



Synthesis and Evaluation of Cytotoxicity Effect of New Ligand (LBe) and its Complexes on a Cervical Cancer

REHAM FAEK HAMEED, AREEJ ALI JARULLAH* and FADHIL LAFTA FARAJ

Department of Chemistry, Faculty of Sciences, University of Diyala, Diyala Governorate, Iraq.

*Corresponding author E-mail: Aroo977@gmail.com

<http://dx.doi.org/10.13005/ojc/350342>

(Received: May 27, 2019; Accepted: June 15, 2019)

ABSTRACT

In this research, new ligand (LBe) 2-(1,1-dimethyl-1,3-dihydro-2H-benzo[e] indol-2-ylidene) propane-1,3-diylidene bis(azanylylidene) diphenol was synthesized by the condensation reaction of 2-hydroxy aniline with 2-(1,1-dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene) malonaldehyde (Be) in ratio 2:1. (LBe) was used as ligand to synthesis a series of metal complexes by its reaction with different metal chlorides in a molar ratio 1:1 and 1:2 of M:L in ethanol such as (NiCl₂.6H₂O, CuCl₂.2H₂O, CoCl₂.6H₂O, MnCl₂.4H₂O and ZnCl₂). The chemical structures of the ligand and its complexes were characterized by ¹H-NMR spectroscopy, infrared spectroscopy, ultra violet-visible spectroscopy, magnetic susceptibility, and molar conductivity measurements. According to the results obtained the suggested structures of the complexes, Square planar geometry for [Co(LBe)], [Ni(LBe)], [Cu(LBe)], octahedral geometry for [Mn(LBe)] and tetrahedral geometry for [Zn(LBe)₂]. Cytotoxicity effect of ligand LBe and its complexes have been evaluated against Hella cell line (cervical cancer) in two exposure times 24 and 48 hours.

Keywords: 2-hydroxy aniline, LBe ligand, Metal complexes, Hella cell line.

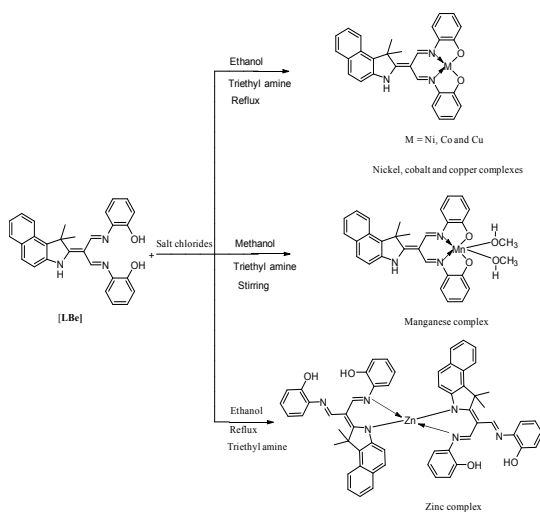
INTRODUCTION

Indole is an aromatic heterocyclic compound¹. A heterocyclic compound is one which possesses a cyclic structure with at least two various kinds of hetro atoms in the ring. Oxygen, nitrogen and sulfur are the most widespread heterocyclic compounds are very vastly distributed in nature and are essential to life in different ways².³. In general, Schiff bases form through the reaction of a primary amine and ketone or aldehyde with removal of water molecule in convenient solvent⁴⁻⁶. Schiff bases have been known by various names

such as azomethines, imines, and anils. Broadly, the Schiff bases that have been derived from aldehydes are named aldimine and from ketones are ketamine^{7,8}. In Schiff base azomethane nitrogen and other donor atoms like oxygen play a major role in coordination chemistry⁹. Schiff bases are beneficial chelates because of their ease of preparation, structural varieties, assorted densities and subtle steric and electronic control on their framework¹⁰. In industry, Schiff bases were used as corrosion inhibitors, rubber accelerators, and antioxidants, also used as plasticizers, and stabilizers for polymers, polymerization, initiators, antioxidants ... etc.^{11,12}.



The transition metal one of the more interesting aspects to form coordination compounds¹³. The coordination compound are of huge interest, because metal ions found in the active sites of a large number of metalloproteins such as, hemocyanin, and in metalloenzymes like in tyrosinase, ureases, lactase and ascorbate oxidase. These proteins are contributory in the various biological processes such as biological electron-transfer reaction, oxygen atom insertion into substrates, dioxygen reduction to hydrogen peroxide or water and hydrolytic reactions¹⁴. Study of coordination chemistry of transition metal ions with unlike types of ligands has been enhanced by the current evolutions in the fields of medicine and bioinorganic chemistry¹⁵. Through the years, Schiff bases have played a particular role as chelating ligands in coordination chemistry, due to their stabilization under a variety of oxidative and reductive conditions, and to the actuality that imine ligands are borderline between soft and hard Lewis bases¹⁶. This research include synthesis and characterization of LBe compound and used as ligand to synthesize a new complexes by its reaction with different salts of metal chlorides in a molar ratio 1:1 and 1:2 of M: L, as shown in scheme 1.



Scheme 1. Synthetic pathway to nickel, cobalt, copper, manganese and zinc complexes

EXPERIMENTAL

Materials and Measurements

All chemical compounds used in this work were purchased from Merck, BDH, Sigma Aldrich, Alpha, GCC and Fulka Chemical Company. The starting material (Be) was synthesized with

modification of a procedure defined by Ali W. B.¹⁷. The purity of the synthesized compounds and ending of reaction was checked by TLC sheet and the spots were detected by using (fluorescence analysis cabinet model CM-10). Melting points were determined by using (Melting point SMP10). FT-IR spectra were registered in the range (400-4000 cm^{-1}) using KBr disk by using (Perkin Elmer Spectrum 65 FT-IR Spectrophotometer). Molar conductivity measurements for metal complexes (10^{-3}) in DMSO at room temperature. Magnetic susceptibility measurements for the complexes were carried out using (Johnson Matthey catalytic systems Division Engineered products). Electronic spectra were recorded on the (UV-Visible double beam spectrophotometer equipped with 10mm quartz cell, JASCO V-650, Japan). NMR-spectra using DMSO- d_6 were registered on a Bruker 400 MHz spectrometer.

Synthesis Methods

Synthesis of (Be) compound

(2g, 0.01mol) of 1,1,2-Tri methyl-1H-benzo [e] indole was dissolved in 10 ml of DMF and cooled in to ice bath. The solution of (4.6 ml, 0.03 mol) of phosphoryl chloride in 10 ml of dimethylformamide was cooled in an ice bath also and then was added dropwise to first solution with stirring for 1 h at below 5°C. After that, the reaction mixture was reflux for 3 hours. The mixture of reaction was poured on ice water, the pH was mend to 8.0 by added aqueous solution of (NaOH 25%), the solid product was precipitated and the product was filtered, washed with water and then dried to afford solid product of yellow crystals of (Be). Yield (91%), m. p.199-200°C.

Synthesis of (LBe)

A mixture of (1 g, 0.008mol) of (Be) and (1.74 g, 0.016mol) of 2-hydroxy aniline was dissolved in toluene 40 ml, then added glacial acetic acid 2 ml to the solution. The mixture was refluxed for 5 hours. The solvent was reduced to one quarter; orange precipitate was formed, filtered off, washed with toluene and dried in oven. Recrystallization was done by using hexane. The purity of compound was determined by using TLC (3:1) hexane – ethyl acetate which gave one spot. Yield (75%), m. p.168-170°C.

Synthesis of [Ni (LBe)]

Solution of (0.2 g, 0.0004mol) of ligand was dissolved in 20 ml hot ethanol, then a few drops of triethylamine (5drops) was added into the solution

followed by addition (0.095 g, 0.0004) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 10 ml of distilled ethanol. The solution was refluxed for 4 h where upon the deep red solid of the product precipitated. Then the mixture was cooled and the precipitate was filtered off, washed with ethanol and dried, m.p decomposition above 300°C . Yield 81%.

Synthesis of [Cu (LBe)]

Solution of (0.2 g, 0.0004) of (LBe) ligand was dissolved in 20 ml hot ethanol, then 5 drops of triethylamine was added into the solution followed by addition (0.068 g, 0.0004) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 8 ml of distilled ethanol. The solution was refluxed for 4 h where upon the dark brown solid of the product precipitated. Then the mixture was cooled and the solid precipitate was filtered off, washed with ethanol and dried, m.p. decomposition above 300°C . Yield 70%.

Synthesis of [Co ((LBe))]

(0.15 g, 0.00034) of (LBe) ligand was dissolved in 20 ml hot ethanol then a few drops of triethylamine was added into the solution and then addition (0.067 g, 0.00034 mol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 8 ml of distilled ethanol. The solution was refluxed for 5 h where upon the brown solid of the product precipitated. Then the mixture was cooled and the brown precipitate was filtered off, washed with ethanol and dried, m.p decomposition above 300°C , yield 93%.

Synthesis of [Mn (LBe)]

Solution of (0.2 g, 0.0004) of ligand was dissolved in 20 ml methanol then trimethylamine was added into the solution followed by the addition (0.079 g, 0.0004) of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 10 ml of methanol. The solution was refluxed in air for 4 h whereupon the solid of the product precipitated. Then the mixture was cooled and the maroon precipitate was filtered off, washed with ethanol and dried, m.p. decomposition above 300°C . Yield 85%.

Synthesis of [Zn (LBe)]

(0.25 g, 0.0006) of ligand was dissolved in 20 ml ethanol then 5 drops of triethylamine was added into the solution followed by the addition (0.041 g, 0.0003) of ZnCl_2 was dissolved in 8 ml of distilled ethanol. The solution was refluxed for 4 h where upon the orange solid of the product precipitated. Then the mixture was cooled to

room temperature and the orange precipitate was filtered off, washed with ethanol and dried, m.p. decomposition above 300°C ., yield 75%.

Cellular Toxicity Test for Raw Extracts in The Growth of Hella Cell Line, A Cervical Cancer Cell Line

Prepare the cell suspension by adding trypsin-fersin solution to the tissue culture pot size (50 cm^2) and add 20 ml of the irrigated medium with the serum. The cell suspension was mixed well and 0.2 ml was taken after each mixture. Each hole of the (96-microtiter plates) was applied using a precise automatic pipette, each hole contained 105×1 (cell/hole). The surface of the dish was covered with a transparent adhesive paper and gently stirred the dish to smooth the distribution Cells in the pits. Leave the dishes in the incubator warm 37°C for a period ranging from 12-18 hours. Until adhesion of the cells in the hole. Then remove the old plant medium in the drilling, and added 0.2 ml of the concentrations prepared for each vessel by using the Serum Free Media (SFM) for control with DMSO and four replicates of control, add phosphate buffer saline (PBS) which was added to it 0.2 ml of serum free medium, incubate the dishes at 37°C . After the expiry time, remove the dish from the incubator and add 50 mL of violet dye to each hole. Return the dish to the incubator for 20 minutes. Remove the dish, remove the contents and wash with PBS until the dye is gone. The results were read using the optical spectroscopy device of the fine calibration dishes with a wavelength of 492 nm. The growth inhibition rate of the cancer cells was determined according to the equation by converting the toxic effect values of the water extract and alkaloids for long-term plant in cellular lines to cancerous proportions.

RESULTS AND DISCUSSION

FT-IR of Ligand (LBe) and its Complexes

The FT-IR spectra of ligand was displayed new absorption bands of new functional group on spectrum, as well as disappearance some absorption bands of starting materials from spectrum like Be, this is a good evidence for designated and approved formation the new ligand. For example appearance a new broad absorption band at the 3372 cm^{-1} which belonged to new functional group of (O-H), absorption band at the 3181 cm^{-1} was assigned to (N-H) group and new functional group at 1644 cm^{-1} for azomethine¹⁸⁻²¹. In addition, the

absorption band at 1608 cm^{-1} and 1580 cm^{-1} was belonged to (C=C) group. Finally a sharp peak at 750 cm^{-1} was attributed to (C-H) bending out of plain²².

FT-IR spectra, for new synthesized complexes, (nickel, copper, cobalt and manganese) were showed shift to lower frequency of absorption bands of (CH=N) from 1644 cm^{-1} to (1589 , 1606 , 1589 and 1592) cm^{-1} respectively. In addition, disappearance absorption bands of hydroxyl group from complexes spectrums in comparison with that of free ligand that supported coordination ligand with central metal ion and formation complexes²³.

FT-IR spectra for new zinc complex shown shift to lower frequency of absorption bands of (C=N)

Table 1: IR spectra data cm^{-1} of free ligand (LBe) and its complexes

Comp.	O-H	N-H	C-H arom.	C-H aliph.	CH=N	C-N	C-O	C-H
(LBe)	3372	3181	3049	2993	1644	1207	1149	750
[Ni(LBe)]	-	3208	3055	2978	1589	1207	1005	731
[Cu(LBe)]	-	3191	3062	2978	1606	1203	1151	752
[Co(LBe)]	-	3252	3069	2971	1589	1207	1103	745
[Mn(LBe)]	-	3269	3063	2976	1592	1208	1051	747
[Zn(LBe)2]	3432	-	3063	2983	1606	1208	1116	747

from 1644 cm^{-1} to 1606 cm^{-1} , and disappearance absorption bands of NH group from complex spectrum in comparison with that of free ligand which supported coordination ligand with central metal ion and formation complexes²⁴. The IR spectra result of ligand and their complexes were listed in Table 1.

Nuclear Magnetic Resonance Spectroscopy Study (NMR)

The $^1\text{H-NMR}$ results for compound (Be) Fig. 1 displayed a single signal at 13.79 ppm was belonged to proton of (NH) of indole ring. A singlet signal at 9.71 ppm was referred to two proton atoms of carbonyl group and signal were appeared between (8.02 - 7.19) ppm were belonged to protons of aromatic ring. Finally, singlet signal at 1.96 ppm was belonged to six protons of two methyl groups^{17,25,26}.

The H-NMR outcomes for ligand, Fig. 2 displayed single signal at 13.65 ppm were belonged to proton of (NH) of indole ring. A signal at 11.95 ppm was referred to two protons of hydroxyl group and single signal at 9.06 ppm was attributed to protons of Schiff base (CH=N). In addition, signals were appeared in the region between (8.70 - 6.90) ppm were belonged to fourteen protons of aromatic ring. Finally, singlet signal at 1.89 ppm was belonged to six protons of two methyl groups^{24,27,28}.

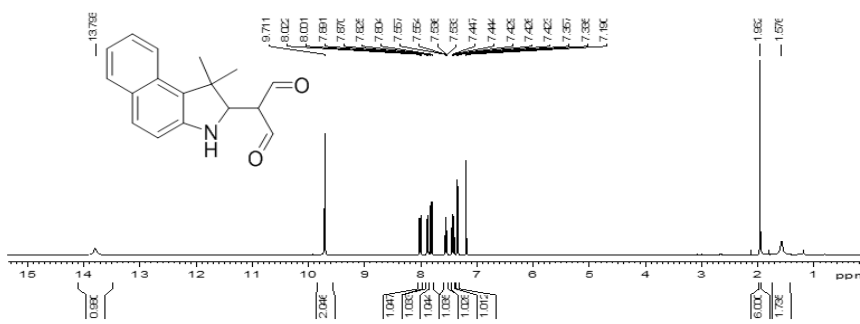


Fig. 1. ^1H NMR spectrum of (Be)

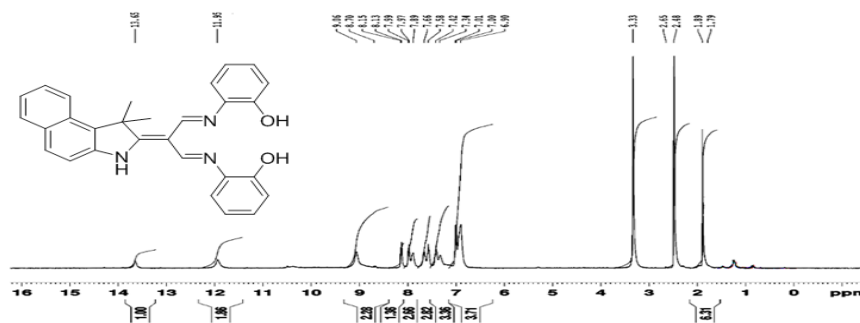


Fig. 2. ^1H NMR spectrum of ligand (LBe)

Magnetic Susceptibility and Molar Conductance

The effective magnetic moment calculated from the following equation²⁹.

$$\mu_S = \sqrt{4s(s+1)}$$

Where, μ_S (magnetic moment for spin only), S (Spin quantum number, $S = n/2$, $n =$ no. of unpaired electrons).

The experimental values corrected for diamagnetic effects using the following relationship³⁰.

$$\mu_{eff} = 2.82\sqrt{X_A * T}$$

$$X_A = X_m - D$$

$$X_m = X_g * M. Wt$$

Where, μ_{eff} (effective magnetic moment), T (absolute temperature in K), X_A (atomic susceptibility), X_m (molar susceptibility), D (correction factor) and X_g (mass susceptibility).

According to the magnetic moment values, the complexes of the LBe ligand were paramagnetic except complexes $[\text{Ni}(\text{LBe})]$ and $[\text{Zn}(\text{LBe})_2]$ were diamagnetic.

The molar conductance of complexes measured at room temperature. The values obtained lie in the range (0-0.2 $\text{S.cm}^2.\text{mol}^{-1}$), this indicates that all these complexes are nonelectrolyte and satisfied

the oxidation state of the central ion (+2)³¹. The molar conductance values and the (μ_{eff}) of all complexes are summarized in Table 2.

Electronic Spectra

The electronic spectrum of ligand showed three absorption bands attributed to ($\pi-\pi^*$) and ($n-\pi^*$) transition³². The Ni(II) complex showed two bands in visible region assigned to (d-d) transition, refer to ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow {}^1B_{1g}$ in a square planar geometry³³. The Co(II) complex show two prominent (d-d) absorption bands attributed to the transitions ${}^2A_{1g} \rightarrow {}^2A_{2g}$ and ${}^2A_{1g} \rightarrow {}^2B_{1g}$, for a low spin square planner. Low spin manganese (II) has the electronic configuration d^5 . The ground term in which octahedral stereochemistry is ${}^2T_{2g}$. The electronic spectra of the complex Mn(II) showed three bands assigned to (d-d) electronic transition ${}^2T_{2g} \rightarrow {}^2A_{2g}$, ${}^2T_{2g} \rightarrow {}^2E_g$ and ${}^2T_{2g} \rightarrow {}^2A_{1g}$ ³⁴. The electronic spectrum of Cu(II) complex show two bands assigned to transitions ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ for a low spin square planner³⁵. The Zinc complex showed no absorption band for (d-d) transition because the d orbital is field. The spectra of Zn complex, show change in the bands position compared to that of the free ligand due to charge transfer between Zn(II) and ligand, that is a good result for zinc(II) tetrahedral complex^{36, 37}. Table 2 explain UV-Vis bands of the ligand and all complexes with their assigned transition.

Table 2: The conductivity measurements, magnetic susceptibility and electronic spectral data of ligand (LBe) and its complexes

Comp.	Wave length $\lambda(\text{nm})$	Wave no. $\nu(\text{cm}^{-1})$	Assignment	μ_{eff} (BM)	Conductivity ($\text{S.cm}^2.\text{mol}^{-1}$)	Suggested Geometry
LBe	283.6	35260	$\pi \rightarrow \pi^*$	-----	-----	-----
	331.8	30138	$\pi \rightarrow \pi^*$			
	393.8	25393	$n \rightarrow \pi^*$			
[Cu(LBe)]	488.8	20458.26	${}^2B_{1g} \rightarrow {}^2E_g$	1.83	0.1	Square planner
	741.2	13491.63	${}^2B_{1g} \rightarrow {}^2B_{2g}$			
[Co(LBe)]	500.1	19996	${}^2A_{1g} \rightarrow {}^2B_{1g}$	1.91	0	Square planner
	740.2	13509.86	${}^2A_{1g} \rightarrow {}^2A_{2g}$			
[Ni(LBe)]	476.6	20981.95	${}^1A_{1g} \rightarrow {}^1B_{1g}$	0.2	0.2	Square planner
	740	13513.51	${}^1A_{1g} \rightarrow {}^1A_{2g}$			
[Mn(LBe)]	506	19747.2	${}^2T_{2g} \rightarrow {}^2A_{1g}$	2	0	Octahedral
	540	18491.12	${}^2T_{2g} \rightarrow {}^2E_g$			
	736	13586.95	${}^2T_{2g} \rightarrow {}^2A_{2g}$			
[Zn(LBe) ₂]	268.2	37285.6	C.T	0.3	0	Tetrahedral
	297.2	33647.37				
	454.2	22016.73				

Biological Activity

Cytotoxicity effect of ligand (LBe) Fig. 4, and its complexes have evaluated against Hella cell

line, a cervical cancer after exposure to (125) $\mu\text{g}/\text{ml}$ for (24 and 48 hours.) as shown in Table 3. The results revealed that the $[\text{Zn}(\text{LBe})_2]$ complex Fig. 5,

had greater inhibition rate on Hella cell line at time of exposure 24 and 48 h respectively. In time of exposure 48 h the results recorded high inhibition rates for the ligands and its complexes.

Table 3: show the hella cell line for ligands LBe and their complexes

Concentration 125 µg/ml	24 h standard error ± Inhibition ratio	48 h standard error ± Inhibition ratio
The control	h 0.00±1.15	h 0.00± 1.17
LBe	f 0.81±7.86	f 0.81± 18.61
[Mn(LBe)]	e 0.30± 13.16	e 0.30±20.95
[Co(LBe)]	d 0.23±24.89	d 0.23±34.90
[Cu(LBe)]	c 0.33± 31.28	c 0.33±47.73
[Ni(LBe)]	b 1.12± 36.21	b 1.12± 61.62
[Zn(LBe) ₂]	a 0.37± 41.28	a 0.37± 70.46

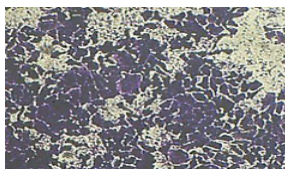


Fig. 3. Cell carcinoma Hella which represents control and illustrates dense line cells, (100 X)

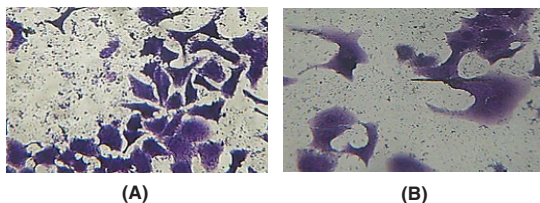


Fig. 4. Hella cell line after exposure to (125) µg/ml of LBe ligand for (A) 24 h and (B) 48 h, (100X)

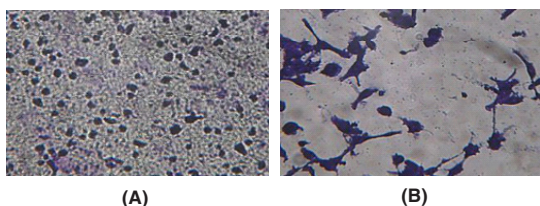


Fig. 5. Hella cell line after exposure to (125) µg/ml of [Zn(LBe)₂] complex for (A) 24 h and (B) 48 h, (100X)

CONCLUSION

The ligand (LBe) was successfully synthesized by condensation reaction. The new ligand behave as tetradentate ligands through coordination with two nitrogen atoms of azomethane group and two oxygen atoms of hydroxyl group with Ni(II), Co(II), Cu(II) and Mn (II) ions and behave as bidentate ligands through coordination with nitrogen atom of azomethane group and nitrogen atom of indole ring with Zn (II) ion. Conductivity measurements showed that all the synthesized complexes to be non-ionic. The results of biological activity of the ligand and its metal complexes at time of exposure 48 h and 24 h for cancer cell line Hella exhibited decrease in inhibition rate according to [Zn(LBe)₂] > [Ni(LBe)] > [Cu(LBe)] > [Co(LBe)] > [Mn(LBe)] > LBe. In addition the highest inhibition rate in time of exposure 48 h than 24 h for the ligands and their complexes.

ACKNOWLEDGMENT

The authors thank Department of Chemistry in College of Science, University of Diyala for supporting this work.

Conflict of Interests

The authors proclaim that there is no conflict of interests concerning the propagation of this paper.

REFERENCES

- Faraj, F.L. Ph.D. Thesis Faculty of Sciences-University of Malaya, Malaysia., **2015**.
- Yadav, P.S.; Prakash, D. and Senthikumar, G.P. *Intrenational Journal of Pharmaceutical Sciences and Drug Research.*, **2011**, 3(1), 01-07.
- Alias, M.F. and Seewan, A.N. *Diyala Journal for Pure Sciences.*, **2013**, 9(4), 93-103.
- Qin, W.; Long, S.; Panunzio, M. and Biondi, S. *Molecules.*, **2015**, 18(10), 12264-12289.
- Tobriya, S.K. *International Journal of Science and Research.*, **2014**, 3(9), 1254-1256.
- Arulmurugan, S.; Kkavitha, H.P. and Venkaraman, B.R. *Rasayan Journal of Chemistry.*, **2010**, 3(3), 385-410.
- Al-mahdawy, A. S. A.; Mohammed, M. Y. and Abd A. N. M.Sc. Thesis College of Science - University of Tikrit, Iraq., **2016**.
- Islam, S.; Siddiki, A. K. M. N. A.; Begum, S. and Salam, M. A. *Open Journal of Inorganic Chemistry.*, **2018**, 8, 55-69.

9. Xavier, A. and srividhya, N. *IOSR Journal of Applied Chemistry.*, **2014**, 7(11), 6-15.
10. Rai, B.K. and Rachana, K. *Orient. J. Chem.*, **2013**, 29(3), 1163-1167.
11. Ahmed, N. K. M.Sc. Thesis College of Science -University of Baghdad, Iraq., **2016**.
12. Lakshmi, B.; Shivananda, K. N.; Prakash, G. A.; Isloor, A.M. and Mahendra, K. N. *Bulletin Korean Chemical Society.*, **2012**, 33(2), 473-482.
13. Govindaraj, V.; Ramanathan, S. and Murgasen, S. *Der Chemica Sinica.*, **2018**, 9(3),736-745.
14. Abass, H. H.; Salih, R. A. and Salih, A. A. *Global Journal of Pure and Applied Chemistry Research.*, **2016**, 4(2), 19-29.
15. Hossain, M. S.; Camellia, F. K.; Uddin, N.; Banu, L. A.; E-Zahan, M. K. and Haque, M. M. *International Journal of Applied Science - Research and Review.*, **2019**, 6(1:2),1-7.
16. Anacona, J. and Santaella, J. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy.*, **2013**, 115, 800–804.
17. Ali, W. B. *Diyala Journal for Pure Sciences* **2018**, 14(3), 206-219.
18. Matela, G.; Aman, R.; Sharma, C. and Chaudhary, S. *Indian Journal of Advances in Chemical Science.*, **2013**, 1(3), 157-163.
19. Ameram, N. and Othman, U. *IOSR Journal of Engineering.*, **2013**, 3(8), 38-50.
20. Kumar, S.; Niranjana, M.S.; Chaluvaraju, K. C.; Jamakhandi, C. M. and Kadadevar, D. *Journal of Current Pharmaceutical Research.*, **2010**, 1, 39-42.
21. Saleem, L.M.N. and Sultan, R.H. *International Journal of Enhanced Research in Science Technology and Engineering.*, **2014**, 3(4), 167-172.
22. Silverstein, R. M.; Webster, F. X. and Kiemle, D. J. *Spectrometric Identification of Organic Compounds*, 7th ed., John Wiley and Sons Inc., New York., **2005**.
23. Niseaf, A. N. *Ibn Al-Haitham Journal for Pure and Applied Science.*, **2017**, 30(1), 131-142.
24. Faraj, F. L.; Ali, W. B.; Jassim, S. A. and Ali, T. R. *Diyala Journal for Pure Sciences.*, **2017**, 13(2), 262-277.
25. Faraj, F.L.; Khaledi, H.; Morimoto, Y. A.; Itoh, S.; Olmstead, M. M. and Ali, H. M. *European Journal of Inorganic Chemistry.*, **2014**, 2014(33), 5752-5759.
26. Matar, S. A.; Talib, W. H.; Mustafa, M. S.; Mubarak, M. S. and Al-Damen, M. A. *Arabian Journal of Chemistry.*, **2015**, 8, 850-857.
27. Zahedifard, M.; Faraj, F. L.; Paydar, M. J.; Looi, C. Y.; Hajrezaei, M.; Hasanpourghadi, M.; Kamalidehghan, B.; Abdul Majid, N.; Ali, H. M. and Abdulla, M. A. *Scientific reports .*, **2015**, 5, 1-17.
28. Singh, T.; Lakhan, R. and Singh, G. S. *Arabian Journal of Chemistry.*, **2017**, 10, S2778-S2781.
29. Housecroft, C.E. and Sharpe, A.G. *Inorganic Chemistry*, 3rd ed., Prentice Hall, Printed and bound by Rotolito Lombarda, Italy., **2008**.
30. Hashim, C. S. and Alias, M. F. M. Sc. Thesis, College of Science for Women-University of Baghdad, Iraq., **2012**.
31. AL-Hashime, S. M.; Sarhan, B. M. and Alazawi, S. A.S. *Journal of Al-Nahrain University.*, **2007**, 10(2), 82-88.
32. Al-Shaalan, N.H. *Molecules.*, **2011**, 16, 8629-8645.
33. Yaseen, A. K. and Al-Karkhi, I. H. T. *Baghdad Science Journal.*, **2013**, 10(1), 198-206.
34. Lever, A. B. P. *Inorganic Electronic spectroscopy* Elsevier publishing Company, New York, London., **1968**.
35. Mishra, A. P. and Jain, R. K. *Journal of Chemical and Pharmaceutical Research .*, **2010**, 2(6), 51-61.
36. Saraireh, I. A. M.; Altarawneh, M.; Alhawarin, J.; Salman, M.; Abu-Yamin, A. and Alasad, R. *Journal of Chemistry.*, **2019**, 2019, 223-232.
37. Dhabab, J.M.; Aljoobori, M. N. and Albajlan, H. H. *Ibn Al-Haitham Journal for Pure and Applied Science.*, **2012**, 25(1), 1-17.