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Eco-friendly Synthesis, Characterization and Antibacterial activity Study of Novel Ligand Derived from 2-Amino Benzothiazole and 6-Bromo-2-Phenyl-(4H)-4-Benzopyranone and its Transition Metal Complexes

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ABSTRACT

The novel Ligand was prepared by irradiation of 2-amino-1-methyl benzimidazole and 3',5'-dimethoxy-4'-hyroxy acetophenone, in scientific microwave oven and its transition metal complexes were prepared from Ni(II), Mn(II), Cd(II), Fe(III), Cu(II), Zn(II), Co(II), Ag(I) salts. The synthesized Schiff base ligand and its complexes were characterized by elemental analysis, spectral technics such as UV-Visible, FT-IR, ^{1}HNMR, LC-MS and Thermo gravimetric analysis. The biological activity of novel ligand and its complexes were tested against *Staphylococcus aureus*, *Salmonella typhi* and *Aspergillus Niger*.

Keywords: 2-amino benzothiazole, 6-Bromo-2-phenyl-(4H)-4-Benzopyranone, *Staphylococcus aureus*, *Salmonella typhi*, *Aspergillus niger*, Thermo gravimetric analysis.

INTRODUCTION

The Eco-friendly approach for synthesis is now a day most efficiently used in the field of research. One of the most useful methods is microwave assisted synthesis[1]. For this eco-friendly method of organic synthesis with or without any solvent in microwave oven method is environmentally safe and more effective than traditional method[2]. In 1955 this microwave assisted synthesis approach was introduced[3]. The microwave assisted method is time saving, solvent-free, having simple reaction condition, giving larger yield[4-8] low cost, easy to handle and safe[9-11]. This method has more selectivity and easier product separation and purification than conventional method. The Schiff bases are condensation product of primary Amine with Aldehyde or Ketone[12-14]. The Schiff bases have been known since 1864, when Hugo Schiff reported the condensation of primary amine

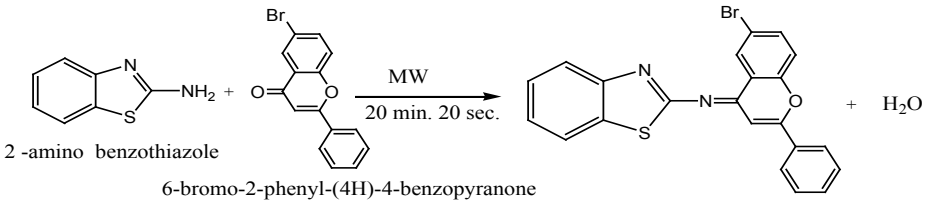
with carbonyl compound[15]. The azomethine group present in Schiff base is responsible for antimicrobial activity[16-17]. This Schiff bases are used biological and analytical field[18-19]. They exhibit biological activities like anticancer[20], bactericidal[21], analgesic[22-23], fungicidal[24-26], antiviral properties[27-29], Plant growth inhibitors[30], anti-inflammatory and anti-tuberculosis[31-33], antibiotic[34]. They are also used as dyes, catalyst, intermediate and stabilizers[35].

MATERIALS AND METHODS

For the synthesis of novel ligand and its complexes, all chemicals are of analytical grade. All the chemicals were purchased from Sigma Aldrich, LOBA CHEM, and Merck Chemicals. By using electro-thermal digital apparatus the melting point of all newly synthesized compounds were recorded. On a Brukers (400MHz, 100MHz) Spectrometer the ^{1}HNMR were recorded. LC-MS is used to find out the molecular weight of compounds. UV-Visible Spectra were recorded at wavelength range 200-800 nm. The Shimadzu Dr.8031 instrument was used for Infrared spectral studies. The Perkin Elmer thermal analyzer was used for thermo gravimetric analysis of the Complexes. TGA was performing in dynamic nitrogen atmosphere.

Preparation of novel ligand

The novel ligand was prepared by the reaction of 2-Amino Benzothiazole and 6 bromo-2-Phenyl-(4H)-4-Benzopyranone. The reaction was carried out in scientific microwave oven for nearly about 20 min 20 sec at 750 W. The Colour change is observed. The melting point was recorded after recrystallization with dry ether. The formation of product was confirmed by TLC technique.



2 -amino benzothiazole

6-bromo-2-phenyl-(4H)-4-benzopyranone

N-(6-bromo-2-phenyl-4*H*-chromen-4-ylidene)benzo[*d*]thiazol-2-amine

Preparation of Complexes

Complexes were prepared by mixing the metal nitrate and metal chloride with the required amount of ligand. The reaction mixtures were irradiated at 750 w in microwave oven nearly about 5 to 8 minutes. The irradiated products were washed with ether and filtered through whatman filter paper. The final product was recrystallized from absolute ethanol to give product.

RESULTS AND DISCUSSION

In this research it was realize that the reaction completed in very short time and higher yield were obtained. The new microwave assisted synthesis procedure was developed. The microwave irradiation was completed in 5-8 min and yield is 80 to 90%. All complexes obtained were solid, colored and stable at room temperature. All complexes are soluble in DMF and DMSO. The final complexes obtained were identified by their melting point, color, UV-Visible spectroscopy, FT-IR, and TG analysis. The products were confirmed by repeating the synthesis process[36].

Elemental analysis

The elemental analysis (CHNSOBr) data for ligand is summarized in Table 1.

Table 1: Elemental composition analysis of novel ligand

Sr. No	Compound	Molecular weight	% of CCal. (found)	% of HCal. (found)	% of NCal. (found)	% of SCal. (found)	% of OCal. (found)	% of BrCal.) (found
1	($C_{22}H_{13}N_2SOBr$)	433.214	60.99(59.30)	3.04(3.73)	6.46(7.00)	7.38(6.88)	3.69(3.91)	18.44(19.18)

Physical properties

The detail physical properties of the novel ligand and its metal complexes summarized in Table 2.

Mass spectrum

The fragmentation pattern shows peak at m/z 320, these equates to the molecular weight 319.35 of the novel ligand.

UV-Visible Study

The UV-Visible spectra was recorded in 200-800 nm in DMSO[37]. Mn(II) complex shows absorption maxima at 220 and 300. Fe(III) complex shows absorption Maxima at 250 and 290. These transition metal have charge transfer band, these indicates coordination of ligand to metal ion.

Table 2: Physical properties of novel ligand and metal complexes.

Sr. No	Ligand/ Complex	Color	Melting point (°C)	Time (sec)	%Yield
1	$(C_{22}H_{13}N_2SOBr)$	Pacement color	180	1220	82
2	$[(C_{22}H_{13}N_2SOBr)_2(H_2O)_2]Ni$	Pale yellow	235	205	87
3	$[(C_{22}H_{13}N_2SOBr)_2(H_2O)_2]Mn$	Dark brown	230	147	83
4	$[(C_{22}H_{13}N_2SOBr)_2(H_2O)_2]Fe$	Reddish Brown	310	122	90
5	$[(C_{22}H_{13}N_2SOBr)_2(H_2O)_2]Cd$	Dark brown	315	24	86
6	$[(C_{22}H_{13}N_2SOBr)_2(H_2O)_2]Cu$	Aquamarine	220	217	85
7	$[(C_{22}H_{13}N_2SOBr)_2(H_2O)_2]$ Zn	Light orange	189	159	90
8	$[(C_{22}H_{13}N_2SOBr)_2(H_2O)_2]Co$	Purple	190	120	90
9	$[(C_{22}H_{13}N_2SOBr)_2(H_2O)_2]Ag$	Lemmonish yellow	182	179	87

Table 3: Electronic spectral data and probable geometry of the metal complexes

Sr. No	Complex	Absorption Maxima (nm)	Assignment	Geometry
1	$[(C_{22}H_{13}N_2SOBr)_2(H_2O)_2]Mn$	220	π -π^*	Octahedral
		300	n-π^*	
2	$[(C_{22}H_{13}N_2SOBr)_2(H_2O)_2]Ag$	250		
		290	π-π^*	Octahedral
			n-π^*	

Infrared spectral studies

In the IR Spectrum of novel ligand band appeared at 1666.3 cm^{-1} is due to C=N, azomethine stretching[38-41]. The novel ligand shows band at 3300 cm^{-1} is due to N-H stretching. The band at 1540 cm^{-1} indicates the C=C stretching.

Table 4: Selected frequencies of infrared spectra of novel ligand and its complexes

Sr. No	Ligand/Complex	υ(C=N)cm^{-1}	υ(N-H)cm^{-1}	υ(C=C)cm^{-1}	υ(C-H)cm^{-1}	υ(OH)cm^{-1}	υ(M-N)cm^{-1}	υ(M-S)cm^{-1}	υ(C-Br)cm^{-1}
1	$(C_{22}H_{13}N_2SOBr)$	1666.3	3300	1540	2950	-----	-----	-------	744
2	$[(C_{22}H_{13}N_2SOBr)_2(H_2O)_2]Mn$	1592.8	3250.9	1535	2900	3605.8	471.1	430.8	728
3	$[(C_{22}H_{13}N_2SOBr)_2(H_2O)_2]Ag$	1643.0	3220.4	1503	2907	3609.9	510	447.4	750

Analysis of ligand-Mn complex

The IR spectrum of Mn complex clearly shows the shifting of azomethine band from 1666.3 cm^{-1} to 1592.8 cm^{-1}. The band due to imidazole NH stretching is at 3250 cm^{-1}. Also the band appeared at 1535 cm^{-1} is due to (C=C) stretching vibration. The aromatic C-H stretching vibration is observed at 2965 cm^{-1}. The most characteristic band appeared at 471.1 cm^{-1} is due to M-N stretching[42] which is absent in novel ligand. The band at 430 cm^{-1} indicates (M-S) stretching vibration[43-44]. The band at 3605.8 cm^{-1} is indicating the water of crystallization[45]. These changes indicate the formation of the metal complex.

Analysis of ligand-Ag complex

The IR spectrum of ligand-Ag complex clearly shows shifting of azomethine band from 1666.3 cm^{-1} to 1643 cm^{-1}. The band due to imidazole NH stretching vibration is shifted 3300 cm^{-1} to 3220 cm^{-1}. The band due to C=C stretching is shifted from 1540 cm^{-1} to 1503 cm^{-1}. The band due to aromatic C-H stretching vibration is shifted from 2950 cm^{-1} to 2907 cm^{-1}. The most characteristic band appeared at 447.47 cm^{-1} is due to M-N stretching, which is absent in the novel ligand. The band at 3709.95 indicates the water of crystallization in metal complex. This confirms the formation of complex.

^{1}H NMR spectral Study

The ^{1}HNMR data of novel ligand shows band at 7.124 ppm to 8.015ppm is due to H of aromatic ring[46-47]. The band appeared at 2.51ppm is

due to H from CH_3 group[48]. The H from Benzimidazole showed band at 6.7ppm.

Table 5: Observed ^{1}HNMR peaks (ppm) of novel ligand

Ligand	H from aromatic ring in ppm	H from methyl group in ppm	H from azomethine in ppm	H from dimethoxy Group in ppm
($C_{22}H_{13}N_2SOBr$)	7.124 - 8.015	2.521	8.136	3.332

Thermo gravimetric analysis

The TGA of ($C_{22}H_{13}N_2SOBr$)Mn was carried out in nitrogen atmosphere from room temperature to 500°C with heating rate 10°C/minute. The thermogram of complex shows total weight loss of 82.29% up to 500°C. From 0°C to 80°C water of crystallization lost with 10% weight loss is observed, loss of organic moiety with total weight loss up to 81.40% at 500°C. A stable curve indicates formation of copper oxide.

The TGA of ($C_{22}H_{13}N_2SOBr$)Ag was carried out in nitrogen atmosphere from room temperature to 500°C with heating rate 10°C/ minute. Thermogram of Complex shows weight loss of 83% up to 500°C. From 0°C to 80°C water of crystallization lost with 10% weight loss is observed, lastly loss of organic moiety with total weight loss 83% at 500°C. A stable curve shows the formation of nickel oxide.

Bioactivity study

The biological study of novel ligand and its complexes were summarized in Table 7. Disc diffusion assay was used. The zone of diameter measured in mm.

Table 6: Thermo gravimetric analytical data of metal complexes

TGA data for ($C_{22}H_{13}N_2SOBr$)Mn		TGA data for ($C_{22}H_{13}N_2SOBr$)Ag	
Weight loss%	Temperature°C	Weight loss%	Temperature°C
0	33.00	0	32.60
10	201.00	10	185.00
20	224.50	20	220.00
30	335.00	30	240.90
40	341.99	40	279.70
50	348.00	50	345.80
60	355.01	60	360.70
70	361.00	70	376.80
80	488.00	80	426.18
81.40	500	83.00	500
(Total weight loss)		(Total weight loss)	

Table 7: Zone of Inhibition of novel Schiff base ligand and its metal complexes

Sr. No	Ligand/complexes	Salmonella typhi	Staphylococcus aureus	Aspergillus Niger Fungi
1	($C_{22}H_{13}N_2SOBr$)	6.7	7.6	12.7
2	[($C_{22}H_{13}N_2SOBr)_2(H_2O)_2$]Ni	7.5	11.6	15.2
3	[($C_{22}H_{13}N_2SOBr)_2(H_2O)_2$]Mn	8.7	7.2	15.8
4	[($C_{22}H_{13}N_2SOBr)_2(H_2O)_2$]Fe	7.6	6.7	8.0
5	[($C_{22}H_{13}N_2SOBr)_2(H_2O)_2$]Cd	19.5	13.1	24.2
6	[($C_{22}H_{13}N_2SOBr)_2(H_2O)_2$]Cu	9.2	NZ*	NZ*
7	[($C_{22}H_{13}N_2SOBr)_2(H_2O)_2$]Zn	1.31	8.2	11.0
8	[($C_{22}H_{13}N_2SOBr)_2(H2O)_2$]Co	6.5	11.2	8.9

The biological activity of novel ligand and its complexes were tested against *Staphylococcus aureus*, *Salmonella typhi* and *Aspergillus niger*. The antimicrobial activity was carried on *In vitro* and disc diffusion and agar well diffusion assay[49]. The culture used were *Staphylococcus aureus* strain NICM 2029, *Salmonella typhi* strain MTCC 3224 and *Aspergillus niger* strain NCIM 545. This culture of microorganism was collected from NICM and NCL Pune. The nutrient media of microbiological

used for bacteria and potato dextrose agar media for Fungi. This culture of microorganism was grown for overnight at 37°C[50-51]. All investigated compound except complex of copper showed remarkable biological activity against *Staphylococcus aureus*. The entire investigated compound shows good biological activity against *Salmonella typhi* in Table 7. The Complexes of Cd, Ag and Zn are shows excellent antibacterial activity against salmonella typhi, showing the zone of inhibition in diameter 19.5mm, 15.5mm and 11.3mm respectively. The Schiff base ligand and complex of Cd, Ag and Ni complex show good antibacterial activity against *Staphylococcus aureus* showing the zone of inhibition in diameter 13.8mm, 11.7mm and 11.6mm respectively. The novel ligand and complex of Cd, Ag, and Mn exhibited excellent antibacterial activity against *Aspergillus niger* fungi, showing the zone of inhibition in diameter 24.2mm, 19.5mm and 15.8mm respectively. The result obtained clearly shows that complexes are more active against each organism[52]. The comparative study of ligand and its complexes shows that complexes are more active than their parent ligand.

CONCLUSION

In this research microwave oven is used for synthesis of novel ligand and its complexes. This method shows advantage like better yield and less reaction time. This method shows new, easy, simple, pollution-free way for metal complexes synthesis. That synthesized novel ligand and its complexes show remarkable activity against *Staphylococcus aureus*, *Salmonella typhi* and *Aspergillus niger* fungi.

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REFERENCES

1. Polshettiwar, V. Aqueous Microwave Assisted Chemistry Synthesis and Catalysis. *Royal Society of Chemistry*, Cambridge, UK., **2010**, ISBN 978-1-84973-938-9.
2. Agarwal, V.S.; Rajan, K.S.; Sen, P.K. United States Patent., **1992**, 5147567.
3. Anjali Jha. **2021**, https://doi.10.5772/ interhopen 98224.
4. Sravanthi, M.; Kavitha, B.; Reddy, Saritha P.; *International Research Journal of Pharmacy*., **2019**, *10*(3), 215-220.
5. Garima Shrivastava.; Manjul Shrivastava., *Int. Res. J. of Pharmacy.,* **2018**, *95*, 81-84.
6. Vinoth, G.; Indira, S.; Bharathi, M.; Alves, L.G.; Martins, A M.; Shanmuga Bharathi. *Inorg. Chem. Acta.,* **2021**, *514*, 128297, http: //doi. org/10.1016/j.molstruc.2920.128297.
7. Sinkar, S.N.; Moharir, S.; Undegaonkar, M. G.; Mirgane, S.R. *International Journal for Research in Applied Science and Engineering Technology*., **2021**, *9*(IV), 44-98.
8. Al Zayd, K.M. *Arabian Journal of Chemistry*., **2009**, *2*, 89-95
9. Mahajan, K.; Swami, M.; Singh, R.V. *Russian Journal of Coordination Chemistry.,* **2009**, *35*, 179-185, https://doi.org/10.1134/ S1070328409030038.
10. Manimohan, M.; Pugalmani, S.; Sithique, M.A. *International journal of Biological Macromolecules.,* **2019**, *136*, 738-754, https:// doi org/10.1016/j.ijbiomac.2019.10.052.
11. Sharma, K.; Singh, R. V.; Fahmi, N.; Singh, R. V. *Chimica. Acta*., **2010**, *75A*, 422 – 427. https://doi.org/10.1016/j.saa.2009.10.052.
12. Xavier, A.; Srividhya, N. IOSR *Journal of Applied Chemistry*., **2014**, *7*(11),6-15.
13. Asriri, A M.; Khan, S.A. *Molecules.,* **2010**, *15*, 6850-6858, https://doi.org/10.3390/ molecules 15106850.
14. Noorussabah, N.; Chaudhary,M.; Das, N.; Mohan, B.; Singh, K.; Dingh, R.K.; Ahmad, K.; Muhammad, S.; Kumar, S. *Journal of Inorganic and Organometallic Polymer and Materials.,* **2020**, *30*, 4426-4440, https://doi. org/ 10.1007/ s10904-020-01610-w.
15. Cimerman, Z.; Miljanic, S.; Galic, N. *Crotica Chemica Acta.,* **2000**, *73*, 81-85.
16. Mishra, A.; Pawar, H.; Jain, R.; Gupta, B. E. *Journal of Chemistry*., **2012**, *9*(a), 77- 85.
17. Bell, S.C.; Corklin, G. L.; Vhildress, S. J. *J AM Chem SOC*., **1963**, *18*, 2868-2869.
18. Yadaw, G.; Mani, J. *International Journal of Science and Research*., **2015**, *4*(2), 121-127.
19. Jahannes karges; Seth M. *Cohen. Rechim* **2021**. https://doi.org./10.1016/j. Ft rechim, 2021.03.006.

20. Renata Paprocka.; Anna Helmin Basa. *Co-ordination Chemistry Reviews.,* 2022. 214307. https:// doi org.10.1016/ j.ccr.201.214307.
21. Concha, C.; Quintana, C.; Klahn, A H.; Artigay, V.; Fuentealba, M.; Biot, C.; Halloum, L.; Kremer, L.; Lopez, R.; Romanos, J; Huentupil, Y. **2017**, *131*, 40-45. https://doi.org/19.1016/j. poly.2917.04.031.
22. Shaharyar, M.; Mazumder, A.; Salahuddin, Garg R.; Pandey, R.D. *Arabian Journal of Chemistry.,* **2016**, *9*, 342–347. https://doi. org/10.1016/j. arabjc. 2011.04.013.
23. Refaat, H. M. *European Journal of Medicinal Chemistry.*, **2010**, *45*, 2949 -2956. https://doi. org/10.1016/j. ejmech. 2010.03.022.
24. Padalkar, V S.; Borse, B. N.; Gupta, V D ; Phatangare, K R.; Patil, V.S.; Umape, O.G.; Sekar, U.N. *Arabian Journal of Chemistry.,* **2016**, *9*, 1125-1130, https://doi.org/10.1016/j. arabic. 2011.12.006.
25. Khan, M.I.; Xu, S.; Ali, M. M.; Ali, R.; Kazmi, A.; Akhatar, N.; Bilal, M.; Hu, Y.; Li, F. *J.Rad. Res. And Appl. Sci.*, **2020**, *13*, 267-275, https:// doi.org/10.1080/16878507. 2020. 1730589.
26. Poernie, M.; Kontree, D.; Miljanie, S.; Soldin, Z.; Budiy, A.; Galie, N. *J. Mol. Struct.*, **2020**, 1227. https://doi.org/10.1016/j.molstruc. 2020, 129564.
27. Tonelli, M.; Paglietti, G.; Boido, V.; Sparatore, F.; Marongiu, F.; Morongiu, E.; La, Colla P.; Loddo, R. *Chem Biodiverse.*, **2008**, *5*(2), 386-401. https://doi org/10.1002/cbdv.200890203.
28. Shaharyar, M.; Mazumder, A.; Salahuddin, Garg R.; Pandey, R.D. *Arabian Journal of Chemistry.*, **2016**, *9*, 342–347, https://doi org/10.1016/j.arabjc.2011.04.013.
29. Oswale, A.; Ott, I. Ogunlana. *International Journal of Inorganic Chemistry.*, **2012**, *7*, 1-6.
30. Cirri, D.; Baroli, F; Pratesi, A.; Baglini, Eb.; Barresi,E.; Marzi,T. *Biomedicines.*, **2021**, *9*, 504. https://doi.org./10.3390/ Biomedicines. 9050504.
31. Dielly, Oliveira morais; Alexandre, Pancatti Jiale; Wang. *Journal of Materials Science and Materials in Medicine.*, **2021**, *32*, 101.
32. Hoyer, Carolin.; Schwerk, Peter.; Sarkar, Biprajit., **2021**. https://doi.org./10.001/ejic. 202100024.
33. Umekar, M.J.; Lohiya, R. T.; Gupta, K.R. *Journal Pharm Sci.*, **2021**, *7*, 233. https://doi. org./10.1186/43094-021-00379-0.
34. Kareem, J.K.; Waddai, F.Y.; Abbas, G. J. *J Pharm. Sci. and Res.*, **2019**, *11*(1), 119-124.
35. Venugopal, P.; Krishnakuty, K. *J. Indian Chem Soc.,* **1997**, *74*, 523-563.
36. Sharma, S T.; Mehta, M.K.; Shah, *Der. Chem. Sin.*, **2013**, *4*, 141-146.
37. Dharmaraj, N.; Viswanathamurthi, P.; Natarajan, K. *J. Transition Met Chem.*, **2001**, *26*,105-109.
38. Omidi, S.; Kakanejadifard, A. *RSC Advanced*, **2020**, *10*, 39186-39202, https://doi.org/10. 1039/DORA.05720G.
39. Mishra, A.P.; Jain, Rajendra K. *Journal of Saudi Chemical Society.*, **2014**, *18*, 814-824, https://doi.org/10.1016/j.jses.2011.09.013.
40. Moharir, S. P.; Undegaonkar, M.G.; Sinkar S.N.; Mirgane, S. R. *Journal of Chemistry and Chemical Sciences.*, **2021**, *11*(4), 43-51.
41. Rehab, K.; Al- Shemary; Ali, Al- Khazraji, M. A.; Ali, N. Niseaf. *The Pharma Innovation Journal.,* **2016**, *5*(1), 81-86.
42. Sinn, E.; Morris, C. M. *Co-ord. Chem. Rev.*, **1969**, *4*, 891.
43. Nakagawa, L.; Shimanonchi, T. *Specro. Chem. Acta.*, **1964**, *20*, 429.
44. Salami, H.A.; Haruna, A.U.; Fzeala F.T.; Salawu, O.W. Scholars research Library, *Der Pharma Chemica.*, **2015**, *7*(4), 261-165.
45. A. A. Khandar, R J. Butecher, M. Abedi, S.A.H. Yazdi, M Akkurt and M.N.Tahir. *Polyhydron.*, **2011**, *30*, 942.
46. Jayaseelan, P.; Prasad, S.; Vedanayaki S.; Rajavel, R. *Eur. J. Chem.*, **2011**, *2*(4), 480.
47. CODEN (USA). *IJCRGG.,* **2014**, 2534-2538.
48. Selbin, *J. Co-ord. Chem. Rev.,* **1966**, *1*, 293-314.
49. Banfi, E; Scialino, G.; Monti-Bragadin, C. *Journal of Antimicrobial Chemotherapy.*, **2003**, *52*, 796-800. https://doi.org/10.1093/ jac/dkh439.
50. Stalons, D. R.; Therosberry, C. *Antimicrob Agents Chemother.*, **1975**, *7*, 15-21. https:// doi.org/19.1128/AAC.7.1.15.
51. Nwabueze, J.N.; Salami, H.A. *International Journal of Research in Inorganic Chemistry.*, **2013**, *3*(1), 1-3.