in the SAIF, IIT Bombay Powai, Mumbai. The solubility of all the complexes was examined by different polar and non-polar solvents. The molar conductivity of ligand and complexes were recorded using 1×10^{-3} M solution in DMSO on Equip-tronics conductivity meter EQ-660A. The electronic absorption spectra of ligand and complexes were recorded in the UV-visible region using DMSO as solvent on UV-1800 PC UV-Vis spectrophotometer. IR spectra were recorded using KBr

pellet on IR-Prestige 21 FTIR. ^1H NMR spectra were carried out at SAIF, IIT Bombay Powai; Mumbai from 600 MHz NMR spectrometer. TGA was carried out at Kirti M. Doongursee College.

RESULT AND DISCUSSION

The Schiff base is synthesized by using equimolar quantities of (2E)-3-Phenylprop-2-enal and 2-Naphthylamine. The metal complexes of Rh (III), Pt (II) and Au (III) were synthesized using 1:1 stoichiometric proportions. The metal complexes derived varied in their colour. All the complexes are air stable, non-hygroscopic, colored solids. The metal complexes are insoluble in water but soluble in DMSO and DMF. All the complexes show very low molar conductance values which indicate that the complexes are non-electrolytic in nature. The physical, analytical and conductivity data of Schiff base and metal complexes are shown in Table I.

A. The I.R. spectral data of the Schiff base and the Metal Complexes

The I.R. spectral data of the Schiff base and the Metal Complexes are recorded in Table No-II A. Schiff base showed a strong absorption band at 1622 cm^{-1} characteristic of $\nu(\text{C}=\text{N})$. The azomethine $\nu(\text{C}=\text{N})$ band at 1622 cm^{-1} in Schiff base is shifted to lower frequency in Rh(III), Pt(II) and Au(III) complexes by 8 cm^{-1} , 10 cm^{-1} and 6 cm^{-1} resp. which indicates the co-ordination of azomethine nitrogen in complexation (V. Chinnusamy & K. Natarajan, 1993) (Agarwal, R. K., Singh, L., & Sharma, D. K. 2006) and (Chinnusamy, V. & Natarajan, K. 1993). The new frequency band observed from $570\text{-}580 \text{ cm}^{-1}$ indicates formation of M-N bond whereas frequency band observed from $315\text{-}330 \text{ cm}^{-1}$ indicates formation of M-X bond.

B. Electronic Spectral Data

Electronic spectrum of ligand showed three high intensity bands at 22676 cm^{-1} , 25543 cm^{-1} and 36095 cm^{-1} indicates $n \rightarrow n^*$ and $\sigma \rightarrow \sigma^*$ transitions.

Table II A. IR Spectral Data of Schiff's Base and Metal Complexes

| Ligand/Complexes | I.R spectral data cm^{-1} | | |
|---|------------------------------------|--------------------------|--------------------------|
| | $\nu(\text{C}=\text{N})$ | $\nu(\text{M}-\text{N})$ | $\nu(\text{M}-\text{X})$ |
| (HL) | 1622 s | ----- | ----- |
| $[\text{Rh}(\text{HL})\text{Cl}_3 \cdot 2\text{H}_2\text{O}]$ | 1614s | 580m | 330m |
| $[\text{Pt}(\text{HL})\text{Cl}_2\text{H}_2\text{O}]$ | 1612s | 570m | 315m |
| $[\text{Au}(\text{HL})\text{Cl}_2\text{H}_2\text{O}]\text{Cl} \cdot \text{H}_2\text{O}$ | 1616s | 576m | 320m |

* s = sharp br = broad m = medium

Table II B. Electronic Spectral Data

| Ligand/Complexes | Electronic spectral data cm^{-1} |
|--|---|
| (HL) | 22676, 25543 and 36095 |
| $[\text{Rh}(\text{HL})\text{Cl}_3\text{H}_2\text{O}]\cdot 2\text{H}_2\text{O}$ | 22675, 27440 and 38867 |
| $[\text{Pt}(\text{HL})\text{Cl}_2]\text{H}_2\text{O}$ | 21420, 25020, 30790 and 35500 |
| $[\text{Au}(\text{HL})\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ | 21076, 25220, 30959 and 34200 |

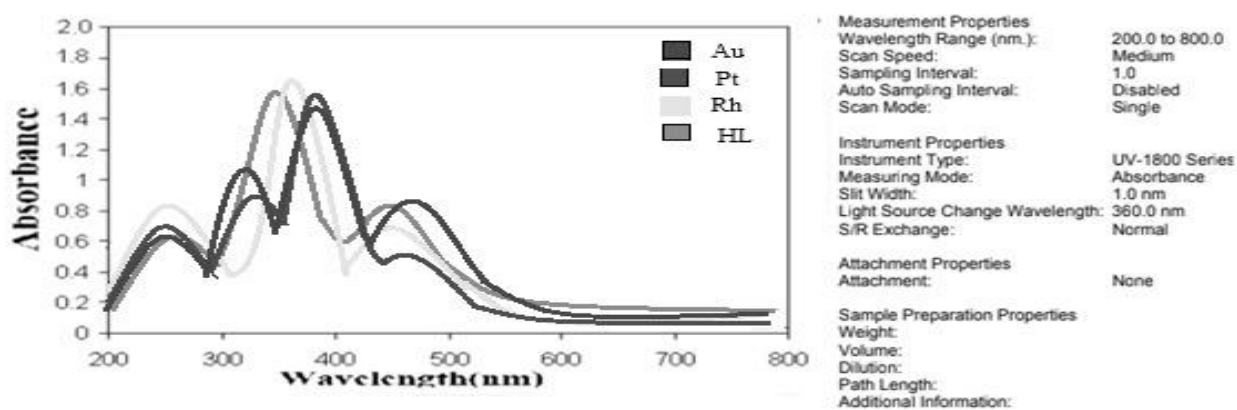


Fig. 2. The overlay of electronic spectra

Table III A. ^1H NMR Spectral Data

| Ligand/Complexes | ^1H NMR (δ ppm) | |
|--|----------------------------------|-----------|
| | CH=N | Ar-H |
| HL | 8.50 | 7.33-8.16 |
| $[\text{Rh}(\text{HL})\text{Cl}_3\cdot 2\text{H}_2\text{O}]$ | 8.69 | 7.33-8.10 |
| $[\text{Pt}(\text{HL})\text{Cl}_2\cdot\text{H}_2\text{O}]$ | 8.86 | 7.33-8.10 |
| $[\text{Au}(\text{HL})\text{Cl}_2\cdot\text{H}_2\text{O}]\text{Cl}\cdot\text{H}_2\text{O}$ | 8.96 | 7.33-8.10 |

Table III B. Thermal Data

| Ligand/Complexes | Calculated loss % | | | Found loss % | | |
|---|-------------------|--------------------|-----------------|-----------------|--------------------|-----------------|
| | Lattice Content | Co-ordinated Water | Organic Content | Lattice Content | Co-ordinated Water | Organic Content |
| [Rh(HL)Cl ₃ ·2H ₂ O] | ---- | 7.15 | 72.07 | ---- | 7.42 | 72.99 |
| [Pt (HL) Cl ₂ H ₂ O] | ---- | 3.33 | 57.89 | ---- | 3.43 | 56.76 |
| [Au(HL)Cl ₂ H ₂ O]Cl·H ₂ O | 8.99 | 3.02 | 55.02 | 8.79 | 3.28 | 55.88 |

21420 cm⁻¹, 25020 cm⁻¹ and 30790 cm⁻¹ which may be assigned to ¹A_{1g}→¹B_{1g}, ¹A_{1g}→¹E_{1g} and ¹A_{1g}→¹A_{2g} respectively. The band at 35500 cm⁻¹ is considered as charge transfer transition. Hence, a square planar geometry may be assigned for Pt(II) complex (Chandra, S., & Singh, R., 1988), (Fülöp, F., Mattinen, J., & Pihlaja, K. 1990) and (Chinnusamy, V. & Natarajan, K. 1993) (Pal, I., Basuli, F., & Bhattacharya, S. 2002).

Similarly the electronic spectra of Au(III) complex showed bands at 21076 cm⁻¹, 25220 cm⁻¹ and 30959 cm⁻¹ which may be assigned to ¹A_{1g}→¹B_{1g}, ¹A_{1g}→¹E_{1g} and ¹A_{1g}→¹A_{2g} respectively. The band at 34200 cm⁻¹ is considered as charge transfer transition. Hence, a square planar geometry may be assigned for Au (II) complex (Mason III, W. R., & Gray, H. B., 1968).

The electronic spectrum of Rh(III) complex showed bands at 22675 cm⁻¹ and 27440 cm⁻¹ which have been assigned to ¹A_{1g}→¹T_{1g} and ¹A_{1g}→¹T_{2g} transitions respectively whereas the band appearing at 38867 cm⁻¹ is a charge transfer transition. (Bertelli, E., Preti, C., & Tosi, G., 1975). The Rh(III) complex may be assigned octahedral geometry (Gudasi, K. B., Patil, S. A., Vadavi, R. S., Shenoy, R. V., & Nethaji, M., 2006) and (Yusof, E. N. M., Ravooof, T. B., Jamsari, J., Tiekink, E. R., Veerakumarasivam, A., Crouse, K. A., & Ahmad, H. 2015). The Electronic spectral data have shown in Table II B and the overlay of electronic spectra is shown in Fig. 2.

C. ¹H NMR

The ¹H NMR spectra of Schiff base and its metal complexes were recorded in DMSO. The aromatic protons in Schiff base were appeared in the range 7.33-8.16 ppm and metal complexes were appeared in the range 7.33-8.10 ppm. The azomethine proton in Schiff base appeared (δ=8.50ppm) have showed downfield shifting in metal complexes (δ=8.69-8.96 ppm) this indicates the co-ordination of azomethine nitrogen atom in metal complexation. The spectral data and have shown in TABLE III A.

D. Thermal Analysis

The TGA/DTA analysis of the metal complexes was carried out to get information about the stability of the metal complexes and amount of organic content present in complexes. TGA/DTA analysis was carried out in the range 0-1000°C at 10°C/min. The

Au(III) complex have shown the initial weight loss of 8.79% respectively in the temperature range 0-100°C which indicates the presence of one molecule of lattice water along with loss of chloride ion from Aurum complex (Alias, M., Kassum, H., & Shakir, C., 2014), (Labisbal, E., Haslow, K. D., Sousa-Pedrares, A., Valdés-Martínez, J., Hernández-Ortega, S., & West, D. X. 2003) and (Mehta, B. H., & Joishar, D. S. 2004).

The Rh (III), Pt (II) and Au(III) complexes have shown weight loss by 7.42%, 3.43 % and 3.28 % in the temperature range 110°C-200°C indicating the presence of one molecule of coordinated water in Rh(III), Pt (II) and Au (III) complexes. Rh(III), Pt(II) and Au(III) complexes have shown weight loss by 72.99 %, 56.46 % and 55.88 % indicating the loss of organic content resulting in the formation of corresponding oxides with further increase in the temperature. The thermal data and graphs have shown in TABLE III B and in Fig. 3, 4 and 5.

E. Structure of Rh(III), Pt(II) and Au(III) complexes

The Schiff base of (2E)-3-Phenylprop-2-enal and 2-Naphthylamine and its Rh (III), Pt (II) and Au(III) complexes were characterized by elemental analysis, spectral studies (1H NMR, IR, UV-Vis.), molar conductance and thermal analysis. On the basis of above data Pt (II) and Au (III) complex show square planar structure whereas Rh(III) complex show octahedral structure. The proposed structures of the metal complexes have shown in Fig. 6, 7 and 8.

F. Antimicrobial Studies of Schiff bases and their Rh(III), Pt (II) and Au(III) metal complexes

The majority of metal complexes possessing antimicrobial activity are chelates. The relationship of metal complexes to biological response has been investigated by the Kirby-Bauer test. The Kirby-Bauer test is a standard test used for antimicrobial susceptibility also called as the disc diffusion test. If the organism is killed or inhibited by the concentration of the antibiotic, there will be no growth in the immediate area around the disc. This area is called as the zone of inhibition (West, D. X., Padhye, S. B., & Sonawane, P. B., 1991) (Padhye, S., & Kauffman, G. B. 1985) and (Sharma, V. K., Shrivastava, S., & Shrivastava, A. 2007)

The biological screening effects of the investigated compounds were tested against the bacteria: Staphylococcus

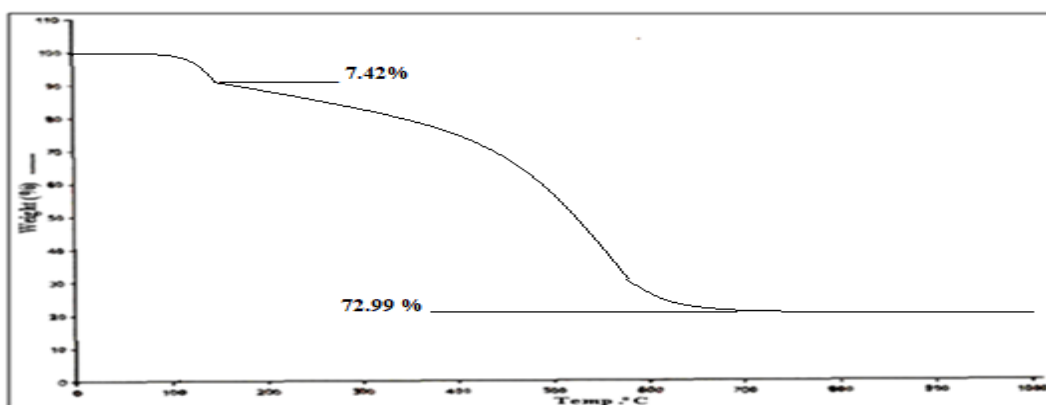


Fig. 3. TGA of Rh(III) complex

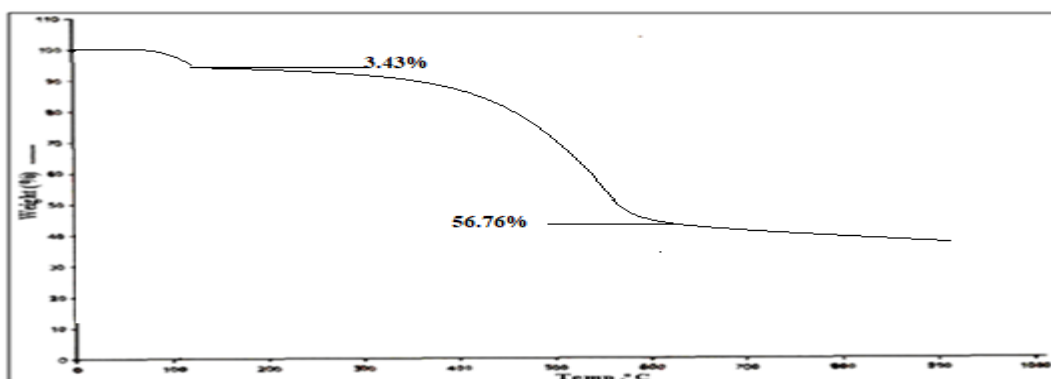


Fig. 4. TGA of Rh(III) complex

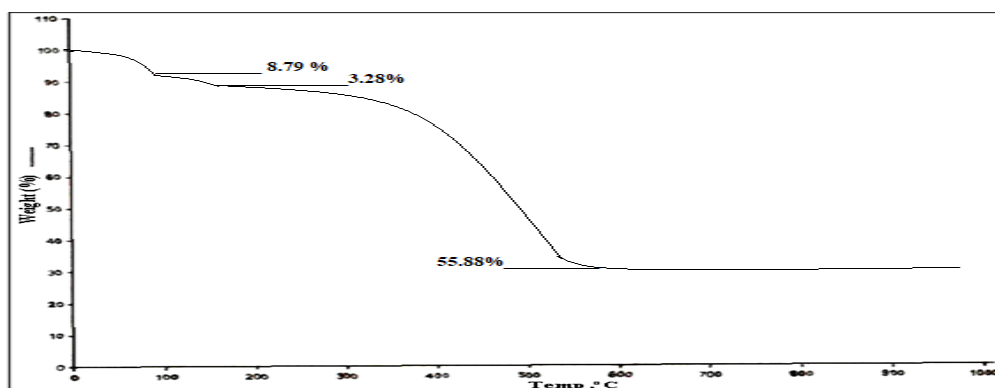


Fig. 5. TGA of Rh(III) complex

aureus, Staphylococcus pyogenes, Escherichia coli and Klebsiella Pneumonia, this was carried out by the disk diffusion technique, using agar nutrient as the medium. The stock solution (5mmol) of new compounds was prepared by dissolving the compounds in DMSO. In a typical procedure, a well was made on the agar medium inoculated with bacterial strains. The well was filled with the test solution using a micropipette and the plate was incubated for 24 h at 37 °C. During this period, the test

solution diffused and the growth of the inoculated microorganisms was affected. The results were recorded by measuring the growth inhibition surrounding the disk. The results (Table IV and Fig. 9) reveal that the ligand is less active towards the bacterial strain. All metal complexes were found to have moderate activity and quite better activity over the ligand. In general it is concluded that metal complexes are more active than that of the corresponding ligand.

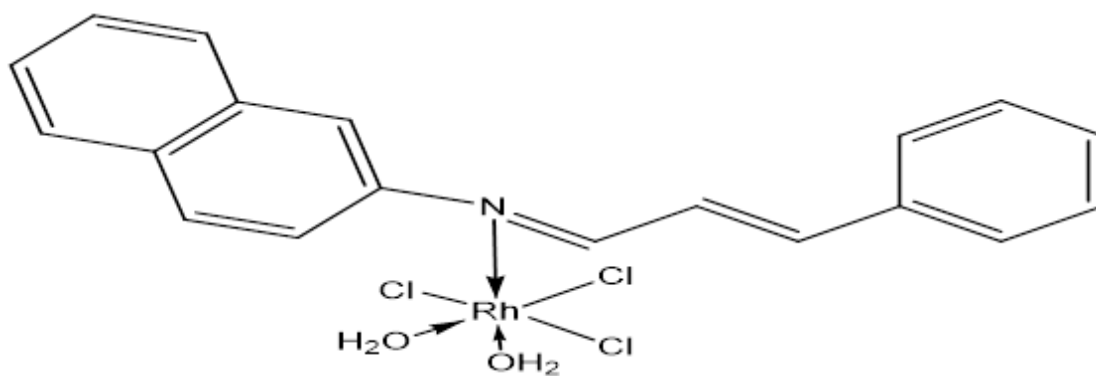


Fig. 6. Structure of Rh(III) complex

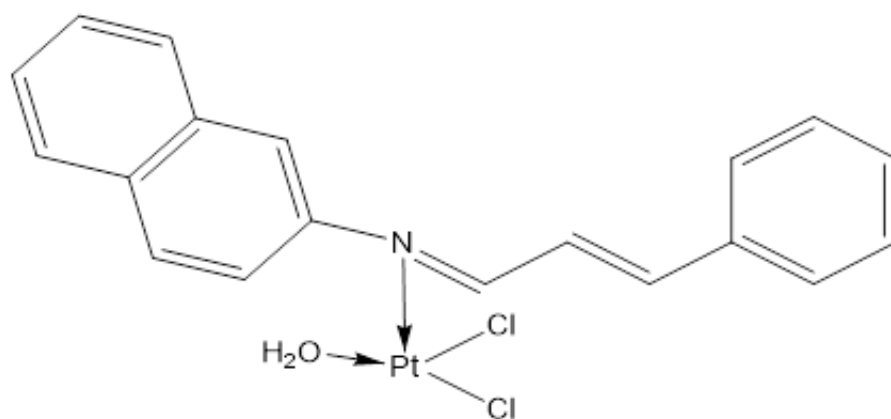


Fig. 7. Structure of Pt(II) complex

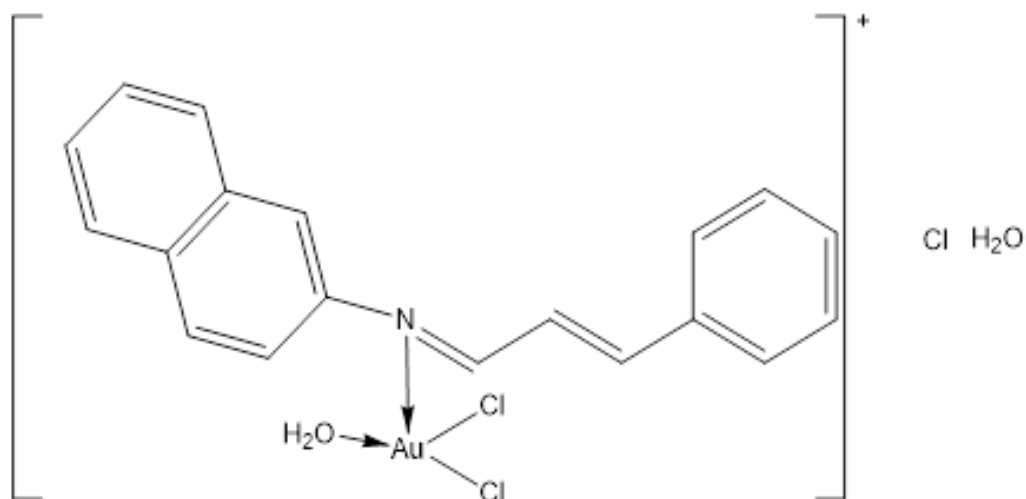
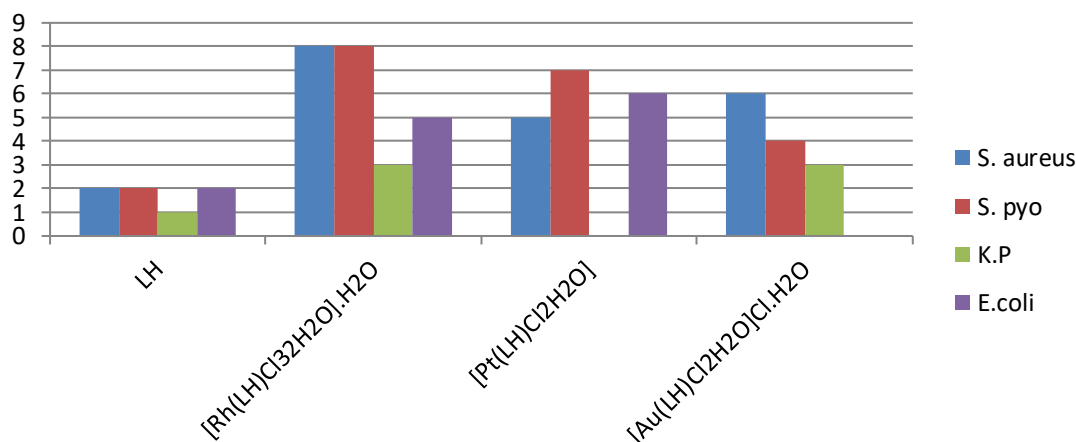


Fig. 8. Structure of Au(III) complex

Table IV. Antibacterial Studies of Schiff Bases and their Metal Complexes

| Sr. No. | Compound | Zone of inhibition for Gram positive strain (mm) | | Zone of inhibition for Gram negative strain (mm) | |
|---------|--|--|---------------|--|---------------|
| | | <i>S. aureus</i> | <i>S. pyo</i> | <i>K.P</i> | <i>E.coli</i> |
| 1 | HL | 02 | 02 | 01 | 02 |
| 2 | [Rh(HL)Cl ₃ ·2H ₂ O] | 08 | 08 | 03 | 05 |
| 3 | [Pt(HL)Cl ₂ ·H ₂ O] | 05 | 07 | - | 06 |
| 4 | [Au(HL)Cl ₂ ·H ₂ O]Cl·H ₂ O | 06 | 04 | 03 | - |

Fig. 9. *S. aureus*:- *Staphylococcus aureus*
E.coli:- *Escherichia coli**S. pyo*:- *Staphylococcus pyogenes*
K.P:- *Klebsiella Pneumonia*

CONCLUSION

The Schiff base of (2E)-3-Phenylprop-2-enal and 2 Naphthylamine and its Rh(III) Pt(II) and Au(III) complexes were synthesized and characterized by elemental analysis, spectral studies (1H NMR, IR, UV-Vis.), molar conductance and thermal analysis. On the basis of above data Pt(II) and Au(III) complex show square planar structure whereas Rh(III) complexes show octahedral structures.

Comparative study of antimicrobial activities of Schiff base ligand their metal coordinated Schiff base ligand showed better activity as compared to former.

All metal complexes were found to have moderate activity and quite better activity over the ligand. In general it is concluded that metal complexes are more active than that of the corresponding ligand.

REFERENCES

Acharyya, R., Basuli, F., Rosair, G., & Bhattacharya, S. (2004). Synthesis, structure and electrochemical properties of some oxime complexes of rhodium. *New Journal of Chemistry*, 28(1), 115-119.

Agarwal, R.K., Singh, L., & Sharma, D.K. (2006). Synthesis, spectral, and biological properties of copper (II) complexes of thiosemicarbazones of Schiff bases derived from 4-aminoantipyrine and aromatic aldehydes. *Bioinorganic Chemistry & Applications*, 2006.

Alias, M., Kassum, H., & Shakir, C. (2014). Synthesis, physical characterization and biological evaluation of Schiff base M (II) complexes. *Journal of the Association of Arab Universities for Basic and Applied Sciences*, 15, 28-34.

Bertelli, E., Preti, C., & Tosi, G. (1975). Synthesis and characterization of O, O'-bonded benzeneseleninate complexes of rhodium (III) and iridium (III). *Journal of Inorganic and Nuclear Chemistry*, 37(6), 1421-1424.

Chandra, S., & Singh, R. (1988). Pd (II), Pt (II), Rh (III), Ir (III) & Ru (III) Complexes of Some Nitrogen-Oxygen Donor Ligands. *Indian Journal of Chemistry*, 27A, 417-420.

Chinnusamy, V. and Natarajan, K. (1993). Synthesis and Reactivity in Inorganic. *Metal-Organic and Nanometal Chemistry*, 23, 889

Çukurovali, A., Yilmaz, I., Özmen, H., & Ahmedzade, M. (2002). Cobalt (II), copper (II), nickel (II) and zinc (II) complexes of two novel Schiff base ligands and their antimicrobial activity. *Transition Metal Chemistry*, 27(2), 171-176.

- Fülöp, F., Mattinen, J., & Pihlaja, K. (1990). Ring-chain tautomerism in 1, 3-thiazolidines. *Tetrahedron*, 46(18), 6545-6552.
- Gudasi, K.B., Patil, S.A., Vadavi, R.S., Shenoy, R.V., & Nethaji, M. (2006). Crystal structure of 2-[2-hydroxy-3-methoxyphenyl]-3-[2-hydroxy-3-methoxybenzylamino]-1, 2-dihydroquinazolin-4 (3H)-one and the synthesis, spectral and thermal investigation of its transition metal complexes. *Transition Metal Chemistry*, 31(5), 586-592.
- Kawamoto, T., & Konno, T. (2003). Analytical and Inorganic-Synthesis and Characterization of Nickel (II) Schiff Base Complexes with Methoxy or Methyl Groups at 2, 6-Positions of the Pendant Phenyl Ring: The Control of cis and trans. *Bulletin of the Chemical Society of Japan*, 76(1), 127-132.
- Kikukawa, Y., Yamaguchi, S., Tsuchida, K., Nakagawa, Y., Uehara, K., Yamaguchi, K., & Mizuno, N. (2008). Synthesis and catalysis of di- and tetranuclear metal sandwich-type silicotungstates $[(\gamma\text{-SiW}_{10}\text{O}_{36})_2\text{M}_2(\mu\text{-OH})_2]_{10-}$ and $[(\gamma\text{-SiW}_{10}\text{O}_{36})_2\text{M}_4(\mu_4\text{-O})(\mu\text{-OH})_6]_{8-}$ (M= Zr or Hf). *Journal of the American Chemical Society*, 130(16), 5472-5478
- Labisbal, E., Haslow, K.D., Sousa-Pedraes, A., Valdés-Martínez, J., Hernández-Ortega, S., & West, D.X. (2003). Copper (II) and nickel (II) complexes of 5-methyl-2-hydroxyacetophenone N (4)-substituted thiosemicarbazones. *Polyhedron*, 22(20), 2831-2837.
- Leovac, V.M., Divjakovič, V., Petrovič, D., Argay, G., & Kálmán, A. (1983). Synthesis and characterization of two Ni (II) complexes with furfural s-methylthiosemicarbazone. *Polyhedron*, 2(12), 1307-1312.
- Mason III, W.R., & Gray, H.B. (1968). Electronic structures and spectra of square-planar gold (III) complexes. *Inorganic Chemistry*, 7(1), 55-58.
- Mehta, B.H., & Joishar, D.S. (2004). Synthesis and Spectral Properties of Cobalt (II) and Nickel (II) Complexes Derived from Bidentate Schiff Bases. *Asian Journal of Chemistry*, 16(2), 910.
- Padhye, S., & Kauffman, G.B. (1985). Transition metal complexes of semicarbazones and thiosemicarbazones. *Coordination Chemistry Reviews*, 63, 127-160.
- Pal, I., Basuli, F., & Bhattacharya, S. (2002). Thiosemicarbazone complexes of the platinum metals. A story of variable coordination modes. *Journal of Chemical Sciences*, 114(4), 255-268.
- Rawal, B., & Gupta, K.P. (1972). Phase equilibria in the Chromium-Germanium system at the high chromium end. *Journal of the Less Common Metals*, 27(1), 65-72.
- Sharma, V.K., Shrivastava, S., & Shrivastava, A. (2007). Bioinorganic Chemistry and Applications. Article ID, 68374(10).
- Shimakoshi, H., Kaieda, T., Matsuo, T., Sato, H., & Hisaeda, Y. (2003). Syntheses of new water-soluble dicobalt complexes having two cobalt-carbon bonds and their ability for DNA cleavage. *Tetrahedron letters*, 44(28), 5197-5199.
- Singh, J., & Gupta, S.P. (1976). Pd (II) Chelate of 2, 4-Dihydroxyvalerophenone. *Indian Journal of Chemistry*, 14A, 710-712.
- Singh, N.K., & Singh, S. B. (2001). Synthesis, characterization and biological properties of manganese (II), cobalt (II), nickel (II), copper (II), zinc (II), chromium (III) and iron (III) complexes with a new thiosemicarbazide derivative. *Indian Journal of Chemistry*, 40A, 1070-1075.
- West, D.X., Padhye, S.B., & Sonawane, P.B. (1991). Structural and physical correlations in the biological properties of transition metal heterocyclic thiosemicarbazone and S-alkyldithiocarbamate complexes. *Complex Chemistry*, 1-50.
- Yusof, E.N.M., Ravooof, T.B., Jamsari, J., Tiekink, E R., Veerakumarasivam, A., Crouse, K. A., & Ahmad, H. (2015). Synthesis, characterization and biological studies of S-4-methylbenzyl-β-N-(2-furylmethylene) dithiocarbamate (S4MFuH) its Zn²⁺, Cu²⁺, Cd²⁺ and Ni²⁺ complexes. *Inorganica Chimica Acta*, 438, 85-93.
- K. Lal, Gupta S.P., & Singh, J., *Journal of Inorganic & Nuclear Chemistry*, 40, 356(1978)
