Synthesis, characterisation and biological investigation of some third-row elements with halo-substituted coumarin Schiff base with N and O as donors

Pratiba Patil\textsuperscript{1,4}, Virupaxappa S Betageri\textsuperscript{1}, Shivashankar M Kinnal\textsuperscript{1} and Latha M S\textsuperscript{2}

\textsuperscript{1} Research Centre, Department of Chemistry, GM Institute of Technology (GMIT), Davangere, Karnataka, India- 577006  
\textsuperscript{2} Department of Chemistry, K. L. E. Society’s R. L. S. Institute (Autonomous), Belagavi, Karnataka, India.  
\textsuperscript{3} P. G. Department of Chemistry, Karnataka University, Dharwad- 580003, Karnataka, India.  
\textsuperscript{4} Visvesvaraya Technological University, Belagavi, Karnataka, India  
Corresponding Author: betagerivs@gmit.ac.in, lathamschem97@gmail.com

Abstract. The present work involves in the synthesis, spectral characterisation and the biological analysis of the metal complexes which were derived from 3-Chloro-8-formyl-7-hydroxy-4-methylcoumarin and benzylamine. The molar conductivity values indicated that the complexes are non-electrolytes. Elemental analysis was carried out to assign the [ML\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}] stoichiometry to the metal complexes, where M= Co (II), Ni (II) and Cu(II) and L= deprotonated ligand. The IR data confirmed coordination of metal ions to the ligand. The presence of a coordinated water molecule was investigated by thermal studies and the electronic spectral results were helpful in assigning the geometry to synthesised complexes. The both Schiff base and the derived metal complexes were subjected various biological activities to check their potency.

Keywords: Halogenated Schiff Base, Fluorescence, and Antituberculosis, anthelmintic, antimicrobial.

1. Introduction  
Coumarin and its derivatives have the enormous properties have attracted many researchers. As it occurs naturally in some of the plants and can be extracted using various methods [1]. When comes to the chemical synthesis, there are several routes [2-7] and one of the best method is Pechmann Condensation. Substituted phenols; can be used to relocate the various groups in the ring. 7-Hydroxycoumarin is the parent coumarin between all the complex coumarin structures. [8]. Coumarin derivatives has the ability to exhibit pharmacological property, such as antiplasmodial [9], anticancer [10], cytotoxic [11], antimicrobial [12], antioxidant [13], antitubercular [14], anti-HIV [15], anti-inflammatory and anticoagulant [16], antispermatogenic [17], anthelmintic [18] and inhibition of platelet aggregation [19] activities. The ability of coumarins to chelate [21] and form the complexes have been studied [20].

Recent survey suggested that the halo-substitution at various positions in an aromatic ring brings about more changes in their activities. These derivatives obtained can be used as potent drugs against various
disorders. Such compounds are known to work against several protein kinases as inhibitors [22]. Recent work indicates that the halogen-bonded ligands probe shows increasing affinity to act like a potential cancer drugs [23]. Solubility of the compounds in water is decreased upon halogen substitution and helps to penetrate the lipid membrane. Less bulky atoms such as fluorine are capable of blocking the metabolically active positions.

Based on the above observations, in the present study it is planned to synthesise biologically active complexes of some 3rd row elements with halogen substituted coumarin Schiff Base. This part of work includes the synthesis of Nickel, Cobalt and Copper complexes within the Schiff Base obtained as a condensation product of benzylamine and 3-Chloro-8-formyl-7-hydroxy-4-methylcoumarin. The spectral characterisation of the synthesized compounds were carried out with the help of (UV-visible, IR, ESI-MS, NMR, Mass.), molar conductivity, thermal and fluorescence studies. Later various biological activities were conducted to test their potency towards some species.

2. Experimental Section

2.1 Reagents used
Chemicals utilized in the present research work are purely reagent grade and they are used without purification.

2.2 Physical measurements
The percentage composition of Hydrogen, Carbon and Nitrogen were investigated using TRUSPEC CHN analyser. The Infrared spectra of the corresponding Schiff base and its metal complexes were recorded on HITACHI-270 IR spectrophotometer in the region 4000-400 cm\(^{-1}\) with the help of KBr disk. The metal complexes' UV spectra were reported on a VARIAN CARY 50-BIO UV-spectrophotometer in the region of 200 -1100 nm using HPLC grade DMF solvent. The proton and carbon NMR spectrum of the corresponding Schiff Base was measured using TMS as internal reference. HITACHI F-7000 Fluorescent Spectrophotometer was used to study the characteristic fluorescent property of coumarins. GCMS of the corresponding Schiff base, ESI-MS spectra of the synthesized compounds were reported using THERMO Finnegan and QP 2010S LCQ Advantage max ion trap mass spectrometer. In TGA, heating rate of 10 °C / min from a range of room temperature to 1000 °C was varied to calculate the data and the instrument used was PERKIN-ELMER DIAMOND TG / DTA. Conductivity Bridge ELICO-CM-82 T was used to record the values of molar conductivity showed cell constant 0.51 and the faraday balance were used to record the values of the magnetic moment.

2.3 Synthesis Part

2.3.1 Synthesis: 3-Chloro-7-hydroxy-4-methylcoumarin.
Mixture of 0.2 mol each dry resorcinol and ethyl-2-chloroacetoacetate was gradually added to Con. Sulfuric acid in a cool atmosphere (0-5 °C) and then kept in a refrigerator overnight. It was quenched in ice with continuous stirring until solid separated out. The solid so obtained was subjected to filtration and recrystallized using ethanol. Yield: 78% M. P. 241- 243 °C.
2.3.2 Synthesis: 3-Chloro-8-formyl-7-hydroxy-4-methylcoumarin.
Mixture of 0.03 M of 3-Chloro-7-hydroxy-4-methylcoumarin and 0.07 M of hexamine were subjected for heating in acetic acid for 4-5 hr followed by the addition of HCl and proceeded to heat for another 20 min. The mixture was then dissolved in ether, and removed. The desired product was the pale-yellow solid obtained after pouring in crushed ice, and it was filtered and dried. Yield: 25.0 percent; point of melting: 163-166°C.

2.3.3. Schiff Base Synthesis.
The pre-hot ethanolic solution of benzylamine was combined with the 3-Chloro-8-formyl-7-hydroxy-4-methylcoumarin hot ethanolic solution, and then refluxed for 4-5 hours (few drops of acetic acid). As a result of refluxion, the precipitate which is obtained is being filtered, washed and recrystallized using acetic acid.
Process-1. Schiff Base Synthesis

2.3.4 NMR spectral study

$^1H$ NMR

One singlet detected at range 14.90 ppm is attributed to the phenolic -OH in the (figure 1) Schiff base spectrum. A single proton resonance is -CH = N, methylene and -CH3 at 9.10, 4.85 and 2.43 ppm respectively. Furthermore, aromatic protons activate during multiplet signals between 6.05-7.63 ppm.

![Figure 1. Schiff base-$^1H$ NMR spectrum](image-url)
The **Schiff base** spectrum of signals $^{13}$C NMR showed resonance at 173.22 (C=N), 160.45 (C=O), 164.01 (C-Cl), 56.84(-CH$_2$) and 18.33(-CH$_3$) ppm. Signals showed appearance in the respective range 104.039 - 159.39 ppm which were further assigned to the aromatic carbon substitutes. The $^{13}$C NMR spectrum is embedded in figure 2.

![Figure 2. Schiff base-$^{13}$C NMR spectrum](image)

### 2.3.4.1. Infrared Spectral Studies.

In spectrum of ligand (Fig.3) due to the presence of -C=N exhibits a very high intense band at 1626 cm$^{-1}$ which ensures the complete formation of Schiff base. Due to the presence of $\nu$(O-H) another band of high intensity at 1257 cm$^{-1}$ is assigned to the phenolic $\nu$(C-O) stretching frequencies and 1719 cm$^{-1}$ for the lactonyl carbon. Appearance of a broad band under the region 3397 cm$^{-1}$ observed.

![Figure 3. Schiff Base- Infrared Spectrum](image)
2.3.4.2. GC- Mass Studies.

The Formation of the respective ligand showed confirmation by a crest at m/z 327 which clearly showed correspondence to its molecular weight. A fragmentation crest at m/z 310 was mainly by the cleavage of –OH group of coumarin (figure 4).

![Schiff Base- Mass Spectrum](image)

**Figure 4. Schiff Base- Mass Spectrum**

2.3.4.3 Synthesis of Cobalt, Nickel and Copper Complexes.

2 M Schiff base was dissolved in alcohol with combined refluxion in 1 M of the metal salts on the water tub for about 1h. Reflux is to be continued for 2 more hours after the addition of 3 h sodium acetate (1mmol). After separation the metal complex was subjected to filtration followed by washing with water; ether and alcohol. It was vacuum dried over fused CaCl$_2$ to remove any moisture.

![Scheme 2. Metal Complexes- Synthesis](image)

**Scheme- 2. Metal Complexes- Synthesis**

2.3.4.4. FTIR Studies of Metal Complexes.

The mode of bounded Schiff base with the metal ion in the complexes were studied by analyzing the IR spectra of the corresponding metal complex which is further studied in comparison with the Schiff base.
The lowered values of azomethine group confirm the coordination complexes via nitrogen. The respective bands observed in Cobalt, Nickel and Copper complexes at 1598, 1592 and 1591 cm\(^{-1}\) are the shifted values of \(\nu(C=\text{N})\) from the ligand. The absence of \(\nu(O-H)\) band in the metal complexes spectrum reveal that the coordination via deprotonation and formation of M-O bond. Bands which are observed at 1327 and 1719 cm\(^{-1}\) are the shifted values of \(\nu(C=\text{O})\) and \(\nu(\text{O}\text{-H})\) respectively. The representative IR spectrum of Cobalt complex has been depicted in figure. 5.

Table 1. Elemental Analyses of Schiff Base and its Metal Complexes Along with Molar Conductance Data

| Compound Name | Empirical Formula | Yield % | M% Obs. Cal. | C% Obs. Cal. | H% Obs. Cal. | N% Obs. Cal. | Molar Cond. (Ohm\(^{-1}\) cm\(^2\) mole\(^{-1}\)) | \(\mu_{\text{eff}}\) (BM) |
|---------------|------------------|----------|--------------|--------------|--------------|--------------|--------------------------------|----------------|
| Schiff Base   | C\(_{17}\)H\(_{12}\)N\(_{3}\) | 80%      | 68.68 68.65  | 4.07 4.09 4.71 4.68 | - - | | - - | |
| Co(II)L\(_{2}\)(H\(_2\)O)\(_2\) | Co(C\(_{17}\)H\(_{12}\)N\(_{3}\))\(_2\)(H\(_2\)O)\(_2\) | 59% 59.40 | 8.57 8.54 | 59.43 3.81 3.79 4.07 4.04 | 22.10 | 4.90 |
| Ni(II)L\(_{2}\)(H\(_2\)O)\(_2\) | Ni(C\(_{17}\)H\(_{12}\)N\(_{3}\))\(_2\)(H\(_2\)O)\(_2\) | 63% 59.45 | 8.16 8.14 | 59.42 3.81 3.83 4.08 4.11 | 12.45 | 3.15 |
| Cu(II)L\(_{2}\)(H\(_2\)O)\(_2\) | Cu(C\(_{17}\)H\(_{12}\)N\(_{3}\))\(_2\)(H\(_2\)O)\(_2\) | 56% 59.05 | 9.18 9.15 | 59.00 4.07 4.05 4.08 | 27.40 | 1.77 |

2.3.4.5. Electronic Absorption Spectra and Magnetic Studies of complex.
Stereochemistry of metal ions was studied by recording the spectra along with ligand in DMF. The absorption spectra provide the valuable information to allocate the stereochemistry of metal ions, the assignment occurs in conjunction with the d-d transition peaks.

Ranging between 255 and 330 nm two bands were observed for the ligand, the bands which appear below the range 350 nm are ligand-based transitions of the azomethine group’s aromatic ring and the non-bonding electrons of nitrogen [24, 25].

Table-2 contains the results of electronic spectra which are recorded in DMF. Two absorption bands of Cobalt complex occurred in the region 568 and 980 nm correspond to
$^{4}T_{1g}(F) \rightarrow ^{4}T_{2g}(F)$ ($\nu_1$) and $^{4}T_{1g}(F) \rightarrow ^{4}T_{1g}(P)$ ($\nu_3$) transitions respectively, which are well matching with high spinning octahedral geometry [26] and magnetic moment of 4.90 BM proves it [27].

Nickel complex exhibits following bands at 989, 674 and 365 nm attributable to $3A_2g(F)3T_2g(F)(1)$, $3A_2g(F)3T_1g(F)(2)$ and $3A_2g(F)3T_1g(P)(33)$ transitions respectively indicate the octahedral geometry [28] and magnetic momentum value of 3.15 BM is also stand by the octahedral geometry around metal ions [29, 30].

The spectrum of Copper complex (figure-6) exhibited two bands of absorption. $2E_g$ a $2T_2g$ transition, evidently it supports the distorted octahedral configuration to the metal complex [31] is given at a very low intensity band in the range 690 nm. Correspondingly the high-intensity bands are observed at 391 nm is prohibited to pass metal load due to symmetry. The magnetic moment obtained value for Copper complex is 1.77 BM, which in further supports the electronic spectral data [32, 33].

Figure 6. Electronic Absorption Spectrum-Cu(II) Complex

Table 2. Electronic Spectral Results with Magnetic Susceptibility Data of the Metal Complexes (1-3).

| Complex. | Obs $\lambda_{max}$ in cm$^{-1}$ (nm) | Band Assignments | Geometry       | $\mu_{eff}$ (BM) |
|---------|--------------------------------------|------------------|----------------|-----------------|
| 1       | 10152 (985)                          | $^{4}T_{1g}(F) \rightarrow ^{4}T_{2g}(F)$ ($\nu_1$) | octahedral     | 4.90            |
|         | 17730 (564)                          | $^{4}T_{1g}(F) \rightarrow ^{4}T_{1g}(P)$ ($\nu_3$) |                |                 |
|         |                                     | $^{3}A_{2g}(F) \rightarrow ^{3}T_{2g}(F)$ ($\nu_1$) |                |                 |
| 2       | 10131 (987)                          | $^{3}A_{2g}(F) \rightarrow ^{3}T_{2g}(F)$ ($\nu_2$) | octahedral     | 3.15            |
|         | 14880(672)                           | $^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(F)$ ($\nu_3$) |                |                 |
|         | 27624(362)                           | $^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(P)$ ($\nu_3$) |                |                 |
| 3       | 14450 (692)                          | $^{2}T_{2g} \leftarrow ^{2}E_{L} \rightarrow ^{2}E_{M}$ | distorted      | 1.77            |
|         | 25380 (394)                          |                  | octahedral     |                 |

2.3.4.6. Fluorescence study of Schiff base and its metal complexes.
Fluorescence being one among the spectrochemical analytical methods in which an analyte’s molecules is being excited through irradiation at a particular wavelength and emits radiation from a different wavelength.

The present research is been analysed to the fluorescent nature of the base of the Schiff and its metal complexes at 27°C temperature within the concentration of $10^{-5}$ M in DMSO solution. It is observed
that, as a result of interaction between phenolic oxygen and metal ion, the emission band at 482 nm of Schiff base disappears upon complexation. Synthesized complexes Co (II), Ni (II) and Cu (II) shows the bands of emission at 466, 452, 437 nm respectively. Diminishing electron density on ligand decreases the complexes' emission rate. The decrease in metal complex intensities was compared to the base of Schiff and the order is Co (II) > Ni (II) > Cu (II) is shown in figure 7.

2.3.4.7. ESI-MS Study.
The Cobalt, Nickel, and Copper complexes ESI-MS analysis were reported a M+1 crest at m / z 747, 748, 753 respectively, and it is also equal to their corresponding molecular weight. This facilitates development of ML$_2$(H$_2$O)$_2$ type metal complexes. The representational Cobalt complex spectra is in the figure 8.

2.3.4.8. Thermal analysis of metal complex.
The thermal behaviour of synthesized Schiff base L complexes Co (II), Ni (II) and Cu (II) was subjected for study as a function of temperature. Decomposition was observed to occur in two stages. In other words, all the complexes have the same thermal features. The definition of the symbolic thermogram
Copper complex is discussed here. The first decomposition was observed due to the loss of the coordinated water molecules in range 180-220 °C region centred at 198 °C. Decomposition in the 350-540 °C regions based at 475 °C leading to the loss of organic moulds. The metal oxide then grew above 650 °C.

![Figure 9. TG/DTA spectrum - Copper Complex](image)

**3. Biochemistry**

3.1. **Anti-tuberculosis Activity Study**

The metal complexes which were synthesized were tested for their anti-tuberculosis study against M. Tuberculosis using Microplate Alamar Blue Assay (MABA). The results further reveal that, the metal complexes exhibited better activity than the Schiff base with different MIC values as shown in Table 3. From results we can conclude that, the Cu(II) complex exhibited the prominent activity with the MIC of 12.5 (μg/mL) when compared to other metal complexes.

| Compound | MIC Values |
|----------|------------|
| Schiff base | 50         |
| 1         | 25         |
| 2         | 25         |
| 3         | 12.5       |
| Streptomycin Std. | 6.25      |

3.2. **Antimicrobial Activity**

The activity ensures that, when compared to their parent ligand, the synthesized metal complexes exhibit the greater lethal effect. The Cu (II) complex displayed the prominent antifungal and antibacterial activity against all strains among the synthesized metal complexes. The results are tabulated in below tables (4 and 5). By this it can be suspected that, presence of any metal ions may possibly show increase in the activity.
Table 4. Antibacterial Studies - Schiff Base and its Metal Complexes

| Compound Name/No. | Conc. (µg/mL) | Zone of Inhibition (mm) |
|------------------|---------------|-------------------------|
|                  | E. coli | P. aeruginosa | K. pneumoniae | S. aureus |
| Schiff base       | 200     | 6             | 5             | 6         | 7         |
| 1                | 200     | 9             | 7             | 9         | 8         |
| 2                | 200     | 9             | 8             | 8         | 10        |
| 3                | 200     | 10            | 10            | 11        | 12        |
| Gentamicin       | 200     | 14            | 13            | 14        | 15        |

Table 5. Antifungal Studies of Schiff Base (HL) and its Metal Complexes

| Compound Name/No. | Conc. (µg/mL) | Zone of Inhibition (mm) |
|------------------|---------------|-------------------------|
|                  | P. chrysogenum | A. niger |
| Schiff base       | 200            | 5         | 6         |
| 1                | 200            | 8         | 10        |
| 2                | 200            | 9         | 9         |
| 3                | 200            | 10        | 12        |
| Flucanazole      | 200            | 13        | 16        |

3.3. Anthelmintic Study

Table 6. Anthelmintic Studies - Schiff Base and its Metal Complexes

| Compound          | Concentration (µg/mL) | Paralysed Time (Min) | Lethal time (Min) |
|-------------------|-----------------------|----------------------|-------------------|
| DMSO*             | -                     | -                    | -                 |
| Schiff base       | 2                     | 20.16±0.02           | 24.28±0.12        |
|                   | 10                    | 9.29±0.22            | 14.30±0.12        |
| 1                 | 2                     | 12.16±0.15           | 19.60±0.02        |
|                   | 10                    | 7.51±0.04            | 10.14±0.03        |
| 2                 | 2                     | 16.21±0.24           | 21.30±0.08        |
|                   | 10                    | 9.10±0.01            | 15.60±0.01        |
| 3                 | 2                     | 10.30±0.03           | 16.41±0.05        |
|                   | 10                    | 5.48±0.22            | 9.45±0.01         |
| Albendazole Std.  | 10                    | 3.49±0.06            | 7.26±0.14         |

Results of the ligand anthelmintic activity and the synthesized compounds are shown in Table- 6. From this result it is clear that the metal complexes show more active than its parent ligand. The Copper complex, in particular, exhibits the prominent behaviour against a standard drug Albendazole at concentration of 10µg / mL relative to the other complexes.

3.4. DNA Cleavage Activity

Schiff base's DNA cleavage activity and its metal complexes is subjected for analysis using pBR322 Plasmid DNA and using the agarose gel electrophoresis process. Schiff base's cleavage activity and its complexes is shown in figure 10. In the present investigation, ligand along with the Cobalt and Nickel complexes shows the partial cleavage; but the Nickel complex cleaves the DNA completely.
4. Conclusion

The Schiff base which has been synthesised acts as a bidentate ligand that is coordinated with deprotonation to metal ions by means of oxygen atoms and azomethine nitrogen. The elemental analyzes verified that the synthesized metal complexes have form stoichiometry \([\text{M(L)}_2\cdot(\text{H}_2\text{O})_2]\) where [\text{M}=\text{Co(II)}, \text{Ni(II)} and \text{Cu(II)}] and ‘L’ are doubly deprotonated ligands. The molar conductivity analysis indicates that there are poor conductivity values in all the synthesized metal complexes. Such various spectro-analytical techniques have helped to assign the following preliminary structure to the metal complexes synthesized. The newly synthesized Schiff base and its metal complexes have been subjected for screening for their in-vitro Cleavage studies, Antitubercular, cytotoxic, antimicrobial and DNA. It has been proved to be a strong antitubercular agent among the tested compounds Cu (II) complex. Whereas antimicrobial assays illustrate Schiff Base's enhanced activity upon coordination. Schiff base’s DNA cleavage activity and its metal complexes were analysed using pBR322 Plasmid DNA, an agarose gel electrophoresis method in which the Ni (II) complex showed the successful cleavage compared to any other synthesized compounds. Considering all the above facts the following tentative structure has been assigned to the synthesised metal complexes.

\[
\text{Metal complexes} \\
\text{M} = \text{Co(II)}, \text{Ni(II)} and \text{Cu(II)}. 
\]

References

[1] Celeghini RMS, Vilegas JHY and Lanças FM 2001 Coumarin in Hydroalcoholic Extracts of Mikania glomerata Spreng. (“guaco”) Leaves, Braz Extraction and Quantitative HPLC Analysis of Chem. Soc. 12 706-709

[2] Mali RS and Tilve SG 1791 Useful Synthesis of Coumestans, Synth. Commun. 20 1781-1791
Alarcon, Georgrieva, Silverstein, Mandakmare, Cavettos, Sandhya Tyagi, VP Khan, MSY Trivedi, Zabradnik, Stanchev, Lacy, Gottlieb, Brufola, Cairns, Saidi

Chem. complexes of benzothiazole 403

Some Metal Complexes Of Transition Metal Ions With Coumarin Schiff Bases Having N And 1993, antiviral activity, Shah

Complexes with Ciprofloxacin and Their Evaluation of Antimicrobial, Antioxidant and Anti-Oxime Derivatives (III): Synthesis and Cytotoxic Evaluation. their therapeutic role in the treatment of cancer of organic natural products, Springer Verlag Wein 200-427

Marshall EM, Ryles M, Butler K, Weiss L 1994 Cancer Res. Clin. Oncol. 120 535.

Lacy A, O’Kennedy R 2004 Studies on coumarins and coumarin-related compounds to determine their therapeutic role in the treatment of cancer Curr. Pharm. Des. 10 3797-3811

Stanchev S, Momekov G, Jensen F and Manolov I 2008 6-Substituted 1, 4-Naphthoquinone Oxime Derivatives (III): Synthesis and Cytotoxic Evaluation. Eur. J. Med. Chem 43 694

Patel KS, Patel JC, Dholariya HR, Patel KD 1992 Synthesis of Cu(II), Ni(II), Co(II), and Mn(II) Complexes with Ciprofloxacin and Their Evaluation of Antimicrobial, Antioxidant and Anti-Tubercular Activity Spectrochim. Acta Part A 96 468

Zabradnik M 1992 The Production and Application of Fluorescent Brightening Agents John Wiley and Sons, New York

Patel KS, Patel JC, Dholariya HR, Patel KD 1992 Synthesis of Cu(II), Ni(II), Co(II), and Mn(II) Complexes with Ciprofloxacin and Their Evaluation of Antimicrobial, Antioxidant and Anti-Tubercular Activity Spectrochim. Acta, Part A. 96 468

Trivedi JC, Bariwal JB, Upadhyay KD, Naliapara YT, Joshi SK, Pannecoque CC, Clercq ED, Shah AK 2007 Improved and rapid synthesis of new coumarinylchalcone derivatives and their antiviral activity, Tetrahedron Lett. 48 8472–8474

Khan MSY and Sharma P. Spectrometric Identification of Organic Compounds Indian J. Chem. 1993, 32 817.

Tyagi VP, Dixit BC and Joshi 2018 Synthesis, Characterization and Biological Evaluation Of Some Metal Complexes Of Transition Metal Ions With Coumarin Schiff Bases Having N And O Donor Atom Naturwissenschaften 67 104–109

Sandhya B, Giles D, Vinod M, Basavarajaswamy G and Rekha A 2011 Eur. J. Med. Chem. 46 4696

Cavettos G, Nano GM, Palmisano G and Tagliapietra S 2001 Tetrahedron: Asymmetry 12 707

Ketata I, Mechi L, Ben Ayed T, Dusek M, Petricek V and Ben Hassen R 2012 Open J. Inorg. Chem. 2 33–39.

Mandakmare AU, Navwade ML 1997 Orient. J. Chem. 13 155–158.

Voth AR and Ho PS 2007 Curr. Top Med. Chem. 7 1336.

Wilcken R, Liu X, Zimmermann MO, Rutherford TJ, Fersht AR, Joerger AC and Boeckler FM 2012 J. Am. Chem. Soc. 134 6810

Ramesh R and Maheswaran S. 2003 J. Inorg. Bio. Chem. 96 457

Silverstein R, Bassler C and Morrill T 1981 Spectrometric Identification of Organic Compounds 4th Ed., John Wiley and Sons Inc., New York

Georgrieva I, Trendafilova N. and Bauer G. 2006 Synthesis and characterization of tetratetrad bis-Schiff base complexes of di-and tri-valent transition metals Spectrochim. Acta Part A 63 403

Ul-Hassan M, Chohan ZH and Supuran CT 2002 Chohan ZH, Scozzafava A, Supuran CT. Zinc complexes of benzothiazole-derived Schiff bases with antibacterial activity. Main Group Met. Chem. 25 291

Prakash PD and Patel MN 2004 Syn. React. Inorg. Met. Org. Chem. 34 383.

Alarcon-Payer C, Pivotta T, Chuquisillo-Lazarto D, Gonzalez Perez JM, Crisponi G Castineiras A and Niclos-Gutierrez J 2004 Inorg. Chem. Commun. 7 1277.
[30] Rao TR and Archan P 2005 Synth. React. Inorg. Metal. Org. Chem. 35 299
[31] Liu H, Wang H, Gao F, Niu D and Lu Z 2007 Synthesis and characterization of self-assembled coordination polymers of N-diaminomethylene-4-(3-formyl-4-hydroxy-phenylazo)-benzenesulfonamide J. Coord. Chem. 60
[32] Raman N and Dhaveethu R 2007 Synthesis, spectral characterization of Schiff base transition metal complexes: DNA cleavage and antimicrobial activity studies J. Indian J. Chem 46A1611
[33] Dianu ML, Kriza A, Stanica N. and Musuc AM 2010 SYNTHESIS, Spectroscopic Characterization and Evaluation (Antibacterial & (GOT, G pT) Enzyme) Activity of Mixed Ligand Complexes of M(II) with Amino Acid (L-Asparagine) and Schiff Bases Derived from (Sulfamethoxazo Drug with 2,4Dimethoxybenzaldehyde) J. Serb. Chem. Soc. 75 1515