

Synthesis and Characterization of Transition Metal Complexes of Schiff Bases Derived from 3-Formyl Chromone

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A series of Co(II), Ni(II), Cu(II) and Zn(II) complexes derived from bidentate Schiff bases obtained by condensation of 3-formyl chromone with 5-chloro-2-phenoxy-phenylamine and 2-phenoxy-phenylamine to form 3-[(5-chloro-2-phenoxy-phenylimino)methyl]chromen-4-one (L_1) and 3-[(2-phenoxy-phenylimino)methyl]chromen-4-one (L_2) have been synthesized and characterized by molar conductance, magnetic moment, thermal studies and spectroscopic techniques (FTIR, UV-visible, ^1H NMR, ^{13}C NMR) having general formula $\text{M}(\text{L}_{1,2})_2 \cdot 2\text{H}_2\text{O}$.

Keywords: 3-Formyl chromone, Schiff bases, Transition metal complexes, Spectroscopic studies, Bidentate.

INTRODUCTION

Schiff bases ($-\text{C}=\text{N}-$) play an important role in the development of coordination chemistry as they readily form stable complexes with most of the metal ions, resulting in an enormous number of publications and have variety of applications in biological, medicinal and analytical field [1]. Schiff base ligands are considered as “privileged ligands” because of their easy preparation and are used as flourogenic agent, pesticides, herbicides, blocking agents and in biological applications such as antibacterial, antifungal [2,3], antiviral, antihelmintic [4], antimalarial, antituberculosis [5,6], anticancer [7], analgesic, anti-inflammatory [8]. They serve as a back bone for the synthesis of various heterocyclic compounds of versatile use.

Transition metal complexes of Schiff bases can bind to DNA by non-covalent interactions such as intercalating system, groove binding and are used as antitumor drugs [9,10]. Transition metal compounds are useful for preparation of pigments, dyes, catalysts, organic and inorganic synthesis, polymer stabilizers and optical sensors [11].

Chromones are a group of naturally occurring compounds having extensive biological applications [12-14]. They are used in the synthesis of many heterocyclic compounds, xanthenes and pyrazoles. Inspired by above applications of Schiff bases and their transition metal complexes we have synthesized and characterized two Schiff base ligands (L_1 and L_2) derived from 3-formyl chromone with 5-chloro-2-phenoxy-phenylamine and 2-phenoxy-phenylamine and their Co(II), Ni(II), Cu(II) and Zn(II) complexes.

EXPERIMENTAL

All the chemicals 3-formyl chromone, 5-chloro-2-phenoxy-phenylamine, 2-phenoxy-phenylamine, Co(II), Zn(II), Ni(II), Cu(II) acetates used in the present research work were purchased from Sigma Aldrich and used as such without any further purification. FTIR spectra were recorded on Shimadzu IR affinity-I 8000 FT-IR spectrometer using KBr disc having wavelength range of $4000-400\text{ cm}^{-1}$. Magnetic moment measurements were carried out at room temperature by guoy's method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as standard. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance II 300 MHz NMR spectrometer and the chemical shifts were reported in ppm relative to TMS as internal standard in CDCl_3 . UV spectra were recorded on UV-VIS-NIR Varian Cary-5000 spectrometer in DMF. Molar conductance measurements of a 10^{-3} M solution in DMF were carried out using a model-306 Systronics conductivity bridge. TGA was carried out in the temperature range from room temperature to $800\text{ }^\circ\text{C}$ using a model Perkin Elmer Diamond TG/DTA thermogravimetric analyzer instrument.

Syntheses of Schiff bases

3-[(2-Phenoxy-phenylimino)methyl]chromen-4-one (L_1) and 3-[(5-chloro-2-phenoxy-phenylimino)methyl]chromen-4-one (L_2): 5-Chloro-2-phenoxy-phenylamine (0.66 g, 3 mmol)/2-phenoxy-phenylamine (0.55 g, 3 mmol) dissolved in methanol (30 mL) was added drop-wise to a methanolic solution of 3-formyl chromone (0.522 g, 3 mmol) with continuous stirring for 2 h. The reaction mixture was then refluxed

for 3-4 h. The feasibility of reaction was checked frequently with TLC. The coloured solid product so obtained was recrystallized in hot methanol then filter the mixture and dried to get pure product.

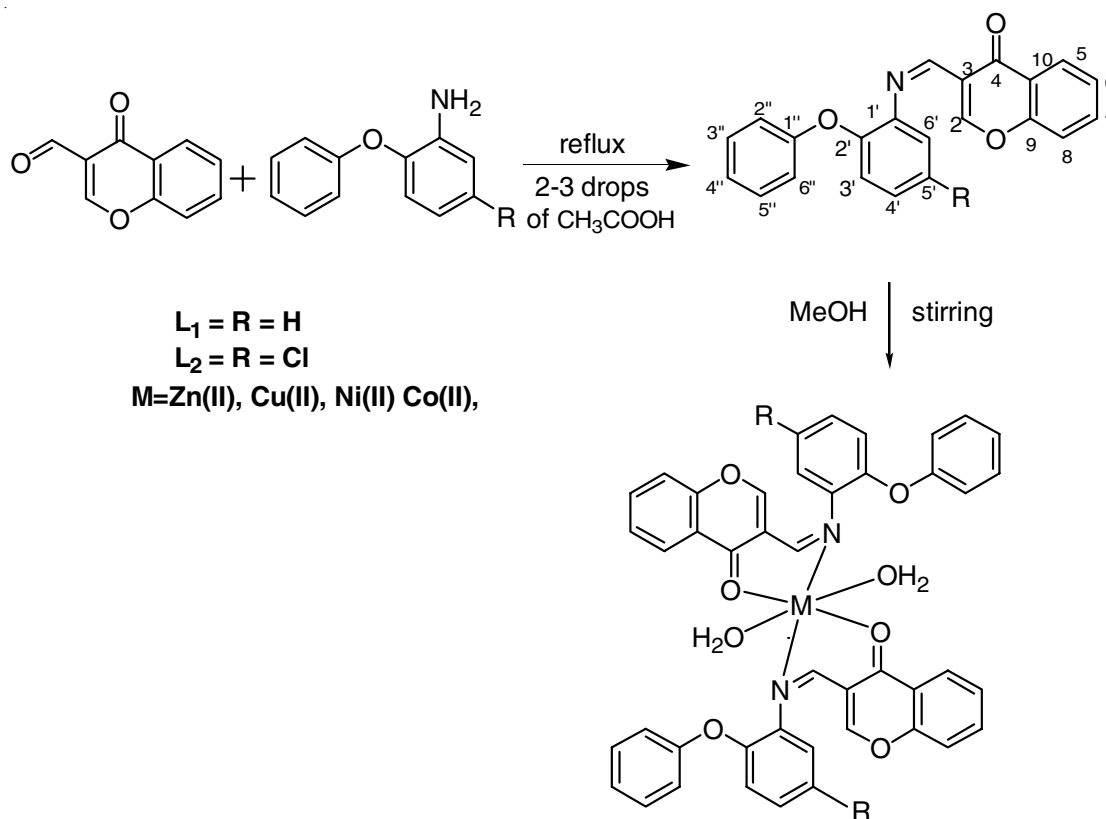
Synthesis of transition metal complexes: Transition metal complexes were prepared by drop-wise addition of 10 mL of hot methanolic solution of the corresponding metal acetates [where M = Co(II), Ni(II), Cu(II), Zn(II)] to 20 mL hot methanolic solution of above prepared Schiff base ligands with continuous stirring in 1:2 molar ratio. The precipitates separated out after sometime were filtered and washed with hot methanol and then finally with hexane and then left at room temperature for drying. All the transition metal complexes in **Scheme-I** were synthesized with same procedure as described.

RESULTS AND DISCUSSION

The Schiff bases have been synthesized by condensation of 3-formyl chromone with 5-chloro-2-phenoxy-phenylamine

and 2-phenoxy-phenylamine to form 3-[(2-phenoxy-phenylimino)methyl]chromen-4-one (L_1) and 3-[(5-chloro-2-phenoxy-phenylimino)methyl]chromen-4-one (L_2) and further reacted with transition metals in molar ratio (2:1) in dry methanol to get metal complexes of type $[ML_{(1-2)} \cdot 2H_2O]$. All the synthesized compounds were coloured, non-hygroscopic, stable at room temperature. These compounds were analyzed by various spectroscopic techniques (1H NMR, ^{13}C NMR, FT-IR, UV-visible), magnetic measurements, elemental analysis. All these metal complexes were insoluble in water, partially soluble in MeOH and $CHCl_3$ and are freely soluble in organic solvents like DMF and DMSO. Molar conductance of the 10^{-3} M solutions of complexes was measured in DMF at room temperature whose values falls in the range of $10-20 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicated that the complexes are non-electrolytic in nature [15] (Table-1).

Infrared spectra: The FTIR spectra of the complexes are compared with those of the free ligands in order to determine the coordination sites that may involve in chelation during



Scheme-I: Synthesis of ligands and their transition metal complexes

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF TRANSITION METAL COMPLEXES

Compound	m.f.	Colour	m.w.	Yield (%)	Elemental analysis (%): Calcd. (Found)			Molar conductivity ($\text{Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
					C	H	N	
L_1	$C_{22}H_{15}NO_3$	Orange	341.36	80	77.41 (77.25)	4.43 (4.48)	4.10 (4.18)	10
L_2	$C_{22}H_{14}NO_3Cl$	Pale yellow	375.80	80	70.31 (70.25)	3.75 (3.78)	3.73 (3.78)	10
$Co(L_1)_2 \cdot 2H_2O$	$C_{44}H_{34}N_2O_8Co$	Brick red	777.68	70	67.95 (68.03)	4.41 (4.47)	3.60 (3.67)	12
$Ni(L_1)_2 \cdot 2H_2O$	$C_{44}H_{34}N_2O_8Ni$	Light green	777.44	76	67.98 (67.92)	4.41 (4.44)	3.60 (3.55)	13
$Cu(L_1)_2 \cdot 2H_2O$	$C_{44}H_{34}N_2O_8Cu$	Brown	782.30	74	67.55 (67.43)	4.38 (4.40)	3.58 (3.51)	16
$Zn(L_1)_2 \cdot 2H_2O$	$C_{44}H_{34}N_2O_8Zn$	Light yellow	784.14	68	67.40 (67.46)	4.37 (4.32)	3.57 (3.24)	18
$Co(L_2)_2 \cdot 2H_2O$	$C_{44}H_{32}N_2O_8Cl_2Co$	Red	846.57	68	62.42 (62.53)	3.81 (3.92)	3.31 (3.54)	17
$Ni(L_2)_2 \cdot 2H_2O$	$C_{44}H_{32}N_2O_8Cl_2Ni$	Green	846.33	75	62.09 (62.01)	3.81 (3.77)	3.31 (3.37)	18
$Cu(L_2)_2 \cdot 2H_2O$	$C_{44}H_{32}N_2O_8Cl_2Cu$	Brown red	851.19	71	62.09 (62.27)	3.79 (3.76)	3.29 (3.25)	14
$Zn(L_2)_2 \cdot 2H_2O$	$C_{44}H_{32}N_2O_8Cl_2Zn$	Light yellow	853.03	65	61.95 (67.94)	3.78 (3.39)	3.28 (3.49)	15

the formation of stable complexes and the respective values are given in Table-2. The ligands showed a band near 1680-1630 cm^{-1} which is due to the presence of $\nu(\text{C}=\text{O})$ group of the chromone moiety which get shifted towards lower regions in the range 25-30 cm^{-1} in their corresponding metal complexes, indicating the coordination of oxygen of carbonyl group of the chromone to metal atom. A characteristic vibration band near 1605-1570 cm^{-1} get appears in the ligands due to $(-\text{CH}=\text{N}-)$ which gets shifted to lower regions in metal complexes by 30-20 cm^{-1} , indicating the participation of nitrogen atom in coordination to metal ion [16]. A sharp band appears near ν 1160-1140 cm^{-1} due to presence of ether linkage *i.e.* Ar-O-Ar which gets shifted in the complexes, also suggests ligational behaviour of the ligands towards the complexes. Appearance of weak bands around 440-420 and 555-520 cm^{-1} due to (M-N) and (M-O) stretching frequencies which confirms the complexation of ligands to the central metal ions through nitrogen and oxygen donor atoms [17]. All the complexes show a broad band near 3445-3420 cm^{-1} which indicates the presence of coordinated water molecules in the complexes [18].

Electronic spectra: The electronic spectrum of the ligands and their metal complexes was recorded in DMF to assume the geometry and ligand field nature around the central atom of the complexes.

The electronic spectra of L_1 and L_2 ligands showed two bands *i.e.* in the range of 26,000-27,000 cm^{-1} due to $n-\pi^*$ transitions and 31,000-36,000 cm^{-1} is due to the $\pi-\pi^*$ transitions with slightly shifted in the energy upon complexation of ligands

with metal atom which suggests ligational behaviour of ligands towards metal centre. The electronic spectra of the Co(II) and Ni(II) complexes exhibits three bands around 8,500, 16,500 and 23,000 cm^{-1} assigned to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ (ν_1), ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ (ν_2) and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3), respectively and three bands around 9,600, 15,885 and 23,500 cm^{-1} assigned to the ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ (ν_1), ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2) and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ (ν_3) transitions, respectively which are characteristics of octahedral geometry and further confirmed by the magnetic moment values, lies in the range of 4.0-5.0 BM for Co^{2+} complex and 2.90-3.20 BM for Ni^{2+} complex which are in good agreement for the same geometry [19]. The electronic spectra of Cu(II) complexes shows three bands at 11,454, 15,112 and 22,500 assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_2$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ and to LMCT transitions and magnetic moment shows a value of 1.80 BM which confirms the distorted octahedral geometry for Cu(II) complexes [20]. All the Zn(II) complexes exhibits a strong band in the range of 28000 cm^{-1} which is assigned for the charge transfer transition from metal to ligand. In the Zn(II) complexes no band is expected in the visible region because Zn(II) is in d^{10} configuration and are diamagnetic in nature.

${}^1\text{H}$ NMR and ${}^{13}\text{C}$ NMR spectra of ligands and their Zn(II) complexes: The ${}^1\text{H}$ NMR and ${}^{13}\text{C}$ NMR spectra of the Schiff bases and their Zn(II) complexes were recorded in CDCl_3 which indicates a shifting of electron density from ligand to the central metal ion in the transition metal complexes (Table-3). The ligand L_1 and L_2 show a singlet at δ 10.42 and 10.12 ppm due to azomethine proton $(-\text{CH}=\text{N}-)$ respectively

TABLE-2
IR SPECTRAL STUDIES (cm^{-1}) OF SCHIFF BASE LIGANDS AND THEIR METAL COMPLEXES

Compound	$\nu(-\text{OH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{Ar-O-Ar})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
L_1	–	1680	1605	1160	–	–
L_2	–	1675	1600	1157	–	–
$\text{Cu}(L_1)_2 \cdot 2\text{H}_2\text{O}$	3440	1641	1585	1140	520	433
$\text{Ni}(L_1)_2 \cdot 2\text{H}_2\text{O}$	3422	1635	1587	1145	530	430
$\text{Co}(L_1)_2 \cdot 2\text{H}_2\text{O}$	3425	1642	1593	1142	527	440
$\text{Zn}(L_1)_2 \cdot 2\text{H}_2\text{O}$	3445	1651	1587	1150	548	442
$\text{Cu}(L_2)_2 \cdot 2\text{H}_2\text{O}$	3438	1642	1583	1140	528	431
$\text{Ni}(L_2)_2 \cdot 2\text{H}_2\text{O}$	3420	1630	1570	1144	532	420
$\text{Co}(L_2)_2 \cdot 2\text{H}_2\text{O}$	3424	1655	1587	1140	525	430
$\text{Zn}(L_2)_2 \cdot 2\text{H}_2\text{O}$	3443	1649	1581	1148	555	422

TABLE-3
 ${}^1\text{H}$ NMR AND ${}^{13}\text{C}$ NMR SPECTRA OF LIGANDS AND ITS ZINC(II) COMPLEXES

Compounds	${}^1\text{H}$ NMR (CDCl_3) δ in ppm	${}^{13}\text{C}$ NMR (CDCl_3) δ in ppm
L_1	10.42 (s, 1H, $-\text{N}=\text{CH}$), 8.41 (s, 1H, $\text{C}_2\text{-Ar-H}$), 7.90-7.44 (m, 6H, Ar-H), 7.23-6.97 (m, 6H, Ar-H)	189.03 (C_4 , $\text{C}=\text{O}$), 163.7 ($-\text{CH}=\text{N}-$), 162.89 (C_2), 157.43 (C_9), 50.31 (C_2'), 148.54 ($\text{C}_{1'}$), 146.21 (C_5'), 140.51 (C_1'), 133.73 (C_7), 132.96 (C_6'), 130.81 (C_{10}), 129.17 (C_3), 128.75 (C_3' , C_5'), 128.22 (C_4'), 127.71 (C_2'' , C_6'), 126.57 (C_3), 124.63 (C_6), 123.41 (C_4'), 120.41 (C_8), 115.81 (C_3)
L_2	10.12 (s, 1H, $-\text{N}=\text{CH}$ proton), 8.25 (s, 1H, $\text{C}_2\text{-Ar-H}$), 7.84-7.51 (m, 6H, Ar-H), 7.47-6.99 (m, 7H, Ar-H)	188.77 (C_4 , $\text{C}=\text{O}$), 162.67 ($-\text{CH}=\text{N}-$), 162.56 (C_2), 157.10 (C_9), 151.71 (C_2'), 148.24 ($\text{C}_{1'}$), 142.38 (C_5'), 138.59 (C_1'), 133.52 (C_7), 132.11 (C_6'), 130.14 (C_{10}), 128.99 (C_3), 128.05 (C_3' , C_5'), 127.88 (C_4'), 126.92 (C_6'' , C_2'), 126.01 (C_3), 124.24 (C_6), 123.22 (C_4'), 119.98 (C_8), 115.79 (C_3)
$\text{Zn}(L_1)_2 \cdot 2\text{H}_2\text{O}$	10.45 (s, 1H, $-\text{N}=\text{CH}$ proton), 8.42 (s, 1H, $\text{C}_2\text{-Ar-H}$), 8.21-7.61 (m, 6H, Ar-H), 7.47-7.18 (m, 5H, Ar-H)	190.44 (C_4 , $\text{C}=\text{O}$), 166.67 ($-\text{CH}=\text{N}-$), 162.90 (C_2), 157.83 (C_9), 150.38 (C_2'), 148.55 ($\text{C}_{1'}$), 145.76 (C_5'), 141.68 (C_1'), 133.53 (C_7), 132.98 (C_6'), 130.83 (C_{10}), 129.19 (C_3), 128.74 (C_3' , C_5'), 128.25 (C_4'), 127.73 (C_6'' , C_2'), 126.55 (C_3), 124.60 (C_6), 123.39 (C_4'), 120.21 (C_8), 116.47 (C_3)
$\text{Zn}(L_2)_2 \cdot 2\text{H}_2\text{O}$	10.16 (s, 1H, $-\text{N}=\text{CH}$ proton), 8.26 (s, 1H, $\text{C}_2\text{-Ar-H}$), 7.83-7.52 (m, 6H, Ar-H), 7.42-7.08 (m, 7H, Ar-H)	190.01 (C_4 , $\text{C}=\text{O}$), 165.85 ($-\text{CH}=\text{N}-$), 162.57 (C_2), 157.12 (C_9), 151.77 (C_2'), 148.25 ($\text{C}_{1'}$), 141.98 (C_5'), 140.19 (C_1'), 133.92 (C_7), 132.14 (C_6'), 130.19 (C_{10}), 128.94 (C_3), 128.04 (C_3' , C_5'), 127.89 (C_4'), 126.94 (C_2'' , C_6'), 125.99 (C_3), 124.14 (C_6), 123.19 (C_4'), 119.48 (C_8), 116.11 (C_3)

which gets deshielded in their Zn(II) complexes at δ 10.45 and δ 10.16 ppm suggests the coordination of azomethine nitrogen to the central metal ion [21]. The aromatic protons of the synthesized Schiff base ligand (L_1) shows a singlet at δ 8.41 ppm of C_2 proton and two multiplets of twelve protons in the range δ 7.90-6.97 ppm. Further, in Schiff base ligand (L_2) a singlet of C_2 aromatic proton at δ 8.25 ppm is observed and two multiplets in the range δ 7.84-6.99 ppm is for thirteen protons which shows further shifting in the peaks of 1H NMR spectra of the Zn(II) complexes indicating the binding of N and O donor atoms of the ligands to the metal ion on complexation.

In ^{13}C NMR, the azomethine carbon of L_1 and L_2 ligand gives a peak at δ 163.7 and δ 164.5 ppm which shows downward field in Zn(II) complexes indicating the linkage through azomethine nitrogen [22]. Sharp singlets at δ 189.03 and δ 188.77 ppm appears due to carbonyl carbon of chromone which also gets shifted downward in complexes. Further, a number of peaks in the range of δ 160-115 ppm are observed due to aromatic carbons.

Thermal studies: Thermal studies for Co(II), Ni(II), Cu(II), Zn(II) complexes were carried out at room temperature to 800 °C that helps to determine the decomposition stages, decomposed products, observed and calculated mass loss percentage of metal complexes. Thermal decomposition pattern followed by all complexes is same and ended with formation of metal oxide. All the complexes shows three stages of decomposition in which first stage corresponds with the loss of two coordinated water molecules in the range of 50-250 °C with a loss of mass in the range of 6.12-6.40 %. In the second and third steps the complexes get decomposed by loss of ligand molecules within the range of temperature between 240-345 °C and 350-450 °C leaving the metal oxide as residue.

Conclusion

In the present work, Schiff base ligands *i.e.* 3-[(2-phenoxyphenylimino)methyl]chromen-4-one (L_1) and 3-[(5-chloro-2-phenoxyphenylimino)methyl]chromen-4-one (L_2) and their Co(II), Ni(II), Cu(II), Zn(II) complexes have been synthesized and characterized. Spectroscopic data suggested the coordination of azomethine nitrogen and carbonyl oxygen of chromone moiety to the metal atom in a bidentate manner. All the complexes of Co(II), Ni(II), Zn(II) possess octahedral geometry, while Cu(II) complexes exhibits distorted octahedral geometry.

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REFERENCES

1. N.S. Abdel-Kader and R.R. Mohamed, *J. Therm. Anal. Calorim.*, **114**, 603 (2013).
2. K. Kawakami, M. Miya-Uchi and T. Tanaka, *J. Inorg. Nucl. Chem.*, **33**, 3773 (1971).
3. A. Shama and H. Omara, *Spectrosc. Lett.*, **34**, 49 (2001).
4. M.I. Husain, M.A. Shukla and S.K. Agarwal, *J. Indian Chem. Soc.*, **56**, 306 (1979).
5. M.A. Bhat, M. Imran, S.A. Khan and N. Siddiqui, *J. Pharm. Sci.*, **67**, 151 (2005).
6. A.A. Abu-Hussen, *J. Coord. Chem.*, **59**, 157 (2006).
7. R. Villar, I. Encio, M. Migliaccio, M.G. Gil and V. Martinez-Merino, *Bioorg. Med. Chem.*, **12**, 963 (2004).
8. R. Nirmal, K. Meenakshi, P. Shanmugapandiyam and C.R. Prakash, *J. Young Pharm.*, **2**, 162 (2010).
9. N. Raman, R. Jeyamurugan, R.U. Rani, T. Baskaran and L. Mitu, *J. Coord. Chem.*, **63**, 1629 (2010).
10. A.A. Emara, A.M. Ali, E.M. Ragab and A.A. El-Asmy, *J. Coord. Chem.*, **61**, 2968 (2008).
11. A. Mobinikhaledi, M. Zendehele, P. Safari, A. Hamta and S.M. Shariatzadeh, *Synth. React. Inorg. Met.-Org. Chem. Nano-Metal Chem.*, **42**, 165 (2012).
12. N.K. Singh, A. Srivastava, A. Sodhi and P. Ranjan, *Transition Met. Chem.*, **25**, 133 (2000).
13. N. Raman, K. Pothiraj and T. Baskaran, *J. Mol. Struct.*, **1000**, 135 (2011).
14. M.T. Hussain, N.H. Rama and K.M. Khan, *Lett. Org. Chem.*, **7**, 557 (2010).
15. K.M. Khan, A. Ahmad, N. Ambreen, A. Ameen, S. Perveen, S.A. Khan and M.I. Choudhary, *Lett. Drug Des. Discov.*, **6**, 363 (2009).
16. S. Bhatnagar, S. Sahi, P. Kackar, S. Kaushik, M.K. Dave, A. Shukla and A. Goel, *Bioorg. Med. Chem. Lett.*, **20**, 4945 (2010).
17. X. Tai, X. Yin, Q. Chen and M. Tan, *Molecules*, **8**, 439 (2003).
18. B.D. Wang, Z.Y. Yang, M. Lü, J. Hai, Q. Wang and Z.-N. Chen, *J. Organomet. Chem.*, **694**, 4069 (2009).
19. P. Kavitha and K. Laxma Reddy, *Arab. J. Chem.*, **9**, 596 (2016).
20. Y. Li, Z.Y. Yang, Z.C. Liao, Z.C. Han and Z.C. Liu, *Inorg. Chem. Commun.*, **13**, 1213 (2010).
21. M. Odabasoglu, F. Arslan, H. Olmez and O. Buyukgungor, *Dyes Pigments*, **75**, 507 (2007).
22. K.H. Chang, C.C. Huang, Y.H. Liu, Y.H. Hu, P.-T. Chou and Y.C. Lin, *Dalton Trans.*, 1731 (2004).