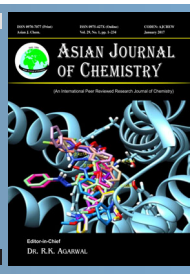
Asian Journal of Chemistry; Vol. 29, No. 1 (2017), 119-123

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2017.20152



Synthesis, Characterization and Antibacterial Activity of Nanocrystalline Ni(II)-6-methyl-4-oxo-4*H*-chromene-3-carbaldehyde Complex

N.H. KOLHE[1], S.S. JADHAV[1,*], S.J. TAKATE[1], D.V. AWARE[2] and A.E. ATHARE[1]

[1]Department of Chemistry and Research Centre, New Arts, Commerce and Science College, Ahmednagar-414 001
[2]Department of Chemistry, Arts, Commerce and Science College Sonai, Tal. Newasa, Dist. Ahmednagar-414 603, India

*Corresponding author: Fax: +91 241 2324715; Tel: +91 241 2324023; E-mail: ssjadhav1957@gmail.com

Received: 22 June 2016; *Accepted*: 21 September 2016; *Published online*: 29 October 2016; AJC-18110

The methyl substituted 3-formyl chromones was synthesized by Vilsmeier-Haack reaction. Nickel(II) complex was synthesized by refluxing the mixture of ligand solution taken into ethanol:acetic acid as 1:1 ratio and Ni(II) salt solution. The nature of bonding and geometry of the Ni(II) complex have been characterized from elemental analysis, FTIR, UV-visible spectral studies, thermal methods like TGA, the magnetic susceptibility, XRD, SEM, ESI-MS and molar conductance measurement, *etc*. Nickel(II) chloride is forming 1:2 (M:L) complex. The FTIR spectrum shows characteristic frequency band at 1614 cm^{-1} and 1695 cm^{-1}, which belongs to carbonyl of pyron ring and neighboring aldehyde carbonyl in ligand respectively. The Ni(II)-ligand complex shows characteristic frequency of M-O- bonding in 545-466 cm^{-1} region. The electronic spectrum shows three absorption bands and confirmed complex has octahedral geometry. The formation of nanocrystalline complex and their bird feather like morphology was identified by powder XRD and SEM. Finally, NiO residue was obtained in thermogravimetric study of the complex. The ligand and its Ni(II) complex were screened for antimicrobial activities by the agar well diffusion technique.

Keywords: Substituted 3-formylchromones, Nanocrystalline complex, Antibacterial activity.

INTRODUCTION

Several metal complexes are known to accelerate the drug action and efficacy of the organic therapeutic agent. The original observations that cisplatin complex had antibacterial properties led to the discovery of their antitumor properties and the development of the highly successful platinum anti-cancer drugs cisplatin and nidoplatin [1]. The complexes of gold have also been reported to have a wide range of antimicrobial activities [2]. Compounds containing the chromones skeleton are an important chelating agents belonging to the flavonoid group that occur naturally in different parts of the plants. They are minor constituents of the human as well as wild animal diet and have been reported to exhibit bioactivities [3]. The bioactivities like antifungal, antibacterial, antitumor [4], antioxidant [5], anti-HIV [6], antiallergenic and antiviral [7] are common.

In order to begin our efforts for such new medicines as effective anti-infective agents against bacteria and fungi, we thought of substituted heterocyclic chromones derivatives to β-diketones ligand with best complex forming ability with d-block metals [8]. The present research work deals with the synthesis, characterization of Ni(II)-6-methyl-4-oxo-4*H*-chromene-3-carbaldehyde and its antibacterial activity. The Ni(II)-chromone complex antibacterial activity was checked by well diffusion methods [9,10] and the inhibition zone was measured in mm-scale.

EXPERIMENTAL

Nickel chloride hexahydrate, phenol, acetic anhydride, pyridine, anhydrous sodium sulphate, anhydrous $AlCl_3$, aryl acetate, acetophenone, dimethyl formide, $POCl_3$, dimethyl sulfoxide and ethanol and solvent were of A.R. grade quality and were purchase from Loba Chem and Merck chemicals.

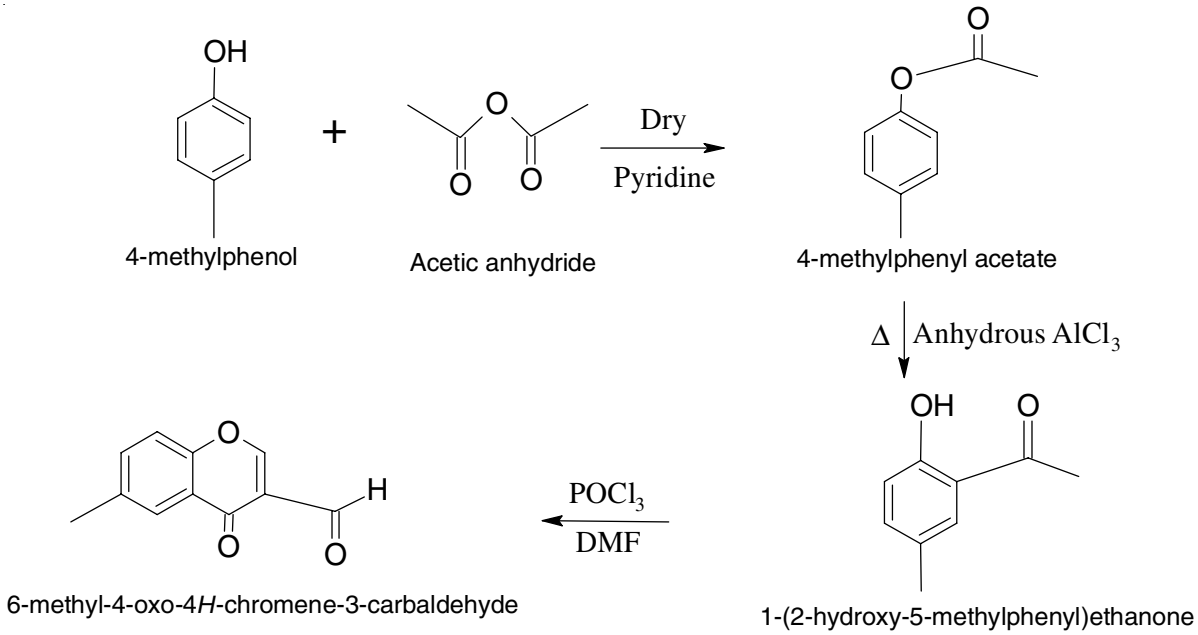
Fourier transformer infrared spectra were recorded in KBr disc on a IR Affinity-1 FTIR-Spectrophotometer Shimadzu in the range 4000-400 cm^{-1}. The electronic spectra was obtained using UV-1800 Shimadzu Spectrophotometer at 25 °C in 10^{-3} M concentration in DMSO solvent. Elemental analysis of C, H, N, O was done using Perkin Elmer analyzer. Magnetic properties were determined from Gouy balance method using analytical single pan balance. The solubility of the prepared complex was checked using solvent DMSO, acetonitrile, water

and ethanol. The conductivity of metal complexes was measured in DMF:H_2O using Conductivity Bridge, Model Systronics type 304 and a dip type cell which is calibrated with KCl solution. Thermal study was recorded on TGA-50, Shimadzu, thermogravimetric analyzer having TGA-50 H thermal analyzer detector. The synthesized complex was characterized by powder X-ray diffraction patterns recorded on a model Philips X-ray diffract meter with diffraction angle 2θ in between 20° to 80° using CuK_α radiation of wavelength 1.54058 Å. The grain size was calculated by Scherer's formula. The Surface morphology and elemental analysis of the samples were carried out using scanning electron microscopy characterization conducted using a JEOL-JEM-6360A analytical scanning electron microscope (Oxford). Also the complex was analyzed by the ESI-Mass Bruker Impact QTOF to gives the information about molecular weight and the possible structures of complex.

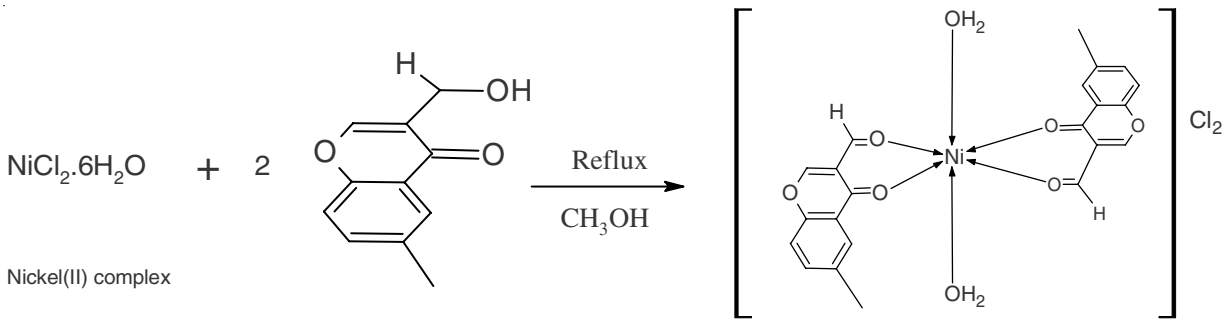
Synthesis of 6-methyl-4-oxo-4*H*-chromene-3-carbaldehyde: The ligand 6-methyl-4-oxo-4*H*-chromene-3-carbaldehyde was synthesized using the Vilsmeir-Haack reaction by reported methods [11-15] (**Scheme-I**). Yield 76.03 %, m.w. 188.17.

Synthesis of Ni(II) complex: 6-Methyl-4-oxo-4*H*-chromene-3-carbaldehyde ligand (0.395 g) was dissolved in 25 mL acetic acid: ethanol (1:1) and was reflux for 0.5 h. To this reflux ligand solution an 25 mL methanolic solution of appropriate Ni(II) chloride solution (0.25 g) was added drop by drop with continuous stirring and the resulting reaction mixture was further refluxed for 3 h and allow to stand for overnight. The spring green solid was separate out and it was filtered, washed with methanol. The complex was dried at room temperature in vacuum (**Scheme-II**). Anal. calcd. (found) for $C_{22}H_{20}O_8Cl_2Ni$: C, 48.75 % (48.09 %); H, 3.69 % (3.28 %); O, 27.05 % (27.17 %); Ni, 10.41 % (10.83) %, Colour: Spring green, m.w. 541.98, m.p. 251 °C, Yield: 69.48 %. The complex is soluble in chloroform, DMF and DMSO.

Antimicrobial activity: *in vitro* Antibacterial activity of the synthesized ligand 6-methyl-4-oxo-4*H*-chromene-3-carbaldehyde and the its Ni(II) complex was checked against Gram-negative bacteria *Escherichia coli* and Gram-positive bacteria *Bacillus subtilis*. The antibacterial activity was measured by agar well diffusion method at 100 µg/mL concentration [16-18]. Bacterial cultures were prepared in nutrient broth. 100 µL of 24 h old bacterial culture was spread on sterile, solidified nutrient agar plates. Wells were made using borer of 7 mm diameter. 100 µL samples were loaded in respective wells. Ciprofloxacin and DMSO were also loaded as positive and negative control respectively. The plates were incubated overnight at 37 °C in incubator. Next day zone of inhibition were observed and measured. All the experiments were performed in duplicate.



Scheme-I



Scheme-II

RESULTS AND DISCUSSION

Infrared spectra: The free ligand shows a high intensity band observed at 1651 cm^{-1} is assigned to ν(C=O) vibration suggesting the pyron carbonyl group [19]. The sharp intense band around 1695 cm^{-1} is assigned to ν(C=O) of the aldehyde carbonyl of the ligand [20]. The band at 1566-1485 cm^{-1} is assigned to the combination of ν(C=C) of the aromatic ring. A high intensity band in the region 1350-1336 cm^{-1} is assigned to oxo ν(C-O) vibration.

In the IR of Ni^{2+} complex, the band of ν(C=O) was shifted from 1651 to 1614 cm^{-1} indicates the bonding towards Ni^{2+}. The another band at 1695 cm^{-1} was shifted toward 1604 cm^{-1} which is attributed to donation of electron from ν(C=O) group of cyclic ketone. The frequency was decreased by 69-83 cm^{-1} unit toward 1267 cm^{-1} from 1350-1336 cm^{-1}. The infrared of prepared complexes have shown weak bands in the range of 545-486 cm^{-1}. This band was attributed to the ν(Ni-O) coordination [21].

Electronic spectra: The electronic spectrum of Ni(II) complex (Fig. 1) shows bands at 9670, 14415 and 24465 cm^{-1} assignable to ^3A_2g (F) - ^3T_2g (F) (ν_1), ^3A_2g (F) - ^3A_1g (F) (ν_2) and ^3A_2g (F) - ^3T_1g (P) (ν_3) transitions respectively, in an octahedral environment [22]. The band ν_1 (10 Dq) was observed at 27472.50 cm^{-1}. However, it is calculated by using equation suggested by Billing and Underhill. Racha parameter B_1 is 382.67 cm^{-1}, which is less than the free ion value of 1030 cm^{-1} indicating the covalent character of the complex (β = 0.371). The ratio ν_2/ν_1 and 1.15 % are further support the octahedral geometry [23,24] around the Ni(II) ion, The electronic spectra of ligand was shown at 277-384 nm indicate n–π* and π–π* transition.

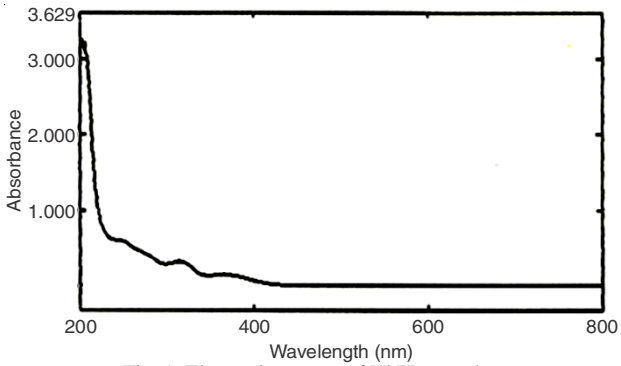


Fig. 1. Electronic spectra of Ni(II) complex

Magnetic susceptibility: The magnetic susceptibility of the nickel(II) complex in the solid state was determined by Gouy balance using $Hg[Co(SCN)_4]$ as a calibrate at room temperature. The magnetic moment of Ni(II)-6-methyl-4-oxo-4*H*-chromene-3-carbaldehyde complex has been found to be μ_{eff} 3.23 BM, suggesting that the octahedral geometry of the complex and the magnetic moment goes on increases due to the second order Zeeman effect [25].

Molar conductance: Molar conductance of the complex was measured in DMF:H_2O (90:10) water at a concentration of 0.0002 M. The observed conductance value for nickel complex is 154.1 Ohm^{-1} cm^2 mol^{-1}, indicates that the complex is 1:2 electrolyte [26].

Thermal analysis: The thermal stability of Ni(II) complex is studied by controlling heating rates 8 °C per min under static air atmosphere. The first decomposition temperature start from 102.20 °C and end with 125.64 °C with % weight loss 7.52 % is attributed with calculated % weight loss 7.63 % indicates the presence of coordinated water molecules [27,28] (Fig. 2). In second step, the % weight loss was 54.44 % was attributed with calculated % weight loss 53.57 % indicate the loss of four $C_{11}H_6O_4$ molecules at 199.79 to 260.98 °C. The final decomposition product was only 3.17 % which was attributed to weight loss 3.21 % indicate formation of C_9H_6O. The final residue was form of NiO. Which was stable at > 650 °C.

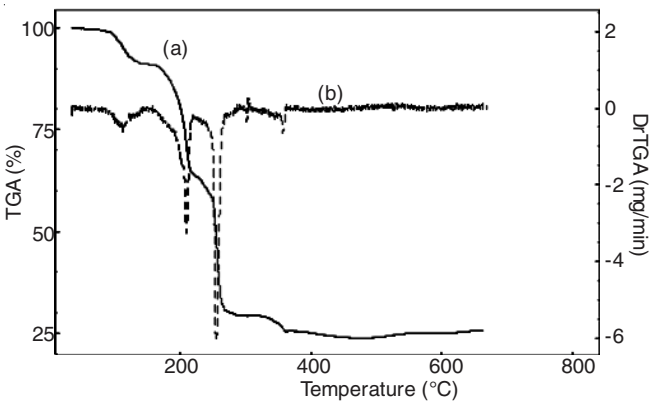


Fig. 2. Thermogram of complex (a) TG and (b) DTG

X-ray diffraction analysis: The confirmation of structure of the complex by taking the powder XRD recorded at 2θ ranges from 20-80° was performed. The complex XRD pattern shows sharp peak, indicating the complex are crystalline in nature. The line broadening of the XRD diffraction peaks in complex show formation of fine nanocrystalline particles (Fig. 3). By using Scherer's equation, average size of nanocrystalline complex is found to be 17 nm. The decrease in the size indicates the surface to volume ratio goes on increases.

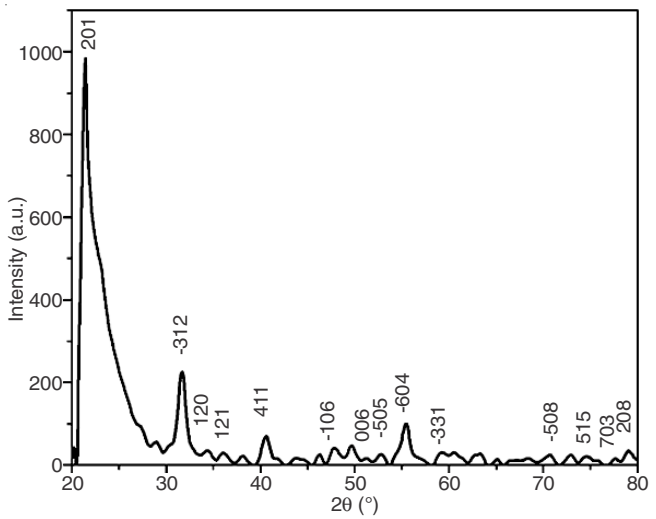


Fig. 3. Powder XRD pattern of Ni(II) complex

The crystallographic data of Ni(II) complex are summarized in Table-1. The complex is stable at room temperature.

TABLE-1
CRYSTALLOGRAPHIC DATA OF Ni(II) COMPLEX

Empirical formula	$C_{22}H_{20}O_8Cl_2Ni$
Formula weight	541.98
Crystal colour	Spring green
Temperature (K)	298
Wavelength (Å)	1.54050
Radiation	CuK_α
Crystal system	Monoclinic (P)
Space group	$P2_1/c$ (14)
A	1.9630
C	2.0556
Z	4
a (Å)	10.6
b (Å)	5.4
c (Å)	11.1
α (°)	90.00
β (°)	106
γ (°)	90
a/b	2.0556
c/b	1.9630
Volume (Å^3)	610.75

Scanning electron microscopy: The complex Ni(II)-6-methy-4-oxo-4*H*-chromene-3-carbaldehyde shows the nano-birds feather like morphology [29] (Fig. 4). The nanocrystalline complex has smaller particles with a high tendency to crystallization and homogeneous size distribution.

ESI-mass studies: Electrospray ionization spectra of complex are shown in Fig. 5. The ESI-mass spectra were measured in order to confirm the composition and the purity of the complexes. The complex was dissolved in DMSO and the spectra of complex displayed the molecular ion peak at *m/z* 628.2466, which is attributable to $[M+1]^+$ corresponding to the molecular weight of the complex formed during the measuring the ESI-mass spectra. The empirical formula of this complex is $C_{26}H_{32}NiO_{10}S_2$. The parent molecular weight of the complex is 541.98. But in the ESI-mass spectra shows *m/z* 628.2466 this is due the DMSO attack on the pyron ring. The successive degradation of the coordinate water molecules from the complex. The mass spectra obtained at *m/z* 589.30324 corresponding to the formation of stable ion $C_{26}H_{28}NiO_8S_2$.

Antimicrobial activity: The 6-methyl-4 oxo-4*H*-chromene-3-carbaldehyde as ligand and their Ni(II) complexes were evaluated for antibacterial activity with different strains of bacteria. The ligand exhibits higher antibacterial activity

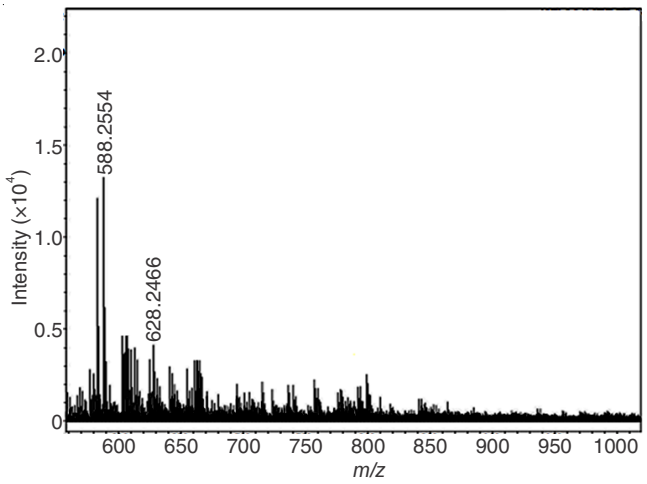


Fig. 5. ESI-mass spectra of complex

against *E. coli* and *B. subtilis* (Table-2). In the present investigation the coordination of ligand with Ni(II) ion the activity go on decrease or the complex become biologically inactive. According to overtone theory and chelation theory on the complexation the polarity decrease and lipophilic nature of metal atom increases. Hence the increase in biological activity. But here in this complex the biological activity decrease due to the formation of ionic complex and this is again showed by electrolytic nature of complex. The antimicrobial activity of ligand get decrease by forming the complex with Ni(II) metal ion and the complex is found to biologically inactive.

TABLE-2
ANTIMICROBIAL ACTIVITY OF
LIGAND AND Ni(II)-COMPLEX

Compound	Diameter of zone (mm) of inhibition			
	E. coli		*B. subtilis*	
1c	23	24	22	22
2a	00	00	00	00
Ciprofloxacin	40	39	35	35

Conclusion

Ni(II) complex have been synthesized using 6-methyl-4-oxo-4*H*-chromene-3-carbaldehyde and characterized by various analytical and spectral data. Based on the electronic spectra, magnetic moment and elemental analysis data, octahedral geometry was proposed for Ni(II) complex. The Ni(II)

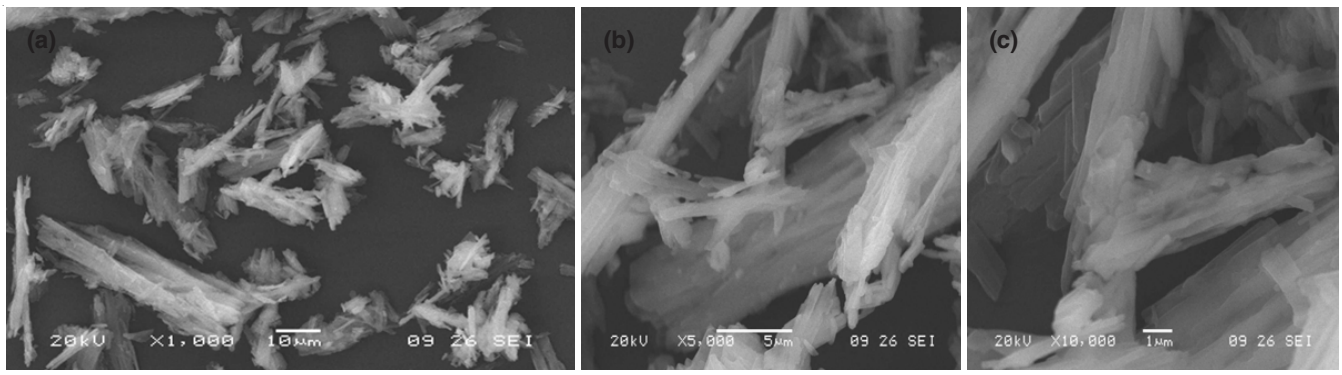


Fig. 4. Scanning electron micrograph of Ni(II) complex with different scales (a) 10 µm, (b) 5 µm and (c) 1 µm

complex shows nanocrystalline in nature with crystal size 17 nm having nanobirds feather like morphology. The powder XRD give the information of complex was monoclinic (P) crystal structure. The coordination between the ligand and Ni(II) metal ion through the both the oxygen of carbonyl from pyron ring and aldehyde group are shown by FTIR spectrum. The complex is 1:2 electrolytic in nature indicated by conductivity measurement. The complex was heated by non-isothermally in presence of air at about 650 °C temperature which shows the formation of NiO as a residue. The antimicrobial activity data has shown that the ligand 6-methyl-4-oxo-4*H*-chromene-3-carbaldehyde displayed higher activity but the activity goes on decrease in complex.

ACKNOWLEDGEMENTS

The authors are grateful to Management of Ahmednagar Jilha Maratha Vidya Prasarak Samaj's, Principal Dr. B.H. Zaware, New Arts Commerce and Science College, Ahmednagar for providing laboratory facilities. Two of the authors (Kolhe and Jadhav) also gratefully acknowledged the financial support of BCUD-Savitribai Phule Pune University, Pune, India (14SCI000295 and 14SCI000729).

REFERENCES

1. B. Rosenberg, E. Renshaw, L. Vancamp, J. Hartwick and J. Drobnik, *J. Bacteriol.*, **93**, 716 (1967).
2. A.M. Elsome, J.M.T. Hamilton-Miller, W. Brumfitt and W.C. Noble, *J. Antimicrob. Chemother.*, **37**, 911 (1996).
3. G.W. Kabalka and A.R. Mereddy, *Tetrahedron Lett.*, **46**, 6315 (2005).
4. S. Martens and A. Mithöfer, *Phytochemistry*, **66**, 2399 (2005).
5. J. Grassmann, S. Hippeli and E.F. Elstner, *Plant Physiol. Biochem.*, **40**, 471 (2002).
6. J. Wu, X. Wang, Y. Yi and K. Lee, *Bioorg. Med. Chem. Lett.*, **13**, 1813 (2003).
7. J. Seijas, M. Vazquez-Tato and R. Carballido-Reboredo, *J. Org. Chem.*, **70**, 2855 (2005).
8. P. Kavitha, M. Saritha and K.L. Reddy, *Spectrochim. Acta A*, **102**, 159 (2013).
9. W.K. Subezynski, W.E. Anholine, J.E. Hyde and O.H. Petering, *J. Am. Chem. Soc.*, **109**, 46 (1987).
10. M. Viswanathan, *Asian J. Chem.*, **20**, 6090 (2008).
11. A. Nohara, T. Ishiguro and Y. Sanno, *Tetrahedron Lett.*, **15**, 1183 (1974).
12. A. Vilsmeier and A. Haack, *Ber. Dtsch. Chem. Ges.*, **60**, 119 (1927).
13. K. Fries and G. Finck, *Chem. Ber.*, **41**, 4271 (1908).
14. K. Fries and W. Pfaffendorf, *Chem. Ber.*, **43**, 212 (1910).
15. W.L. Archer, *Org. Synth.*, **4**, 331 (1953).
16. N. Dharmaraj, P. Viswanathamurthi and K. Natarajan, *Transition Met. Chem.*, **26**, 105 (2001).
17. P.B. Chakrawarti, *J. Indian Chem. Soc.*, **78**, 273 (2001).
18. M.J. Pelczar, E.C.S. Chan and N.R. Krieg, Microbiology, Blackwell Science, New York (1998).
19. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley Interscience, New York, edn 2 (1970).
20. J.R. Ferraro, Low Frequency Vibrations of Inorganic and Coordination Compounds, John Wiley, New York, edn 2 (1971).
21. S. Chandra and L.K. Gupta, *Spectrochim. Acta A*, **62**, 1089 (2005).
22. P.K. Singh and D.N. Kumar, *Spectrochim. Acta A*, **64**, 853 (2006).
23. M.N. Patel and V.J. Patel, *Synth. React. Inorg. Met.-Org. Chem.*, **19**, 137 (1989).
24. E. Sinn and C.M. Harris, *Coord. Chem. Rev.*, **4**, 391 (1969).
25. A. Kumar, G. Singh, R.N. Handa, S.N. Dubey and P.J. Squattrito, *Indian J. Chem.*, **38A**, 613 (1999).
26. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
27. C.K. Modi, S.H. Patel and M.N. Patel, *J. Therm. Anal. Catal.*, **87**, 441 (2007).
28. G.G. Mohamed and Z.H. Abd El-Wahab, *J. Therm. Anal. Catal.*, **73**, 347 (2003).
29. Q. Shao, T. Wang, X. Wang and Y. Chen, *Front. Optoelectron. China*, **4**, 195 (2011).