Asian Journal of Chemistry; Vol. 33, No. 8 (2021), 1819-1823

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2021.23262

Synthesis, Characterization and Biological Evaluation of Metal(II) Complexes Containing Triphenylphosphine and Schiff Base Ligand Based on 3-Methoxysalicylaldehyde

G. GOKULNATH[1], P. ANITHA[2], R. MANIKANDAN[3] and C. UMARANI[1,*]

[1]Department of Chemistry, Government Arts College (Autonomous), Salem-636007, India
[2]Department of Chemistry, Government College of Engineering, Salem-636011, India
[3]Department of Chemistry, Loyola College of Arts and Science, Rasipuram, Namakkal-636202, India

*Corresponding author: E-mail: cuchem1966@gmail.com

Received: 23 April 2021; *Accepted*: 17 May 2021; *Published online*: 26 July 2021; AJC-20433

Schiff base ligand (HL) derived from condensation of 3-methoxy salicylaldehyde with 4-aminobenzoic acid and its metal(II) complexes containing triphenylphosphine of the type $[MCl(PPh_3)(L)]$ (M = Ni^{2+}, Co^{2+} or Cu^{2+}; L = bitendate Schiff base ligand) have been synthesized. All the metal(II) complexes were characterized by analytical and spectroscopic (FT-IR, electronic, ESI-Mass, ESR, ^1H, ^{13}C NMR and ^{31}P NMR) techniques. All the synthesized compounds were evaluated for *in vitro* antimicrobial efficiency against Gram-positive bacteria, Gram-negative bacteria and fungai using the agar well diffusion method. Anticancer activity *in vitro* of the ligand and its metal(II) complexes were also screened against MCF-7 cancer cell lines (human breast cancer cell line).

Keywords: Schiff base, Metal(II) complexes, 3-Methoxy salicylaldehyde, 4-Aminobenzoic acid, Biological activity.

INTRODUCTION

In coordination chemistry, Schiff base ligands have been extensively studied mainly because of their simple syntheses, availability, electronic properties and form complexes with almost all metal ions, coordinating to metal ions *via* azomethine nitrogen [1,2]. Schiff bases and their metal complexes have attracted a number of researchers because of their widespread applications including antibacterial, antifungal, antiviral, antiulcer, anticancer [3], antioxidant [4], anti-inflammatory [5] and herbicidal [6] activities, in addition to catalytic [7], thermal [8] and electrochemical [9] properties.

In the past decades, the chemistry of metal complexes with multidentate Schiff bases containing nitrogen and other donor compounds has been extensively studied [10]. The substituted salicylaldehyde exhibit remarkable antibacterial and antifungal activities, providing it chemotherapy potential [11,12]. Moreover, the metal complexes bearing such ligands have antimicrobial [13-15], antiviral [16], anti-inflammatory [16], cytotoxic [17] or hypoglycemic activities [18]. Schiff bases in combination with other ligands in their metal complexes form mixed ligand complexes, which is another alternative for the synthesis of specific metal complexes. These mixed ligand complexes containing neutral and anionic molecules as addition ligands have been of interest recently in view of their solid-state structures and the complex structure consisting of triphenylphosphine derivatives are of particular importance due to their probable beneficial catalytic activities [19]. Numerous mixed ligand complexes have been synthesised and discovered for their structure-function relationships. Among them, metal-phosphine complexes of biologically important ligands, such as salicylaldehyde, are of great interest [20,21].

In this work, we aimed to present the synthesis and characterization of the Co(II), Ni(II) and Cu(II) complexes containing triphenylphosphine and Schiff base ligand derived from 3-methoxysalicylaldehyde and 4-aminobenzoic acid. The antimicrobial activities and anticancer activities of the Schiff base ligand and its metal(II) complexes have also been explored.

EXPERIMENTAL

The chemicals used were chemically pure and AR grade. The solvents were purified and dried according to standard procedures [22]. The precursors $[MCl_2(PPh_3)_2]$ (M = Co^{2+}, Ni^{2+}

and Cu^{2+}) were synthesized by the literature procedure [23]. Elemental analyses of carbon, hydrogen and nitrogen were carried out using a Vario EL III elemental analyzer. FT-IR spectra were recorded on a Nicolet Avatar model spectrometer from 4000 to 400 cm^{-1} using KBr pellets. Electronic spectra were recorded on Shimadzu UV-1650 PC spectrophotometer in 800-200 nm range using methanol as the solvent. ^{1}H & ^{13}C NMR spectra were recorded in Jeol GSX-400 instrument using TMS as the internal standard. ^{31}P NMR spectrum of the complex was recorded in Jeol GSX- 400 instrument using *o*-phosphoric acid as a reference. Electron spin resonance spectrum (ESR) of the powder sample was recorded with a JEOL JES-FA200 instrument in X-band frequencies at room temperature using 2,22-diphenyl-1-picrylhydrazyl radical (DPPH•) as an internal standard at SAIF-IIT, Madras, India. The ESI-Mass spectra were performed on LC-MS Q-ToF Micro Analyzer (Shimadzu) at SAIF-Panjab University, Chandigarh, India. The melting points were checked on a Technico micro heating table and are uncorrected.

Synthesis of 4-((2-hydroxy-3-methoxybenzylidene)-amino)benzoic acid ligand (HL): A solution of 4-aminobenzoic acid (0.274 g, 2 mmol) in 10 mL of ethanol was added dropwise to a solution of 3-methoxy salicylaldhyde (0.304 g, 2 mmol) in 10 mL warm ethanol and the resulting reaction mixture was refluxed on a water bath for 4 h while yellow solid separated. The yellow solid was filtered off, washed with cold ethanol.

Synthesis of metal(II) complexes: A warm ethanolic solution (10 mL) of 4-(2-hydroxybenzylideneamino)benzoic acid (HL) (0.5 mmol) was added to metal precursors (0.5 mmol) in ethanol (10 mL). The resulting reaction mixture was refluxed for 5 hours. A crystalline powder was obtained on slow evaporation which was filtered, washed with ethanol and dried under *vacuum.*

Antimicrobial activity: The antimicrobial activity of the ligand and its metal(II) complexes was determined by using the agar well diffusion method [24]. The compounds were studied for the inhibitory effect on the growth of different gram bacteria such as *Staphylococcus aureus* (Gram-positive bacteria) and *Escherichia coli* (Gram-negative bacteria). The concentration of the standard (gentamicin), ligands and its metal(II) complexes was added 1000, 500, 200 and 100 µg/mL in DMSO for antibacterial studies.

The antifungal activity of the ligand and its metal(II) complexes were studied against *Aspergillus niger*. Standard amphotericin B, ligands and their complexes were added in 1000, 500, 200, and 100 µg/mL in DMSO for antifungal studies. Each test bacteria was swabbed on sterile Muller-Hinton agar plates by using a sterile cotton swab and then, 6 mm diameter wells were punched on the well by using a sterile cork borer. The spore suspension of test fungi was swab inoculated aseptically on the sterile potato dextrose agar plates followed by making wells of 6 mm diameter by using a sterile cork borer. The plates were incubated at 37 ºC overnight. After 24 h, the antimicrobial activities were expressed in terms of the zone diameter that inhibits (in millimetres) each microbial species by using different samples.

Anticancer activity: In this study, the MTT (3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2*H*-tetrazolium bromide) assay [25] was used to examine the anticancer activity of the ligand and its metal(II) complexes against MCF-7 (human breast cancer cell line). At 37 ºC, the cell lines were grown in an incubator (Thermo-Fisher) with 95% air and 5% CO_2. The compounds were dissolved in DMSO to form 10 mM stock solutions. The DMSO stock solutions were diluted to a concentration of < 0.1% in a cell culture medium to avoid the solvent effect on cell proliferation. Cells were seeded into 96-well plates and allowed to adhere overnight in an incubator at 37 ºC. The seeding densities used were 5×10^4 cells/well. Various concentrations (0.1-100 µg/mL) of ligand and its metal(II) complexes were added to the plates, and the plates were incubated for 48 h at 37 ºC. Then, 20 µL of MTT (5 mg/mL) was added and further incubated for another 4 h. Finally, DMSO (100 µL) was added, and the optical density (OD) of living cells was recorded at a wavelength of 570 nm. MTT colour formation was directly proportional to the number of viable cells, which validates its use in these studies. The half-maximum inhibitory concentration (IC_{50}) values were obtained and analysed according to the non-linear multipurpose curve fitting program GraphPad Prism.

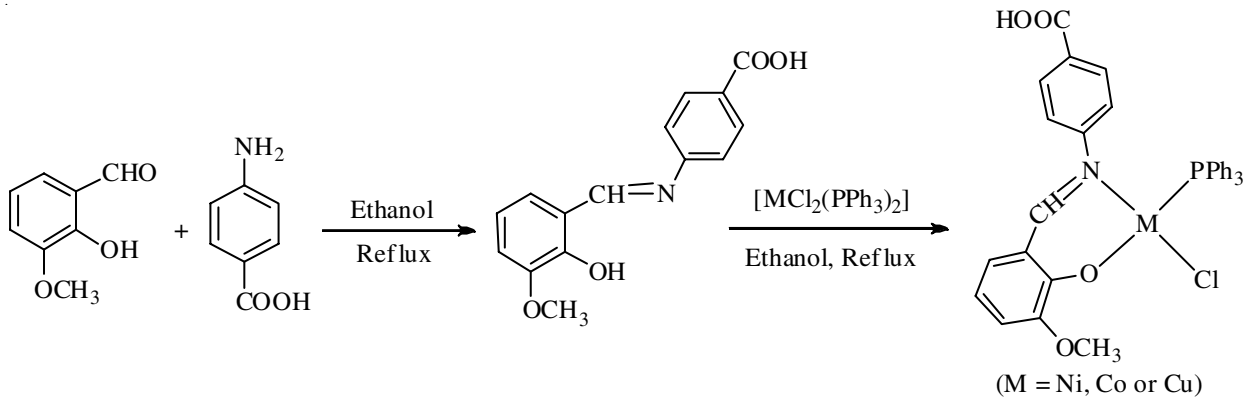
RESULTS AND DISCUSSION

Condensation of 3-methoxysalicylaldehyde with 4-aminobenzoic acid in ethanolic medium yielded the Schiff base (HL). The synthesis of the complexes were achieved by reacting one equivalent ethanolic solution of ligand (HL) with one equivalent metal precursors $[MCl_2(PPh_3)_2]$ (M = Co^{2+}, Ni^{2+} and Cu^{2+}) in ethanol (**Scheme-I**). The elemental analysis and physicochemical data of the ligand and their complexes are provided in Table-1.

IR spectra: The IR spectrum of the free ligand showed a strong vibration at 3500 cm^{-1} due to the presence of hydroxyl group. This band disappeared in the spectra of new complexes, suggesting that the ligands undergo deprotonation before combining with the metal ion. In addition, a band appeared at 1282 cm^{-1} due to phenolic C-O stretching in the free ligand that shifts to 1264-1230 cm^{-1} in the IR spectra of complexes, indicating coordination through phenolic oxygen atom [26]. A medium sharp band at 1676 cm^{-1} due to the azomethine C=N stretching

TABLE-1
PHYSICO-ANALYTICAL DATA OF LIGAND AND METAL(II) COMPLEXES

Compound	Colour	m.p. (°C)	Yield (%)	m.f.	Elemental analysis (%): Calculated (found)		
					C	H	N
HL	Yellow	162	82	$C_{15}H_{13}NO_4$	66.41 (66.87)	4.83 (4.21)	5.16 (5.82)
$[CoCl(PPh_3)L]$	Green	189	78	$C_{33}H_{27}NO_4PClCo$	63.22 (63.54)	4.34 (4.72)	2.23 (2.65)
$[NiCl(PPh_3)L]$	Brown	192	77	$C_{33}H_{27}NO_4PClNi$	63.25 (63.93)	4.34 (4.72)	2.24 (2.83)
$[CuCl(PPh_3)L]$	Yellow	203	78	$C_{33}H_{27}NO_4PClCu$	62.76 (62.13)	4.31 (4.83)	2.22 (2.45)



Scheme-I: Synthetic route of ligand and complexes

frequency of the free ligand was shifted to a lower frequency in the spectra of the complexes (1602, 1656, and 1654 cm^{-1} for **1**, **2** and **3**, respectively) indicating that the other coordination is through azomethine N atom [2]. Both free ligand and its metal(II) complexes shows the broad band in the region of 3396-3286 cm^{-1} can be assigned to -COOH group and this observation suggests that the non-participation of COOH group in bonding. On the other hand, the bands present in the 549-493 and 462-439 cm^{-1} ranges may be taken as an indication to the coordination between the metal ions with oxygen and nitrogen atoms, respectively (Table-2). Bands due to triphenylphosphine were also present in the expected region [27].

Electronic spectra: The electronic spectrum of free ligand exhibited bands at 243 and 302 nm, corresponding to the $n\rightarrow\pi^*$ transition of azomethine and $\pi\rightarrow\pi^*$ transitions of the aromatic ring, respectively. The absorption bands observed for all the complexes in the regions of 228-315 and 365-384 nm were assigned to intra-ligand transitions and ligand-to-metal charge transfer (LMCT) transitions, respectively [28]. The band that appeared in the region 430-480 nm was assigned to a *d-d* transition [29] (Table-2).

NMR spectra: In ^{1}H NMR, the singlet observed at δ 12.15 ppm in the ligand due to phenolic OH proton has disappeared in the ^{1}H NMR spectrum of Ni(II) complex. This revealed the coordination of ligand to Ni(II) through phenolic oxygen atom [30]. The ligand and their nickel complex show a sharp singlet at δ 11.98 and 11.96 ppm, respectively which is due to COOH group. Then a singlet observed at δ 8.33 ppm in the spectra of the free ligand assigned to the azomethine proton, which undergoes a shift to δ 8.41 ppm in nickel(II) complex, indicating the coordination of the azomethine nitrogen atom to the metal ions. Further, the methoxy protons of free ligand and nickel(II) complex appeared at δ 3.98 and 3.76 ppm, respectively. The signals corresponding to the protons of the aromatic moieties of the ligand and their metal(II) complex were observed as multiplets in the range δ 6.46-8.14 ppm.

The ^{13}C NMR spectra of the ligand and its nickel(II) complex showed a sharp peak at δ 187.56 and 191.42 ppm, which was attributed to the -COOH carbon. The phenolic carbon (C-O) and azomethine (CH=N) carbon have exhibited peaks at δ 161.24-167.35 and δ 153.52-160.29 ppm regions, respectively. Sharp peaks at δ 56.03 and 56.16 ppm suggest methoxy carbon. In addition, all aromatic carbon atoms exhibited their corresponding peaks in the regions of 111.07-148.54 ppm as expected (Table-3). The Co(II) and Cu(II) complexes are paramagnetic in nature. Therefore, its complexes cannot be observed on the ^{1}H & ^{13}C NMR spectra.

The ^{31}P NMR spectrum of nickel(II) complex was recorded to confirm the presence of the triphenylphosphine group in the complex (Fig. 1). A sharp singlet was observed at δ 28.24 ppm due to the presence of triphenylphosphine ligand in the complex. Moreover, Co(II) and Cu(II) complexes are paramagnetic in nature. Hence, their complexes cannot be observed in the ^{31}P NMR spectra.

TABLE-2
IR (cm^{-1}) AND ELECTRONIC (nm) SPECTRAL DATA OF LIGAND AND METAL(II) COMPLEXES

Compound	ν(OH)	ν(COOH)	ν(CN)	ν(C-O)	ν(M-O)	ν(M-N)	λ_{max}
HL	3500	3361	1676	1282	–	–	243, 302
[CoCl(PPh_3)(L)]	–	3396	1602	1230	493	439	228, 305, 383, 446
[NiCl(PPh_3)(L)]	–	3286	1656	1272	513	449	235, 315, 365, 430
[CuCl(PPh_3)(L)]	–	3298	1654	1261	549	462	230, 265, 308, 384, 480

TABLE-3
^{1}H NMR AND ^{13}C NMR SPECTRAL DATA OF LIGAND AND Ni(II) COMPLEX

Compound	^{1}H NMR (ppm)	^{13}C NMR (ppm)
HL	12.15 (-OH), 11.98 (COOH), 8.33 (CH=N), 6.65-8.14 (aromatic H), 3.98 (-OCH_3)	187.56 (COOH), 167.35 (phenolic C-O), 160.29 (CH=N), 113.79-132.41 (aromatic C), 56.16 (-OCH_3)
[NiCl(PPh_3)(L)]	11.96 (COOH), 8.41 (CH=N), 6.46-7.54 (aromatic H), 3.96 (-OCH_3)	191.42 (COOH), 161.24 (phenolic C-O), 153.52 (CH=N), 111.07-148.54 (aromatic C), 56.03 (-OCH_3)

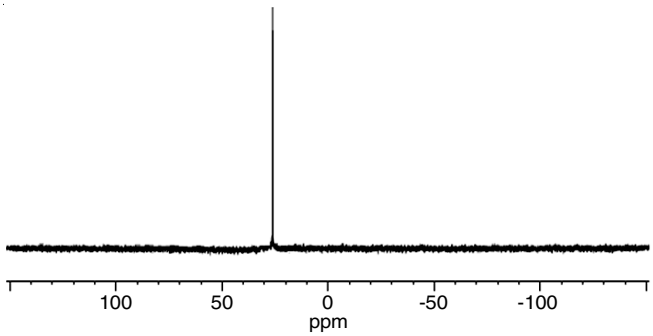


Fig. 1. ^{31}P NMR spectrum of [NiCl(PPh$_3$)(L)]

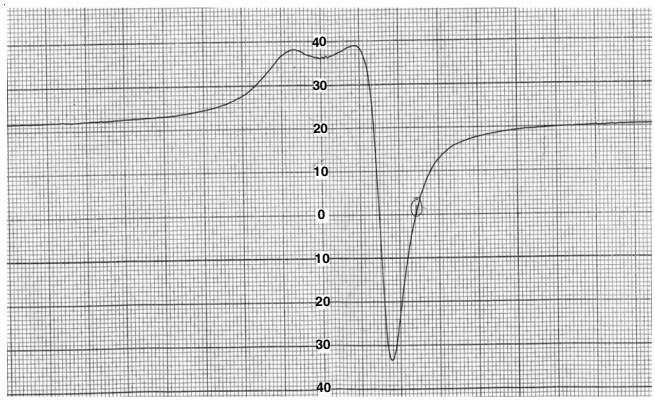


Fig. 2. ESR spectrum of [CuCl(PPh$_3$)(L)]

ESR spectra: The ESR spectrum of copper(II) complex was recorded at room temperature (Fig. 2). It exhibited anisotropic signal with $g_{\parallel} = 2.26$, $g_{\perp} = 2.10$, and $g_{aver.} = 1/3\ (g_{\perp} + 2\ g_{\parallel}) = 2.20$. The trend of the observed "g" values was $g_{\parallel} > g_{\perp} > g_e$ (2.0023), indicating that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital, which is in agreement with the electronic absorption spectroscopic assignments. In square planar complexes, the unpaired electron occupies the $d_{x^2-y^2}$ orbital with the $^2B_{1g}$ ground state, resulting in $g_{\parallel} > g_{\perp}$. The ESR spectra of the solid cobalt(II) and nickel(II) complexes at room temperature do not show the ESR signal because the rapid spin lattice relaxation of the cobalt(II) and nickel(II) broadens the lines at a higher temperature [31].

Mass spectra: ESI-mass spectral analyses of the metal(II) complexes were studied to confirm the molecular mass of the complexes (Fig. 3). The *m/z* values of the molecular ion peaks for the complexes [CoCl(PPh$_3$)L$_1$] (**1**), [NiCl(PPh$_3$)L$_1$] (**2**) and [CuCl(PPh$_3$)L$_1$] (**3**) were obtained at 627.20, 626.95 and 631.07 $[M]^+$, respectively. The calculated molecular masses corresponding to these complexes were 626.93, 626.69 and 631.54, respectively. The obtained *m/z* of molecular ion peaks of complexes were in good agreement with the calculated molecular masses of complexes.

Antimicrobial activity: The antimicrobial activities of ligand and metal(II) complexes (**1-3**) were tested against bacteria (*S. aureus* and *E. coli*) and fungi (*A. niger*). The results of the antibacterial and antifungal screening of the ligand, metal(II) complexes and standard are presented in Table-4. The antibacterial activity data indicate that the ligand and its metal(II) complexes are more active against the Gram +ve strain than the Gram -ve strain. This difference in the activity may be attributed to the fact that the cell wall of Gram +ve bacteria has more antigenic properties because the outer lipid membrane consists of polysaccharides. Furthermore, Co(II), Ni(II) and Cu(II) complexes are more effective than the ligand. The activity of metal(II) complexes is higher compared with that of the free ligand because of the lipophilic nature of metal complexes and can be explained using the chelation theory [32]. Among the active compounds, the Co(II) complex is more active than the standard drug.

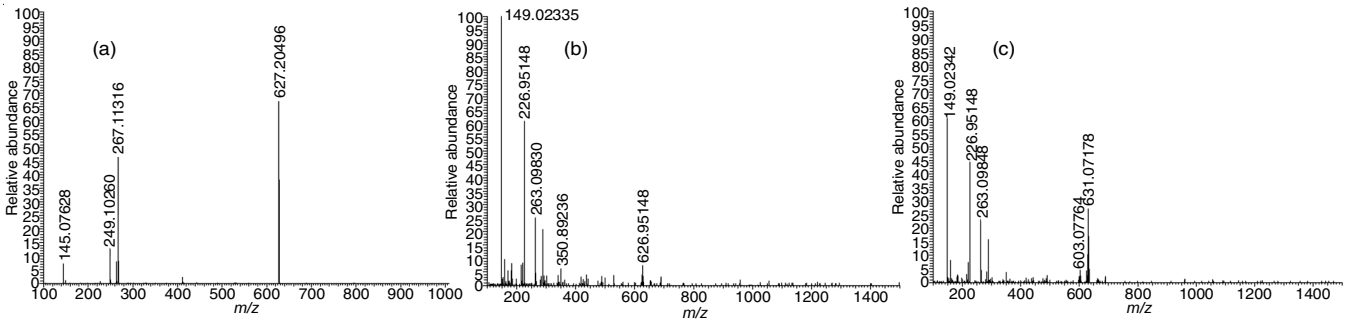


Fig. 3. ESI-mass spectrum of [CoCl(PPh$_3$)(L)] (a); [NiCl(PPh$_3$)(L)] (b); [CuCl(PPh$_3$)(L)] (c)

TABLE-4
ANTIMICROBIAL ACTIVITIES DATA OF FREE LIGAND AND METAL(II) COMPLEXES

Compounds	Zone of inhibition in mm (μg/mL)											
	Bacteria								Fungi			
	Staphylococcus aureus				*Escherichia coli*				*Aspergillus niger*			
	1000	500	200	100	1000	500	200	100	1000	500	200	100
Ligand	15.0	10.5	7.0	7.0	10.0	10.0	5.5	4.5	10.5	9.0	7.5	0
[CoCl(PPh$_3$)(L)]	24.0	22.5	13.5	10.5	18.0	13.5	10.5	10.5	16.5	9.0	9.0	0
[NiCl(PPh$_3$)(L)]	16.0	13.5	13.5	12.0	12.0	10.5	9.0	9.0	13.5	12.0	10.5	9
[CuCl(PPh$_3$)(L)]	16.5	13.5	7.5	7.5	15.0	10.5	9.0	9.0	14.0	9.0	9.0	0
Standard	18.0	18.0	18.0	18.0	17.5	17.5	17.5	17.5	15.0	15.0	15.0	15.0

Anticancer activity: Because the Schiff base ligand HL and its derived metal(II) complexes (**1-3**) showed good antimicrobial efficacy, it has been chosen for further evaluation of *in vitro* anticancer activity with MCF-7 cancer cells by using the MTT assay. The observed anticancer activities (in terms of IC_{50}) of the Schiff base ligand HL and its derived metal(II) complexes (**1-3**) on MCF-7 cancer cell lines are illustrated in Table-5. The test compounds were dissolved in DMSO, and for control, an equal amount of DMSO was used to monitor the activity of solvent alone in this experiment. The compounds exhibited anticancer activity at ≥ 1 µg/mL. Increasing the concentration of complexes from 0.1 to 100 µg/mL, increases cell inhibition. The results showed that on MCF-7 cancer cells (IC_{50} = 5.82 µg/mL), the Cu(II) complex has a higher activity than the ligand and other metal(II) complexes.

TABLE-5
IC_{50} (µG/ML) VALUE OF LIGAND AND ITS METAL(II) COMPLEXES AGAINST MCF-7 CELLS (HUMAN BREAST CANCER CELLS)

Compound	IC_{50} (µg/mL)[a]
Ligand	22.99
[$CoCl(PPh_3)(L)$]	12.86
[$NiCl(PPh_3)(L)$]	21.19
[$CuCl(PPh_3)(L)$]	5.82
Cisplatin	12.33

[a]50% inhibitory concentration after exposure for 48 h in the MTT assay.

Conclusion

Co(II), Ni(II) and Cu(II) complexes containing triphenyl phosphine and a Schiff base ligand have been synthesized and characterized based on analytical data and various spectral studies. Physico-chemical studies have suggested the square planar geometry for Ni(II), Co(II), and Cu(II) complexes. The antimicrobial activities of the ligand and its metal(II) complexes indicate that Co(II) complexes possess higher bacterial and fungal activities than Ni(II) and Cu(II) metal(II) complexes and the ligand. Furthermore, *in vitro* anticancer properties of all compounds were screened against MCF-7 cancer cell lines. Results revealed that the anticancer activity of Cu(II) complex is higher than that of standard, free ligand and other complexes.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. P.A. Vigato and S. Tamburini, *Coord. Chem. Rev.*, **248**, 1717 (2004); https://doi.org/10.1016/j.cct.2003.09.003
2. M. Sonmez, H.G. Sogukomerogullari, F. Oztemel and I. Berber, *Med. Chem. Res.*, **23**, 3451 (2014); https://doi.org/10.1007/s00044-014-0925-0
3. D. Chaturvedi and M. Kamboj, *Chem. Sci. J.*, **7**, 1 (2016); https://doi.org/10.4172/2150-3494.1000e114
4. B. Iftikhar, K. Javed, M.S.U. Khan, Z. Akhter, B. Mirza and V. Mckee, *J. Mol. Struct.*, **1155**, 337 (2018); https://doi.org/10.1016/j.molstruc.2017.11.022
5. M.S. Alam, J.H. Choi and D.U. Lee, *Bioorg. Med. Chem.*, **20**, 4103 (2012); https://doi.org/10.1016/j.bmc.2012.04.058
6. S.B. Desai, P.B. Desai and K.R. Desai, *Heterocycl. Commun.*, **7**, 83 (2001); https://doi.org/10.1515/HC.2001.7.1.83
7. S. Sarkar, S.K. Nag, A.P. Chattopadhyay, K. Dey, S.M. Islam, A. Sarkar and S. Sarkar, *J. Mol. Struct.*, **1160**, 9 (2018); https://doi.org/10.1016/j.molstruc.2018.01.035
8. M.A. Ayoub, E.H. Abd-Elnasser, M.A. Ahmed and M.G. Rizk, *J. Mol. Struct.*, **1163**, 379 (2018); https://doi.org/10.1016/j.molstruc.2018.03.006
9. R.N. Egekenze, Y. Gultneh and R. Butcher, *Inorg. Chim. Acta*, **478**, 232 (2018); https://doi.org/10.1016/j.ica.2018.01.027
10. A. Hasaninejad, S. Mojikhalifeh and M. Beyrati, *Appl. Organomet. Chem.*, **32**, e4380 (2018); https://doi.org/10.1002/aoc.4380
11. G.L. Backes, D.M. Neumann and B.S. Jursic, *Bioorg. Med. Chem.*, **22**, 4629 (2014); https://doi.org/10.1016/j.bmc.2014.07.022
12. E. Pelttari, M. Lehtinen and H. Elo, *Z. Naturforsch. C*, **66**, 571 (2011); https://doi.org/10.1515/znc-2011-11-1206
13. L.A. Saghatforoush, A. Aminkhani and F. Chalabian, *Transition Met. Chem.*, **34**, 899 (2009); https://doi.org/10.1007/s11243-009-9279-8
14. M.S. Refat, I.M. El-Deen, Z.M. Anwer and S. El-Ghol, *J. Coord. Chem.*, **62**, 1709 (2009); https://doi.org/10.1080/00958970802684205
15. C.D. Sheela, C. Anitha, P. Tharmaraj and D. Kodimunthri, *J. Coord. Chem.*, **63**, 884 (2010); https://doi.org/10.1080/00958971003660416
16. M. Gielen and E.R.T. Tiekink, Metalotherapeutic Drugs and Metal-Based Diagnostic Agents: The Uses of Metal in Medicine, John Wiley & Sons: New York (2005).
17. A. Ray, G.M. Rosair, R. Kadam and S. Mitra, *Polyhedron*, **28**, 796 (2009); https://doi.org/10.1016/j.poly.2008.12.040
18. J. Vanco, J. Marek, Z. Travnicek, E. Racanska, J. Muselik and O. Svajlenova, *J. Inorg. Biochem.*, **102**, 595 (2008); https://doi.org/10.1016/j.jinorgbio.2007.10.003
19. M.M. Tamizh, K. Mereiter, K. Kirchner and R. Karvembu, *J. Organomet. Chem.*, **700**, 194 (2012); https://doi.org/10.1016/j.jorganchem.2011.12.016
20. R. Prabhakaran, S.V. Renukadevi, R. Karvembu, R. Huang, J. Mautz, G. Huttner, R. Subashkumar and K. Natarajan, *Eur. J. Med. Chem.*, **43**, 268 (2008); https://doi.org/10.1016/j.ejmech.2007.03.006
21. G. Erre, S. Enthaler, K. Junge, S. Gladiali and M. Beller, *Coord. Chem. Rev.*, **252**, 471 (2008); https://doi.org/10.1016/j.ccr.2007.09.021
22. A.I. Vogal, Textbook of Practical Organic Chemistry, Eds.: 5, ELBS: London (1989).
23. L.M. Venanzi, *J. Chem. Soc.*, 719 (1958); https://doi.org/10.1039/jr9580000719
24. M. Balouiri, M. Sadiki and S.K. Ibnsouda, *J. Pharm. Anal.*, **6**, 71 (2016); https://doi.org/10.1016/j.jpha.2015.11.005
25. J.D. Burton, *Methods Mol. Med.*, **110**, 69 (2005);
26. M.M. Tamizh, B. Varghese, A. Endo and R. Karvembu, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **77**, 411 (2010); https://doi.org/10.1016/j.saa.2010.06.004
27. M.M. Tamizh, K. Mereiter, K. Kirchner, B.R. Bhat and R. Karvembu, *Polyhedron*, **28**, 2157 (2009); https://doi.org/10.1016/j.poly.2009.04.021
28. M.B. Ferrari, S. Capacchi, F. Bisceglie, G. Pelosi and P. Tarasconi, *Inorg. Chim. Acta*, **312**, 81 (2001); https://doi.org/10.1016/S0020-1693(00)00339-X
29. N.C. Kasuga, K. Sekino, C. Koumo, N. Shimada, M. Ishikawa and K. Nomiya, *J. Inorg. Biochem.*, **84**, 55 (2001); https://doi.org/10.1016/S0162-0134(00)00221-X
30. S. Güveli, N. Özdemir, T. Bal-Demirci, B. Ülküseven, M. Dinçer and Ö. Andaç, *Polyhedron*, **29**, 2393 (2010); https://doi.org/10.1016/j.poly.2010.05.004
31. S. Chandra and U. Kumar, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **61**, 219 (2005); https://doi.org/10.1016/j.saa.2004.03.036.
32. B.G. Tweedy, *Phytopathology*, **55**, 910 (1964).