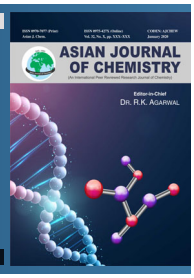
Asian Journal of Chemistry; Vol. 32, No. 10 (2020), 2507-2514

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2020.22754



One Pot Synthesis of Schiff Base Complexes of Cu(II), Zn(II), Ni(II), Co(II) and their Cytotoxicity, Molecular Docking and Antibacterial Activity

A. ASHMA[1,2], A. SUDHA[2] , S.L. ASHOK KUMAR[3], G. SASIKUMAR[2], and S.J. ASKAR ALI[2,*]

[1]Department of Chemistry, Aalim Muhammed Salegh College of Engineering, Avadi-IAF, Chennai-600055, India
[2]PG and Research Department of Chemistry, The New College (Autonomous), Chennai-600014, India
[3]Department of Chemistry, GRT Institute of Engineering and Technology, Thiruthani, Chennai-631209, India

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

Received: 2 April 2020; *Accepted*: 30 May 2020; *Published online*: 25 September 2020; AJC-20061

A novel Schiff base ligand (L), N(4)-cyclohexyl-2-(1-(5-chlorothiophen-2-yl)ethylidene)hydrazine carbothioamide was synthesized from isothiocyanatocyclohexane and hydrazine. All the synthesized transition metal(II) complexes were characterized by functional peak using ^{1}H NMR, ^{13}C NMR, FT-IR, UV-vis spectroscopy and metal complex atomic ratio of complexes of thiosemicarbazones were characterized by elemental analysis. Schiff base and its metal(II) complexes were screened *in vitro* medicinal drug activity against Gram positive and Gram-negative microorganisms and anti-cancer activity against human carcinoma cell line MCF-7 was detected with nickel(II) and cobalt(II) complexes. Further, the cytotoxity of ligand and its metal(II) complexes were tested on a Monkeys normal cell line and found to be non-toxic (< 200 µg/mL). In the present work, the molecular mechanism of anticancer (breast cancer) activity of the compounds were also disscussed.

Keywords: Schiff base ligand, Thiosemicarbazone, Metal complexes, Antibacterial screening, Cytotoxicity activity.

INTRODUCTION

Benzimidazole derivatives represent one in every of the chemical categories that showed potent malignant neoplasm activity particularly against carcinoma cell line (MCF-7) [1-5]. Benzimidazole nucleus was used as biomimetic of G residues and several benzimidazole derivatives inhibit epithelium cell growth and suppress growth each *in vitro* and *in vivo* [6]. Recently, several amalgamate benzimidazoles exhibit promising malignant neoplasm activity [7-14]. The synthesis and biological activities of [1,2,4]triazino-[2,3]benzimidazoles likewise as [1,2,4]triazino-[4,3-*a*]benzimi-dazoles [7-11] are widely reported. However, little work had been reported on the biological activity of [1,2,4]triazino[4,5-*a*]benzimidazoles [8]. Transition metal complexes of thiosemicarbazones have a number of pharmacological applications such as antibacterial, antifungal, antitumor, anticancer and anti-inflammatory activities [4-7]. The metal complexes of thiosemicarbazones have more cytotoxic agent [8,9] than the free ligand. Thiosemicarbazone have the coordination ability to form mononuclear (or) binuclear metal complexes [10-13]. They can bind metal ions as bidentate NS- or tridentate NNS- donor ligands forming five-membered chelate rings. Thiosemicarbazones and their transition metal complexes have good growth inhibiting activity against the MCF-7 cancer cells [14].

In this investigation, a bidentate Schiff base ligand and its transition metal(II) complexes were synthesized using one-pot chemical synthesis. The synthesized Schiff base ligand and its metal complexes were characterized by analytical techniques such as UV-visible, FT-IR, NMR, LC-MS and SEM analysis. Additionally, their toxicity effects on Vero and MCF-7 neoplastic cell lines *in vitro* were evaluated.

EXPERIMENTAL

Cyclohexyl isothiocyanate, 5-chloro acetyl-2-thiophene (Sigma Aldrich), hydrazine hydrate (Sigma Aldrich), nickel(II) perchlorate hexahydrate (Sigma Aldrich), copper(II) perchlorate hexahydrate (Sigma Aldrich), zinc chloride (Sigma Aldrich) and cobalt chloride (Sigma Aldrich) were used. Analytical

grade methanol and other solvents were used without further purification. Antibacterial strains were obtained from microbial type culture collection (MTCC), Indian Institute of Microbial Technology (IMTECH), Chandigarh.

Synthesis of Schiff base ligand (L): Ethanolic solutions of cyclohexyl isothiocyanate (1.4123 g, 10 mmol) and hydrazine hydrate (0.5006 g, 10 mmol) were mixed with constant stirring. The stirring was continued for 1 h and recrystallized from ethanol solution. The recrystallized product yield is 93%.

A Schiff base N(4)-cyclohexyl thiosemicarbazide (1.733 g, 10 mmol) was dissolved in methanol (50 mL) and addition to 5-chloro-2-acetyl thiophene (1.606 g, 10 mmol) dissolved in methanol (10 mL), reflux continuously for 4 h. Then, the above solution with few drops of carboxylic acid. The yellow crystalline product was unbroken aside for slow evaporation at temperature, then filtered, washed with solvent and dried.

Synthesis of Schiff base ligand @ metal complexes: Schiff base ligand and its metal(II) complexes were synthesized by the following standard procedure. A Schiff base (N(4)-cyclohexyl thiosemicarbazide (1.733 g, 10 mmol) was dissolved in methyl alcohol (50 mL) and then 5-chloro-2-acetyl thiophene (1.606 g, 10 mmol) dissolved in methyl alcohol (10 mL) were mixed with constant stirring. Then, 0.1 mmol of copper(II) perchlorate hexahydrate solution was slowly added on top of resolution. The reaction mixture was refluxed in an oil bath at 80 ºC for 4 h. Then, the supernatant solution was filtered using Whatman filter paper. The precipitate was washed thoroughly using diethyl ether and dried in a vacuum oven. The same procedure was repeated using zinc chloride, nickel(II) perchlorate hexahydrate, cobalt nitrate instead of copper(II) perchlorate hexahydrate to synthesize the transition metal(II) based Schiff base ligand (L) complexes. The crude precipitate of Schiff base ligand and its metal(II) complexes was recrystallized from the acetonitrile-methanol mixture.

Cytotoxicity screening by XTT kit method: Cell proliferation assay kit procured from Cayman (Cat. No. 100110200) used for this experiment. Vero cells and MCF-7 obtained from Tamilnadu Veterinary Animal Sciences University, were maintained in our facility and used for this assay.

Vero cells and MCF-7 were grown separately at 2×10^4 cells/mL in T25 flask contains culture medium for 24 h at 37 °C and then cells were seeded in 96 well tissue culture plates for 24 h. Once the confluence reached, the cells were treated with different concentrations of test samples Schiff base ligand (L) and its complexes, and incubated for upto 48 h followed by analysis with XTT proliferation kit by ELISA.

XTT assay was performed according to the (Cayman) manufacturers instruction, briefly, 10 µL of the reconstituted XTT mixture used with pipette. Then mixed with 1 min on an orbital shaker then cells were incubated for 4 h at 37 °C in a CO_2 incubator and plates were mixed gently on an orbital shaker for 1 min to ensure homogeneous distribution of colour. Samples were read at 450 nm wavelength on a microplate reader. Experiments were repeated for three times and the average values were calculated and analyzed as percentage of inhibition.

Molecular docking analysis: The molecular docking studies of ligand and its metal(II) complexes were carried out by maestro program inbuilt in the Schrödinger suite. Initially, the ligand structures are sketched by maestro building tools and then the ligand was pre-processed in the ligand preparation step by using force field OPLS-2005 and gave low energy structure conformers which is suitable for molecular docking studies. The three-dimensional structure of thymidylate synthase (PDB ID: 1HZW) was downloaded from protein data bank (http://www.pdb.org). In the protein preparation step used to assign bond orders, add hydrogen atoms and removed water beyond 5 Å.

Finally, the protein structure was fully optimized by using force field (OPLS-2005). The prepared ligand structure was docked into binding site of the thymidylate synthase using the glide with standard precision mode. The energy calculations were made using genetic algorithms. The outputs were exported to PyMol for visual inspection of the binding modes and for possible π-π stacking, hydrogen bond and hydrophobic exchanges of the compounds with thymidylate synthase.

Characterization studies: The FT-IR spectra were obtained in KBr disc by ABB Bomem (Model-MB 3000) spectrometer from 4000 to 400 cm^{-1}. ^1H NMR and ^{13}C NMR were recorded on Bruker-Advance III 500 MHz NMR instrument using $CDCl_3$ as a solvent and TMS as internal reference (chemical shift in δ ppm). C, H, N, S analyses of the compounds were performed on Vario micro cubes elemental analyzer. The UV-visible spectrum was recorded on UV-vis spectrophotometer (Elico SL159) in DMSO solvent. EPR spectra of the complexes were recorded in the solid state at room temperature using X band EPR spectroscopy. Cyclic voltammetric measurements were made in DMSO solvent on a high-power potentiostat/galvanostat/ZRA using glassy carbon as working electrode with tetrabutylammonium perchlorate as the supporting electrolyte. *in vitro* Antibacterial screening of ligand and its complexes performed against human bacterial pathogens using Kirby Bauer disc diffusion method.

RESULTS AND DISCUSSION

FTIR spectroscopy: The FT-IR range of Schiff base ligand (L) shows a couple of medium intensity groups present at 3400-3200 cm^{-1} region, which compare to $\nu(NH_2)$ extending vibration are appeared in Fig. 1a (inset orange colour). Fig. 1(b-e) show the Schiff base ligand-metal(II) complexes (black-blue colour), these groups are missing in the range. Additionally, no strong absorption band is seen at 1735 cm^{-1} showing the non-appearance of ν(C=O) group of carbothioamide. This demonstrates the buildup of carbonyl groups of benzimidazole and amino group of ligands has occurred [15,16]. Another band for azomethine ν(C=N) extending vibration was recorded because of this complex response at 1596 cm^{-1} [17,18] From this spectra of Schiff base ligand and its metal complexes, metals assume a significant role in the FTIR range.

UV-Visible spectroscopy: The electronic spectra of the ligand (L) and its metal(II) complexes were recorded in DMSO (1×10^{-3} M) solvent are shown in Fig. 2 and spectral data are shown in Table-1. The free ligand showed bands at 266 and

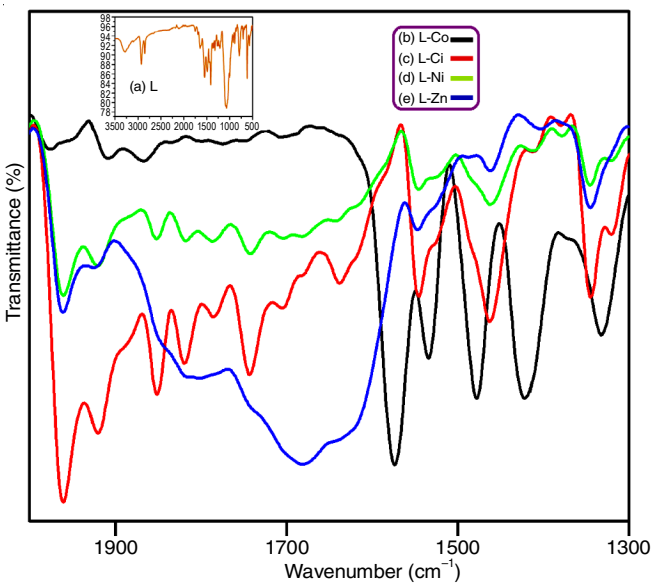


Fig. 1. FTIR spectra of (a) Schiff base ligand (L), (b) L-Co(II), (c) L-Cu(II), (d) L-Ni(II) and (e) L-Zn(II) complexes

TABLE-1
ELECTRONIC SPECTRA OF LIGAND (L) AND ITS METAL(II) COMPLEXES

Compounds	λ_{max} (nm)	Transition assignment	Geometry
Ligand [L]	266 330	π-π* n-π*	–
[L-$CoCl_2$]	269 348 526	π-π* n-π* Charge transfer	Octahedral
[L-Ni]H_2O	268 346 467	π-π* n-π* Charge transfer	Square planar
[L-Cu]H_2O	268 361 514	π-π* n-π* Charge transfer	Square planar
[L-$ZnCl_2$]	264 350	π-π* n-π*	Octahedral

330 nm attributed to π-π* and n-π* transitions respectively of the azomethine (C=N) bond. The electronic spectra of nickel and copper(II) complexes showed band at 467 and 514 nm respectively due to the ligand to metal charge transfer transitions. Such a feature is expected for square planar complexes [19].

In cobalt(II) complex, the transition at 526 nm is revealed to charge transfer band arising from S → M(II) transition *i.e.*, $^4T_{1g}$ (F) → $^4T_{1g}$ (P), which clearly indicate the octahedral geometry of the complex. In Zn(II) complex, the transition at 264 and 250 nm shows that the octahedral geometry of the complex [20].

NMR studies: The ^{1}H NMR spectrum of Schiff base ligand showed two broad singlets at δ 8.44 and δ 7.37 ppm assignable to the NH protons present in the molecule. Ligand showed singlet signal at δ 2.20 ppm corresponding to the ketone methyl group. The ^{13}C NMR spectrum of ligand revealed well defined peaks at 176.09 ppm assignable to thione carbon (C=S). Azomethine carbon (-C=N) appeared at δ 144.05 ppm [21]. The synthesized Schiff base ligand (L) structure are confirmed through the UV-vis spectra and NMR spectral studies.

SEM morphology: The SEM micrographs of the ligand and its metal(II) complexes are presented in Fig. 3(a-e). The larger particles are formed by agglomeration, as predicted by morphological structure. Fig. 3e shows the rod like better morphological structure due to the strong coordination between Schiff base ligand and its Zn(II) complex.

EPR spectral studies: The solid state EPR spectra of Schiff base ligand (L) and its copper complex in the polycrystalline state at 278 K was recorded in the X-band region, using 100 KHz field modulation. The copper complex was found to be anisotropic with g-values g_x = 2.282 g_y = 2.192, g_z = 2.051. The spectrum is slightly rhombic with $g_x > g_y > g_z > 2.0023$. g_x can be considered almost equal to g_y indicates that a d_{x^2}-d_{y^2} is assigned to the complex as a square planar systems. However lack of copper hyperfine data, shows that, there is extensive delocalization on to the ligand or excess of g-/A strain in the system. This can be due to the deviations from stick square planar geometry [22]. The deviation of the g value from that

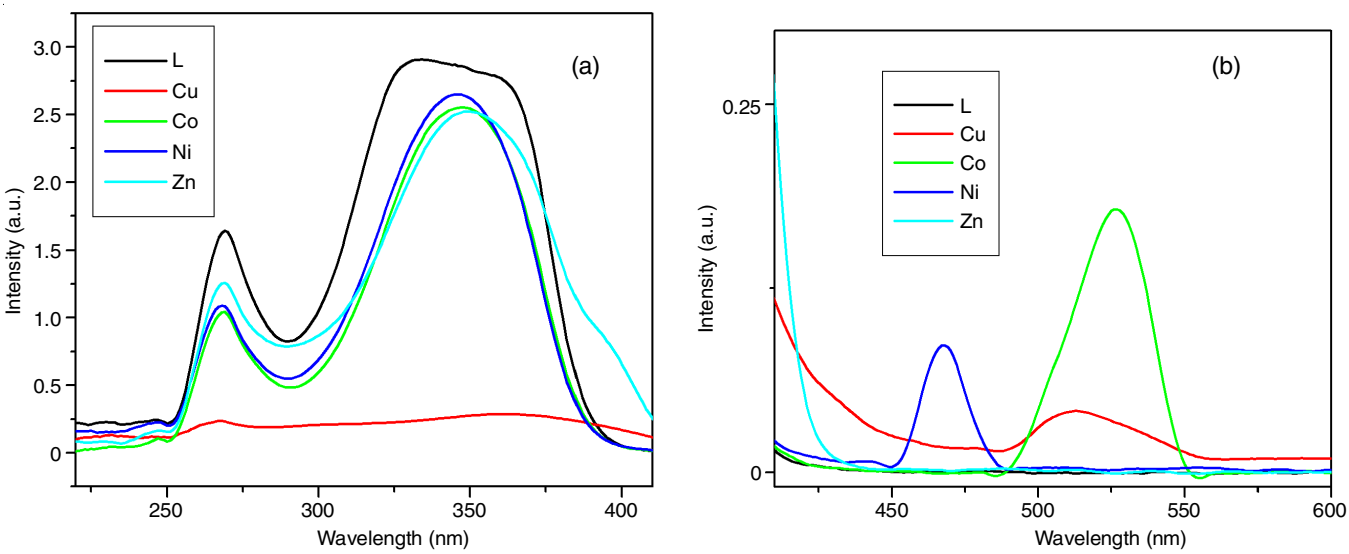


Fig. 2. UV-vis spectra of Schiff base ligand (L) and its metal complexes at 200-400 (a) and 400-600 nm (b), respectively

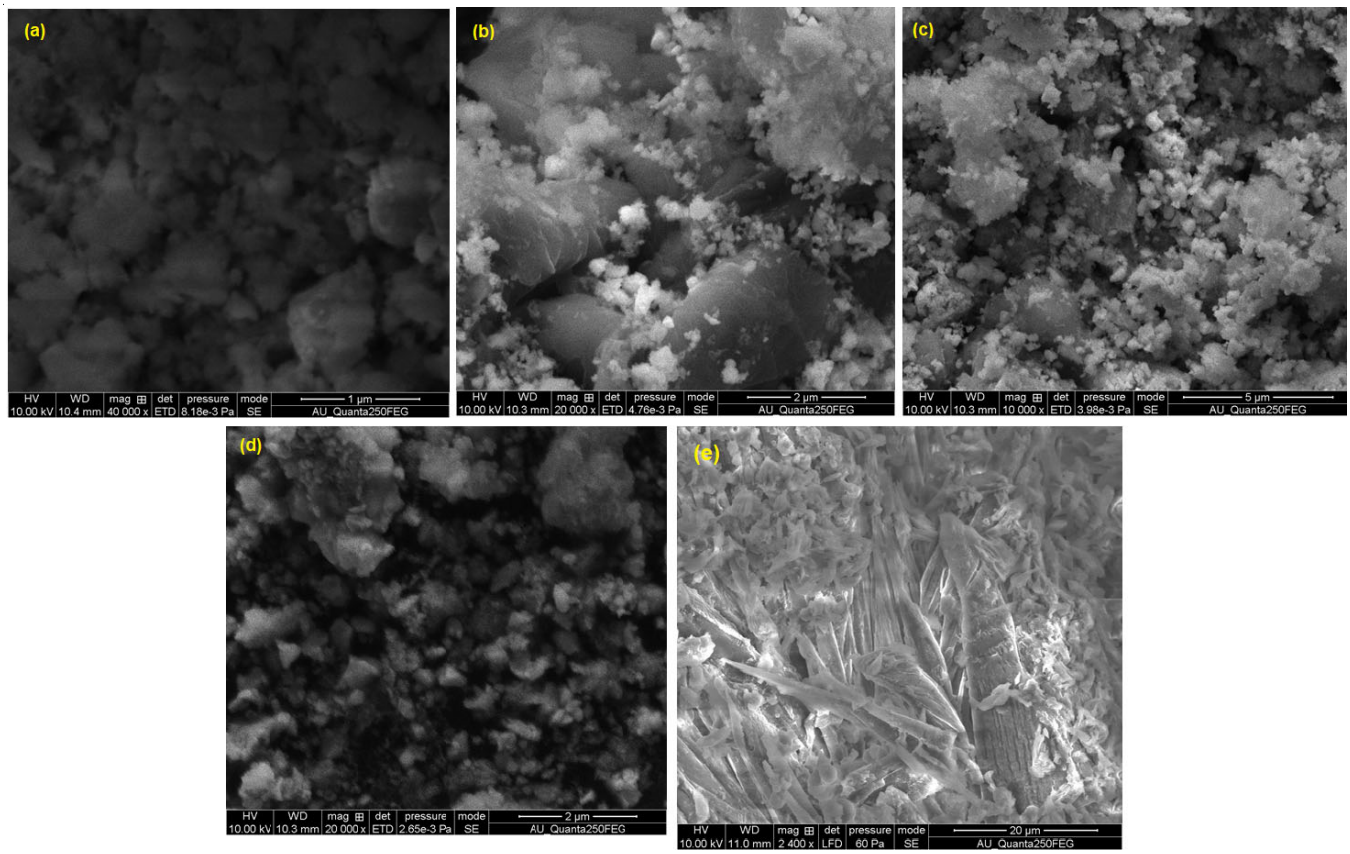


Fig. 3. SEM micrographs of Schiff base ligand and its metal complexes

of free electron (2.0023) is due to the covalent nature of the metal ligand bonding through NS (or) NNS [23-25] (Fig. 4).

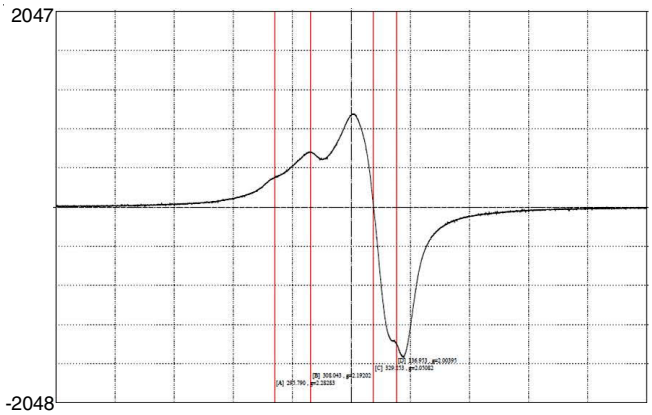


Fig. 4. EPR spectrum of Schiff base copper(II) complex

Antibacterial activity: The antibacterial properties of synthesized Schiff base and its metal complexes against human bacterial pathogens utilizing Kirby Bauer disc diffusion technique. The Gram-negative (*P. aeruginosa*, *Escherichia coli*) and Gram-positive (*Staphylococcus aureus*, *Bacillus subtilis*) bacterial strains were acquired from microbial type culture collection (MTCC), Indian Institute of Microbial Technology (IMTECH), Chandigarh, India. Bacterial inoculum were readied nutrient broths at 37 °C incubate it overnight and the viability of cells were confirmed.

Muller Hilton Agar plates were set up under sterile condition. Spread plating of 10 µL of inoculums of individual life forms were performed on the cemented MH agar plates. Wells were framed utilizing 6 mm stopper borer. Stock arrangement of edifices were readied utilizing DMSO of 5 mg/mL and stacked in the well. Dimethyl sulfoxide concoction was filled in as negative control after 24 h brooding at 37 ºC the hindrance zones were estimated. The trials were performed in triplicate and Understudy's t-test was utilized to assess factually noteworthy contrasts.

The antibacterial activity of schiff base ligand (L) demonstrate the zone of inhibiton of gram positive and Gram-negative bacterial values are given in Table-2.

TABLE-2
ZONE OF INHIBITION (MM) OF SCHIFF BASE LIGAND AND ITS METAL(II) COMPLEXES

Compound	*P. aeruginosa*	*B. subtilis*	*E. coli*	*S. aureus*
Schiff base ligand (L)	8	7	14	15
L(Zn)	15	20	17	19
L(Cu)	16	22	19	20
L(Ni)	20	23	22	18
L(Co)	18	22	15	17
Ciprofloxacin	19	22	21	24

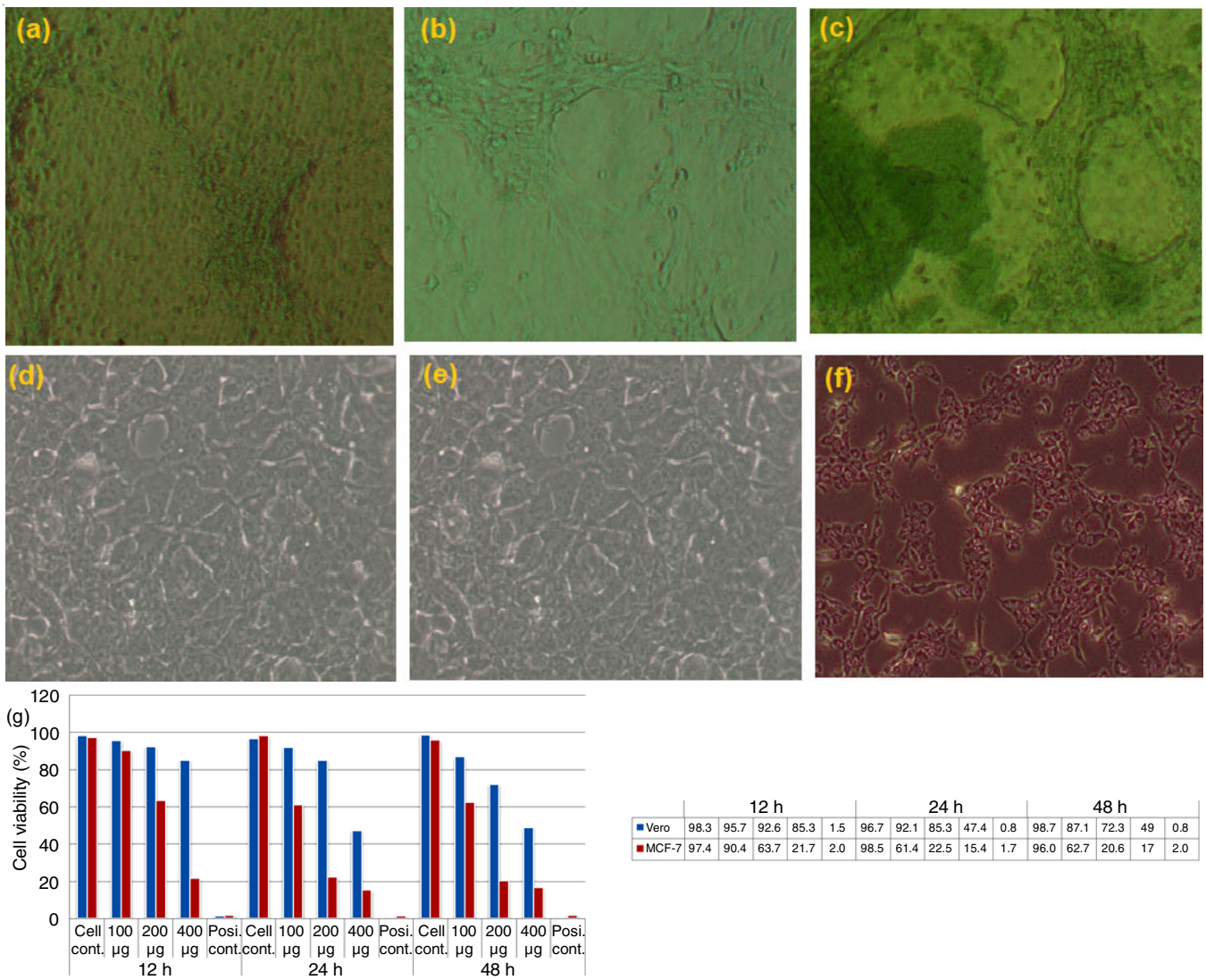
Cytotoxicity studies: *in vitro* Cytotoxicity of Schiff base ligand and its cobalt(II), nickel(II), copper(II) and zinc(II) complexes were tested by XTT cell proliferation assay. Of the

all compounds screened, Schiff base ligand-Ni(II) complex and Schiff base ligands-cobalt complexes have shown the maximum inhibition property against the breast cancer cell line MCF-7. Other compounds have shown minimal or no significant activity (Fig. 5).

As shown in Fig. 6, the formation of apoptotic bodies occurred following the treatment of MCF-7 and vero cells with 100-400 µg/mL Schiff base ligand and its metal complexes for 12-48 h. The results of the cell cycle and apoptosis experiments demonstrate that Schiff base ligand and its nickel(II) complex can effectively induce in MCF-7 and vero cells. Similarly, in an earlier study, curcumin- or catechin-examined different cell lines showed the enrichment of condensed nuclear morphology, chromatin fluorescence and the existence of dead cells. This suggests that Schiff base ligand nickel metal complexes are stimulated the cell death in MCF7 and vero cells by the reactive oxygen species (ROS)-imposed apoptotic process. The enrichment of ROS levels and consequent damage of mitochondria membrane potency could be enhanced the cell death effectively.

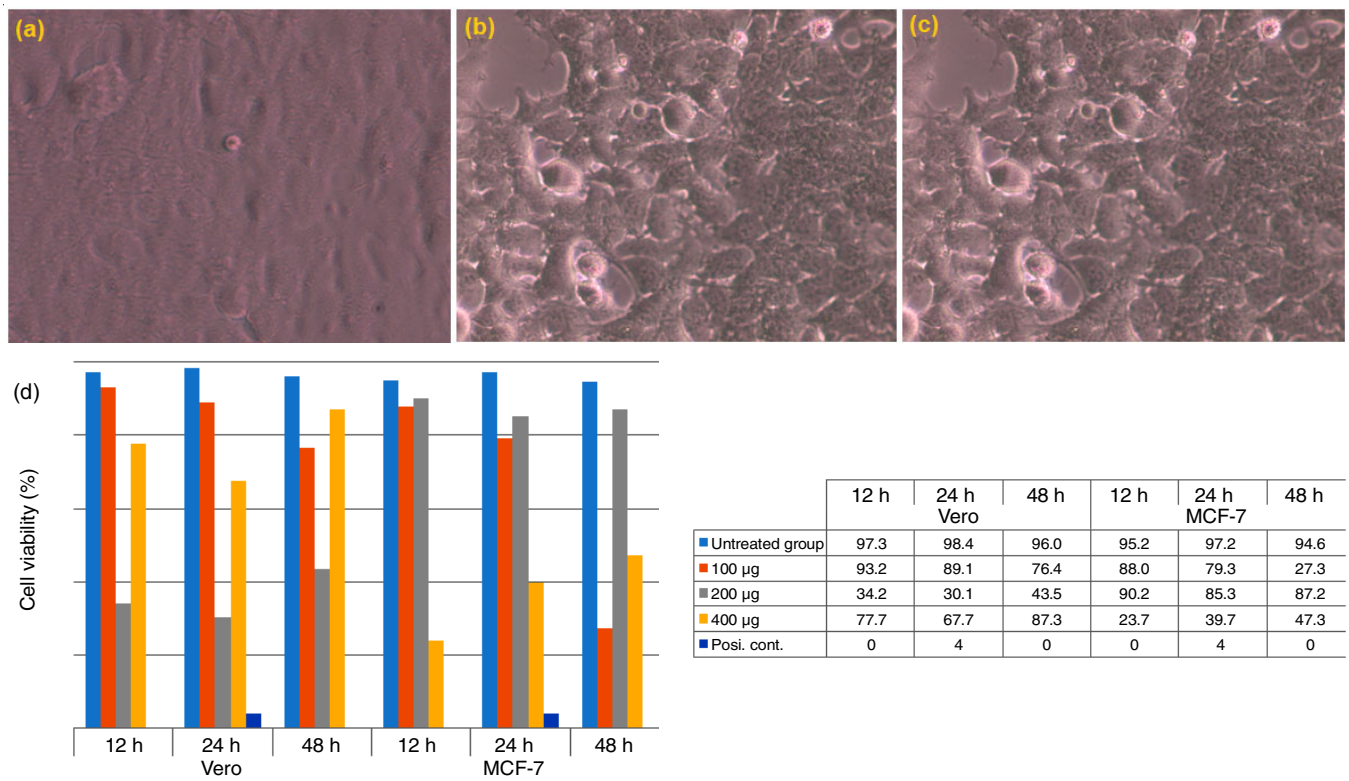
Molecular docking studies: The 3D and 2D interactions site of Schiff base ligand and its metal complexes with thymidylate synthase are shown in Fig. 7. The docking studies results revealed that all the ligands located within the hydrophobic site of thymidylate synthase receptor. The observed docking score values found to be, -5.099, -5.5, -5.45, -4.022, -4.725 kcal mol^{-1} for ligand and complexes L-Co, L-Ni, L-Cu and L-Zn respectively, which showed effective interaction with receptor thymidylate synthase. Moreover, the binding results showed various modes of interaction *via* H-bond, π-π stacking and hydrophobic contacts. Based on the above results, L-Co complex shows the highest docking score with thymidylate synthase.

The complex also exhibit hydrophobic interactions with many amino acid residues: (TYR 258, LEU 221, ILE 108, ALA 111, PHE 80, VAL 79, PRO 224, PHE 225, TRP 109, PRO



	12 h					24 h					48 h				
Vero	98.3	95.7	92.6	85.3	1.5	96.7	92.1	85.3	47.4	0.8	98.7	87.1	72.3	49	0.8
MCF-7	97.4	90.4	63.7	21.7	2.0	98.5	61.4	22.5	15.4	1.7	96.0	62.7	20.6	17	2.0

Fig. 5. Morphological changes induced by ligand and its metal complexes using 25 µg/mL compared with control against vero cell line, cells treated up to 48 h and screened for cytotoxic properties by XTT cell proliferation kit method. (a) Control (b) cobalt complex at 24 h (c) cobalt complex at 48 h, cell viability of cancer cell lines, MCF7 against (d) Schiff base ligand (e) cobalt complex at 24 h, (f) cobalt complex at 48 h and (g) %cell viability



	12 h	24 h	48 h	12 h	24 h	48 h
		Vero			MCF-7	
Untreated group	97.3	98.4	96.0	95.2	97.2	94.6
100 µg	93.2	89.1	76.4	88.0	79.3	27.3
200 µg	34.2	30.1	43.5	90.2	85.3	87.2
400 µg	77.7	67.7	87.3	23.7	39.7	47.3
Posi. cont.	0	4	0	0	4	0

Fig. 6. Illustrates the cancer cells inhibiton property of control (a), Schiff base nickel complex at 24 h (b), nickel complex at 48 h (c) at various concentrations against vero and MCF-7

193, TYR 135, PRO 194, LEU 192, CYS 195 and VAL 84) the values are given in Table-3. Therefore the results obtained from molecular docking analysis concluded that the ligand and their metal complexes could effectively bind with thymidylate synthase receptor and the interaction between them was governed by hydrogen bond, π-π stacking and hydrophobic forces.

Conclusion

A novel synthesized bidentate Schiff base ligand (L) and its metal(II) complexes under investigation supported the suggested structures. Synthesized complexes were confirmed the functional groups by FTIR and UV-vis spectroscopy. The results obtained from molecular docking analysis concluded that the ligand and its metal complexes could effectively bind with thymidylate synthase receptor and the interaction between them was governed by hydrogen bond, π-π stacking and hydrophobic forces. The antibacterial activity results show that most of the synthesized metal(II) complexes possess a good antimicrobial activity against the pathogens tested than the corresponding free Schiff base ligand.

CONFLICT OF INTEREST

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

TABLE-3
MOLECULAR DOCKING STUDIES FOR SCHIFF BASE LIGAND AND METAL COMPLEXES

Complexes	Docking score (kcal mol^{-1})	Active sites with a mode of interaction		
		H-bond	π-π stacking	Hydrophobic contacts (cut off at 5 Å)
Schiff base ligand (L)	-5.099	LEU 221	TRP 109	PHE80, VAL79, PRO224, LEU221, PHE225, ILE108, LEU192, PHE91, TYR135, TRP109.
L-Co	-5.5	–	PHE 225	TYR258, LEU221, ILE108, ALA111, PHE80, VAL79, PRO224, PHE225, TYR109, PRO193, TYR135, PRO194, LEU192, VAL84, LEU192, CYS195.
L-Ni	-5.45	–	PHE 225	VAL223, TYR258, LEU221, ILE108, PHE91, PRO194, PRO193, TYR135, CYS195, TRP109, LEU192, PHE225, ALA111, PRO224, VAL79, PHE80
L-Cu	-4.022	–	–	TYR135, PRO194, ILE108, TYR258, LEU74, VAL79, PRO224, PHE225, PHE80, LEU221, ALA111, TYR109, LEU192, CYS195.
L-Zn	-4.725	LEU 221	–	VAL79, PHE80, VAL106, PRO224, LEU74, LEU221, PHE225, TYR109, PHE91, TYR135, CYS195, ILE108, VAL223.

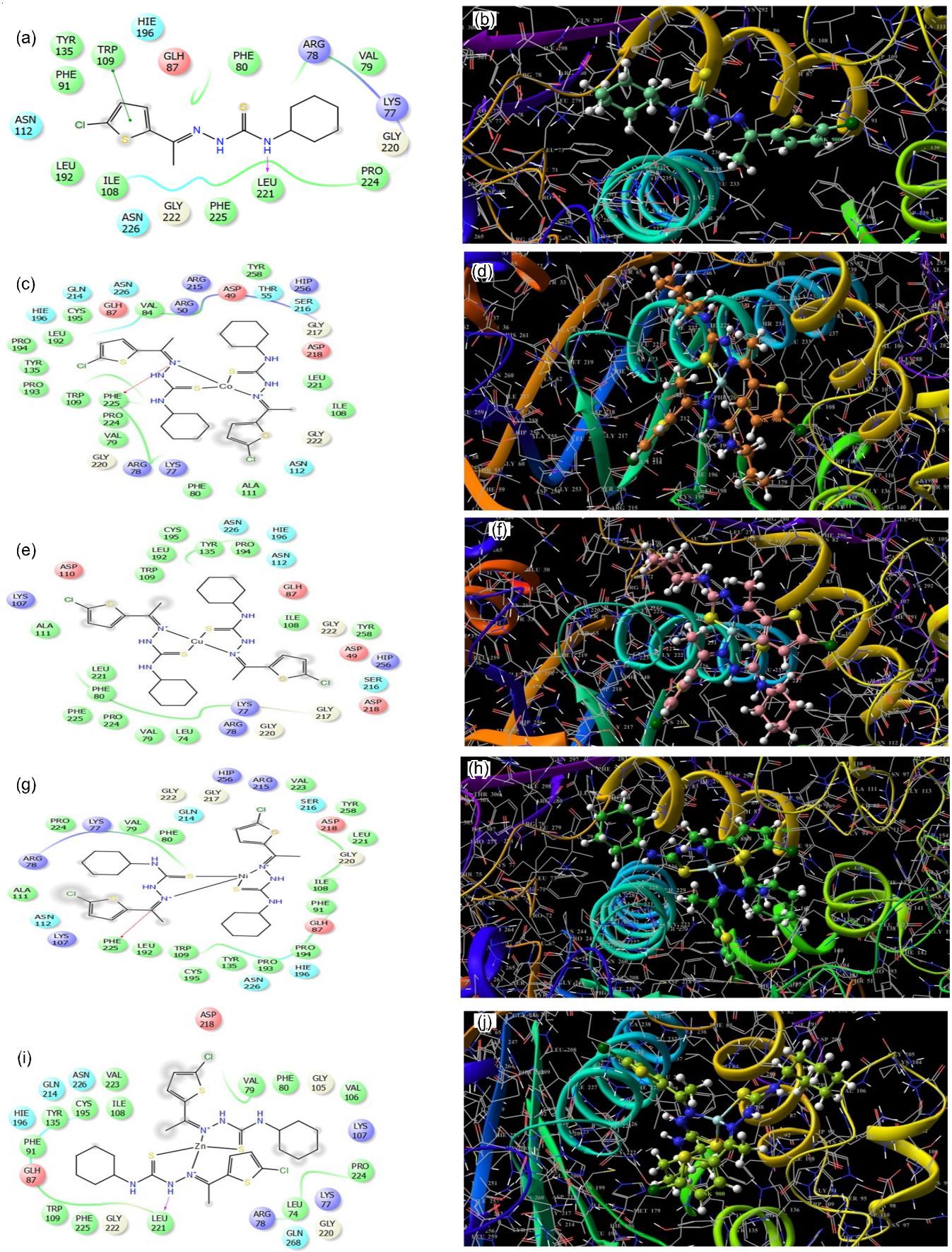


Fig. 7. Molecular docking models of Schiff base ligand 2D (a); 3D (PDB ID: 1HZW) (b); Co(II) complex 2D (c) and 3D (d); Cu(II) complex 2D (e) and 3D (f); Ni(II) complex 2D (g) and 3D (h); Zn(II) complex 2D (i) and 3D (j)

REFERENCES

1. D. Kumar, M.R. Jacob, M.B. Reynolds and S.M. Kerwin, *Bioorg. Med. Chem.*, **10**, 3997 (2002); https://doi.org/10.1016/S0968-0896(02)00327-9
2. C. Le Sann, A. Baron, J. Mann, H. van den Berg, M. Gunaratnam and S. Neidle, *Org. Biomol. Chem.*, **4**, 1305 (2006); https://doi.org/10.1039/b600567e
3. H.M. Refaat, *Eur. J. Med. Chem.*, **45**, 2949 (2010); https://doi.org/10.1016/j.ejmech.2010.03.022
4. S.A. Galal, A.S. Abdelsamie, M.L. Rodriguez, S.M. Kerwin and H.I. El Diwani, *Eur. J. Chem.*, **1**, 67 (2010); https://doi.org/10.5155/eurjchem.1.2.67-72.1
5. H.M. Refaat, *Med. Chem. Res.*, **21**, 1253 (2012); https://doi.org/10.1007/s00044-011-9636-y
6. A. Hori, Y. Imaeda, K. Kubo and M. Kusaka, *Cancer Lett.*, **183**, 53 (2002); https://doi.org/10.1016/S0304-3835(02)00110-6
7. K.M. Dawood and B.F. Abdel-Wahab, *ARKIVOC*, **2010**, 333 (2010); https://doi.org/10.3998/ark.5550190.0011.109
8. K.M. Dawood, N.M. Elwan and B.F. Abdel-Wahab, *ARKIVOC*, **2011**, 111 (2011); https://doi.org/10.3998/ark.5550190.0012.102
9. A. Husain, M.M. Varshney, M. Rashid, R. Mishra and A. Akhter, *J. Pharm. Res.*, **4**, 413 (2011).
10. V.M. Povstyanoy and V.P. Kruglenko, *Org. Farm. Khim.*, **3**, 32 (2005).
11. P.K. Sahoo and P. Behera, *Eur. J. Med. Chem.*, **45**, 909 (2010); https://doi.org/10.1016/j.ejmech.2009.11.031
12. J. Styskala, L. Styskalova, J. Slouka and M. Hajduch, *Eur. J. Med. Chem.*, **43**, 449 (2008); https://doi.org/10.1016/j.ejmech.2007.01.008
13. H.M. Eisa, A.M. Barghash, S.M. Badr and A.A. Farahat, *Indian J. Chem.*, **49B**, 1515 (2010).
14. K. Malarz, A. Mrozek-Wilczkiewicz, M. Serda, M. Rejmund, J. Polanski and R. Musiol, *Oncotarget*, **9**, 17689 (2018); https://doi.org/10.18632/oncotarget.24844
15. X. Yan, J. Xu, X. Wu, Z. Zhang, X. Zhang, Y. Fan and C. Bi, *New J. Chem.*, **39**, 2168 (2015); https://doi.org/10.1039/C4NJ01906G
16. S. Delgado, A. Santana, O. Castillo and F. Zamora, *Dalton Trans.*, **39**, 2280 (2010); https://doi.org/10.1039/b914835c
17. M.M. Omar, G.G. Mohamed and A.A. Ibrahim, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **73**, 358 (2009); https://doi.org/10.1016/j.saa.2009.02.043
18. M. Baghbanzadeh, C. Pilger and C.O. Kappe, *J. Org. Chem.*, **76**, 1507 (2011); https://doi.org/10.1021/jo1024464
19. Manju, N. Mishra and D. Kumar, *Russ. J. Coord. Chem.*, **40**, 343 (2014); https://doi.org/10.1134/S1070328414050091
20. A.L. El-Ansary and N.S. Abdel-Kader, *Int. J. Inorg. Chem.*, **2012**, 901415 (2012); https://doi.org/10.1155/2012/901415
21. L. Thunus and R. Lejeune, *Coord. Chem. Rev.*, **184**, 125 (1999); https://doi.org/10.1016/S0010-8545(98)00206-9