

Synthesis, Characterization, Thermal Analysis, and Antibacterial Activity of New Tetradentate Ligands and their Complexes

Basher J. Kadhim¹, Jasim Alshawi², Tahseen Alslaim³

^{1,2,3}Chemistry Department, Faculty of Education for Pure Sciences, University of Basrah

²Crossponding Author's E-mail: [jasim.salih\[at\]uobasrah.edu.iq](mailto:jasim.salih[at]uobasrah.edu.iq)

Abstract: *New Schiff bases tetradentate ligands N2O2, were prepared from condensation chloroacetylaceton with diamine compounds (ethylenediamine, hydrazine carbothiohydrazide). then synthesis their transition metal complexes by reaction with Cu (II), and Co (II). All synthesized compounds were characterized by spectral techniques such as FTIR, ¹HNMR and electronic spectra, and Mass spectra. The thermal stability and decomposition of complexes were studied. The antibacterial activity against gram-positive and gram-negative bacteria and calculate the diameter of inhibition zone (mm).*

Keywords: Schiff bases, tetradentate, acetylacetone, antibacterial, TG

1. Introduction

A lot of research has been done on Schiff bases because of how many different ways chemicals may be permuted. Schiff bases are a significant group of chemicals in the pharmaceutical and medical fields. They exhibit biological properties like antimicrobial properties [1-4], antifungal [5], anti-cancer [6-8]. A wide range of metal ions can be coordinated using Schiff base ligands [9-11]. Tetradentate N2O2 donor atom Schiff bases have long been recognized to coordinate with a variety of metal ions [12-16]. These ligands can create a wide range of complexes with various stoichiometry, structural, magnetic, and spectroscopic characteristics. Schiff bases generated from acetylacetone and diamine were investigated in various metal complexes [17-19]. In this study synthesis new tetradentate Schiff bases ligands NOON donor atoms derived from acetylacetone or 3-chloroacetylacetone with ethylene diamine or thiocarbodihydrazide and their Cu, Co complexes.

2. Chemistry Section

2.1. Instrumentation

This instrument measures the intensity of the absorption bands between 4000 and 400 cm⁻¹, which is found in the KBr pellet. Using an Agilent Technologies 5975C spectrometer, the researchers used the EI method to scan the mass spectra at 70 eV. The Bruker Avance 500 MHz spectrometer was used to scan the ¹H and ¹³C NMR spectra of the investigated compounds, with TMS serving as the internal standard, DMSO-d₆ was used as a solvent. A measure of a complex's magnetic susceptibility is called the Magnetic Susceptibility Balance Modern Type Indicator (MSB-MKI).

2.2. General method for synthesis ligands (H2L1 and H2L2)

To a solution of 20m. mol b-diketone (acetylacetone or 3-chloroacetylacetone) in 50ml ethanol, was added 10 m. mol of diamine (ethylene diamine or thiocarodihydrazide), the mixture was heated under reflux for 4 hrs. cooled the reaction mixture and the product was collect from filtration and recrystallized from ethanol.

2.2.1 4, 4'-(ethane-1, 2-diylbis (azan-1-yl-1-ylidene)) bis (3-chloropent-2-en-2-ol (H₂L1): Yellow Powder, recrystallized from ethanol, yield: 81%, M. P 131-130°C ¹HNMR (DMSO, δppm) 11.21 (S, 2H, OH), 3.53 (Tre, 4H, CH₂CH₂), 2.17 (S, 12H, -CH₃), ¹³CNMR, 176.3, 164.6, 85.1, 62.7, 15.1, 12.4; EI-Mass (70ev m/z) 292.1, 274, 257, 220, 159, 148.1, 132.1., IR (ν, cm⁻¹) 3377, 2968, 2927, 2872, 1695, 1664, 1516, 1456, 1417, 1352. UV (nm): 230 (ε = 11312.5), 275 (ε = 5410), 300 (λ_{max}950).

2.2.2 4-hydroxypent-3-en-2-ylidene)-2-((Z)-4-hydroxypent-3-en-2-ylidene) hydrazine-1-carbothiohydrazide. (H₂L2): Light Yellow crystallized recrystallized from ether yied: 70%, M. P: 207-206°C, ¹HNMR (DMSO, δppm), 14.38 (S, 2H, NH), 6.25 (S, 6H, CH₂), 2.38 (S, 6H, CH₃), ¹³CNMR: 184.2, 176.3, 151, 87.0, 24.2, 15.2, EI-Mass (70ev m/z): 270, 256, 212, 153, IR (ν, cm⁻¹) 3392, 2972, 2927, 2858, 1676, 1651, 1610, 1514, 1492,

2.3 General method for synthesis transition metal complexes

The complexes prepared from reaction (10 m. mol) of ligand in 50ml (MeOH +DMF 4: 6) mixture with (10m. mol) of transition metal salt (CuCl₂.2H₂O, CoCl₂.6H₂O), the mixture was heated for 5 hrs, the complex was collected by filtration the wash three times by ether.

2.3.1.complex [Cu L₁.2H₂O]:

Brown powder, yield 60%; M. P. >300 °C; IR (ν, cm⁻¹): 3377, 2968, 2927, 2872, 1684, 1656, 1515, 1456, 1417,

1352; UV-Visb, λ_{\max} (ϵ): 366nm (6725.5), 309nm (5840.8), 476nm (519.2), 633nm (43.2); Molar conductance ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) = 5.3; μ_{eff} (B. M.) = 1.8; Anal. calc. for: $\text{C}_{12}\text{H}_{20}\text{Cl}_2\text{CuN}_2\text{O}_4$: M, 16.26; C, 36.89; H, 5.16; Cl, 18.15; N, 7.17. found: M, 16.18; C, 36.65; H, 5.10; Cl, 18.20; N, 7.11.

2.3.2. mComplex [$\text{Co L}_1 \cdot 2\text{H}_2\text{O}$]:

Olive powder; yield 70%; M. P. $>300^\circ\text{C}$; IR (ν , cm^{-1}): 3377, 2968, 2927, 2872, 1686, 1654, 1515, 1456, 1417, 1352; UV-Visb, λ_{\max} (ϵ): 320 nm (10452), 369 nm (9341), 613.9 nm (240), 679 nm (40); molar conductance ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) = 9.8; μ_{eff} (B. M.) = 4.54; Anal. calc. for: $\text{C}_{12}\text{H}_{20}\text{Cl}_2\text{CoN}_2\text{O}_4$; M, 15.26; C, 37.33; H, 5.22; Cl, 18.36; N, 7.25; found: M, 15.28; C, 37.29; H, 5.26; Cl, 18.27; N, 7.21.

2.3.3. complex [$\text{Cu L}_2 \cdot 2\text{H}_2\text{O}$]:

Brown powder, yield 66%; M. P. $>300^\circ\text{C}$; IR (ν , cm^{-1}): 3392, 2972, 2927, 2858, 1674, 1648, 1610, 1514, 1492, 1475, 1452, 1421; UV-Visb, λ_{\max} (ϵ): 299nm (8675), 375nm (6725.5), 304nm (4533.8), 476nm (522.3), 633nm (53.4); Molar conductance ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) = 12; μ_{eff} (B. M.) = 1.6; Anal. calc. for: $\text{C}_{11}\text{H}_{20}\text{CuN}_4\text{O}_4\text{S}$: M, 17.27; C, 35.91; H, 5.48; N, 15.23; S, 8.73, found: M, 17.13; C, 35.89; H, 5.50; N, 15.21; S, 8.69.

2.3.4. complex [$\text{Co L}_2 \cdot 2\text{H}_2\text{O}$]:

Olive powder; yield 80%; M. P. $>300^\circ\text{C}$; IR (ν , cm^{-1}): 3392, 2972, 2927, 2858, 1670, 1649, 1610, 1514, 1492, 1475, 1452, 1421; UV-Visb, λ_{\max} (ϵ): 306nm (9784), 355 nm (5452), 612 nm (241); molar conductance ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) = 15; μ_{eff} (B. M.) = 4.46; Anal. calc. for: $\text{C}_{11}\text{H}_{20}\text{CoN}_4\text{O}_4\text{S}$; M, 16.22; C, 36.37; H, 5.55; N, 15.42; S, 8.83; found: M, 16.19; C, 36.31; H, 5.60; N, 15.39; S, 8.86.

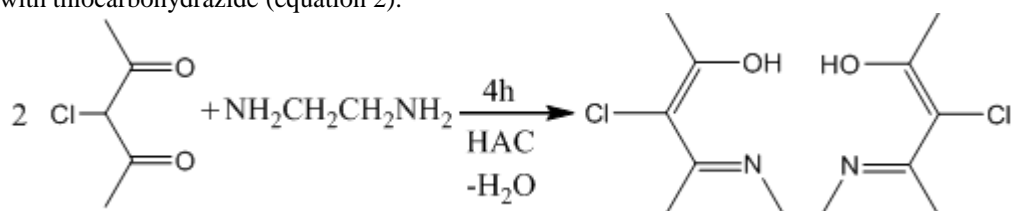
3. Antimicrobial activity

The antibacterial activity was tested by using Agar Well diffusion [20]. The culture medium for bacteria was prepared and poured into the Petri dishes and left for 20 minutes to solidify. The bacteria or fungal were spread on the surface of the culture medium, then 0.1 ml was added (concentration 2000 ppm) of the prepared compounds were added. The Petri dishes were incubated at 37°C .

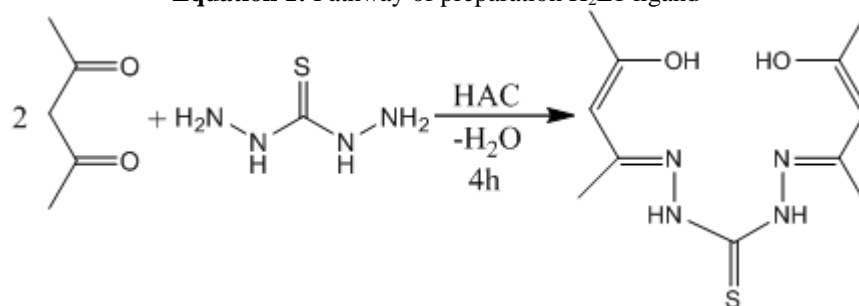
4. Results and Discussion

Two Schiff bases ligands H_2L_1 was prepared from the condensation of 3-chloro-2, 4-pentadion with ethylenediamine (equation 1) and H_2L_2 was prepared from

2, 4-pentadion with thiocarbohydrazide (equation 2).



Equation 1: Pathway of preparation H_2L_1 ligand



Equation 2: Pathway of preparation H_2L_2 ligand

The Cu and Co complexes are prepared from the reaction Schiff bases ligands with transition metal salts ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) in EtOH + DMF (4: 6) as a solvent under reflux [figure 1]

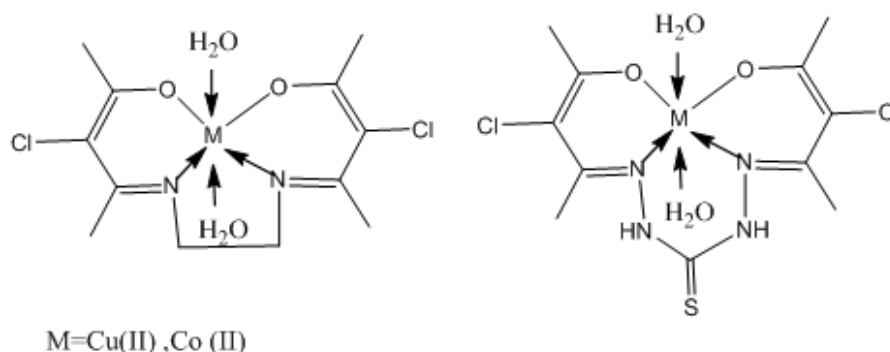


Figure 1: Suggested structure of metal complexes

Volume 10 Issue 11, November 2021

www.ijsr.net

Licensed Under Creative Commons Attribution CC BY

4.1. Characterization of synthesized compounds

The synthesized compounds are characterization by using spectroscopic techniques.

The infrared spectra of ligands shown stretching vibration bands at 3392 and 3377 cm^{-1} attributed of OH for L1 and L2 respectively. The stretching vibration of C-H aliphatic for ligand L1 at 2972 cm^{-1} , and 2983 cm^{-1} for L2. As well as the bands of azomethane at 1651 cm^{-1} for ligand L1 and at 1656

cm^{-1} for ligand L2. The molecular ion of Mass spectrometry and elemental analyzes were consistent with the proposed structures of ligands and complexes. The ^1H NMR spectrum of L1 (figure 2) displays three signals, at 11.21 ppm attributed to OH proton, the second signal is singlet at 3.54 ppm attributed to $\text{CH}_2\text{-CH}_2$ protons, the final signal at 2.47ppm for the CH_3 protons. The NMR spectrum of L2 also shows three singlet signals, at 14.2ppm, 6.2ppm, and 2.18 ppm attributed to OH, $\text{CH}=\text{C}$, and CH_3 respectively.

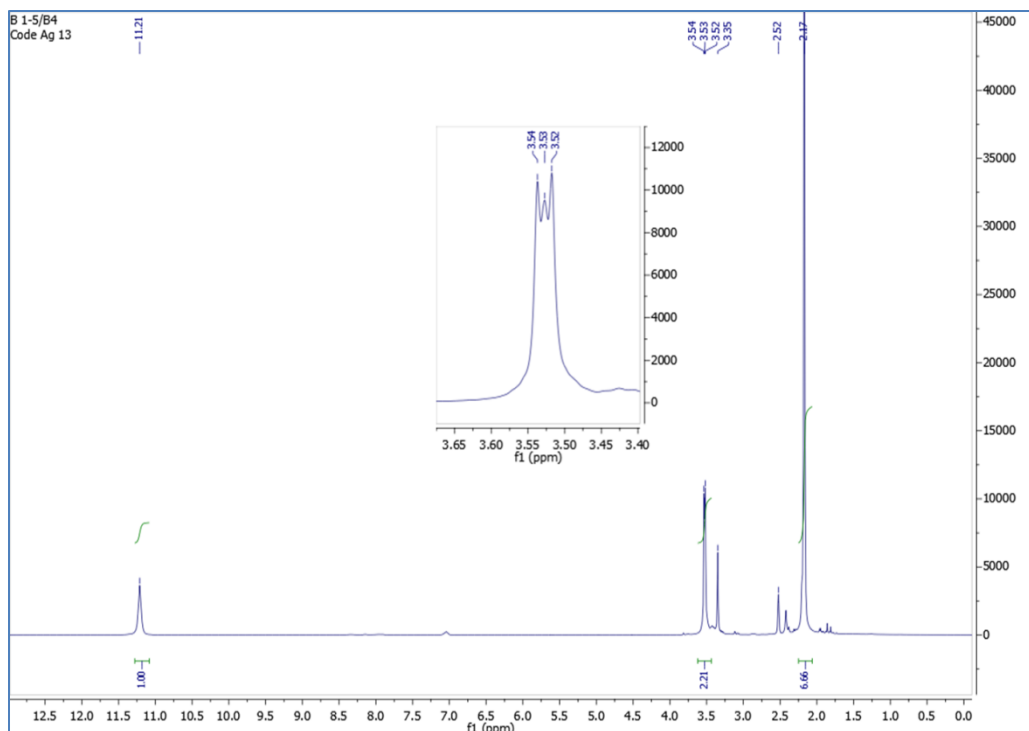


Figure 2: ^1H NMR spectrum of $\text{H}_2\text{L1}$ ligand

4.2. Thermal analysis results

To find out more about the thermal stability of these novel complexes and check whether water molecules are inside or outside the central metal ion's inner coordination sphere, researchers utilized thermal analysis (TG and DTG) on the

Schiff base complexes (table 1 and figure 3-6). The complexes were heated to 600 $^\circ\text{C}$ in a nitrogen environment at a rate of 10 C/min for TG analysis. There is good agreement between the measured mass losses and the predicted values obtained from TG curves. All complexes have different breakdown processes.

Table 1: Thermal analysis data of complexes

Comp.	Decomposition Temp. $^\circ\text{C}$			remaining product at 600 $^\circ\text{C}$	weight Loss% (Calc.)	Assignment
	T_i	T_{max}	T_f			
CuL1	110 210	180	210 600	36.24%	9.4 (9.2) 54.36	$2\text{H}_2\text{O}$, coord
CoL1	110 200	170	200 600	34.65%	9.6 (9.32) 55.75	$2\text{H}_2\text{O}$, coord
CuL2	110 260	250	260 600	38.95%	9.8 (9.8) 51.25	$2\text{H}_2\text{O}$, coord
CoL2	120 260	250	260 600	40.76%	9.26 (9.9) 49.98	$2\text{H}_2\text{O}$, coord

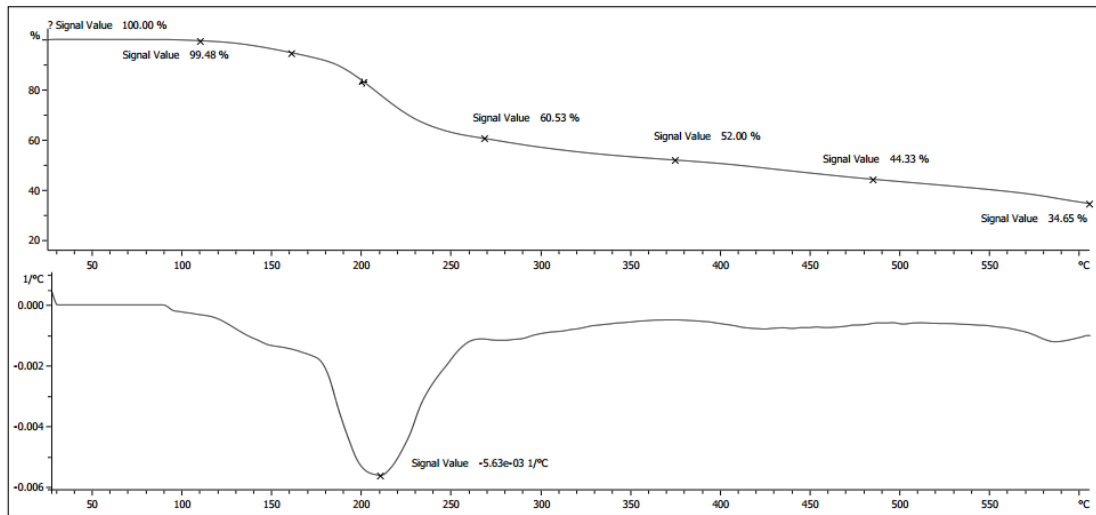


Figure 3: TG diagram of CoL1 complex

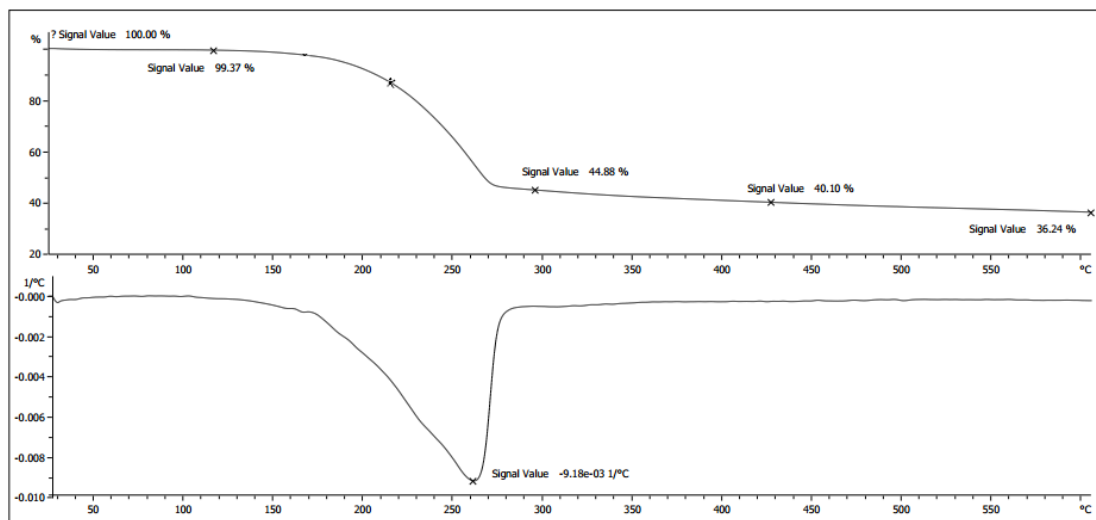


Figure 4: TG diagram of CuL1 complex

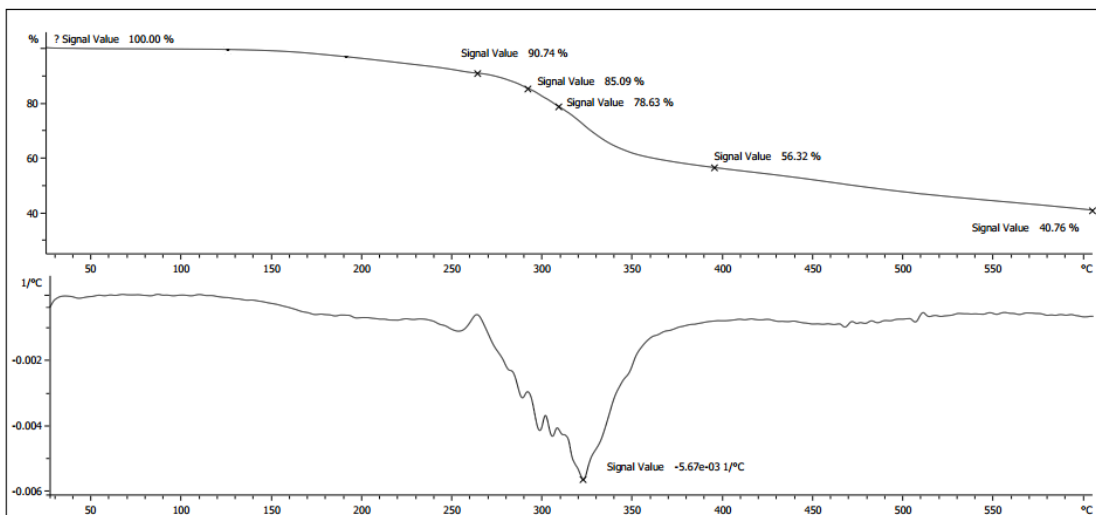


Figure 5: TG diagram of CoL2 complex

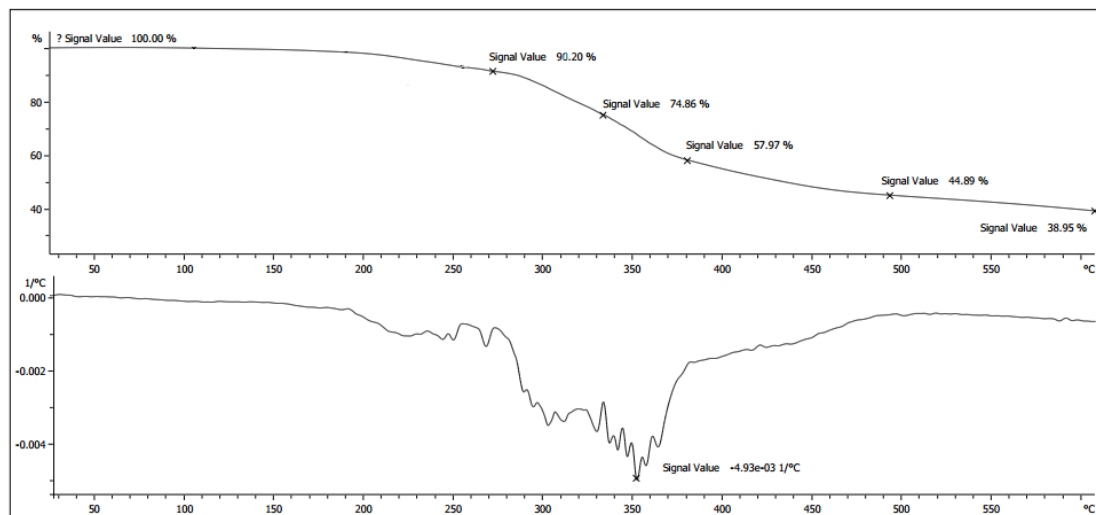


Figure 6: TG diagram of CuL2 complex

5. Antimicrobial Activity

The antibacterial and antifungal activities of the Schiff base ligand and its complexes have screened for their in-vitro antibacterial activity against staphylococcus Escherichia coli Aspergillusniger and A. flavus. The zones of inhibition produced by the test compounds are presented in table (2). It is observed that the metal complexes possess higher growth inhibition potential compared to that of the ligand. It is suggested that the complexes having anti-bacterial and antifungal activities inhibit the multiplication process of the microbe by blocking their active sites.

Table 2: The diameter of inhibition zone (mm) of synthesized compounds

Compound	Diameter of inhibition zone (mm)			
	Bacteria species		Fungi species	
	S. aureus	E. coli	A. niger	A. flavus
L1H ₂	3	9	16	10
L1Cu	10	12	15	11
L1Co	9	10	17	12
L2H ₂	4	8	17	17
L2Cu	8	11	13	15
L2Co	10	14	14	10
Ampicillin	17	8	13	11
Ceftazidime	3	17	18	15

References

- [1] S. N. Sovari and F. Zobi, *Chemistry* 2020, 2 (2), 418-452
- [2] H. Pasdar, B. H. Saghavaz, N. r Foroughifar and M. Davallo, *Molecules* 2017, 22 (12), 2125
- [3] Alegna P. BalianoElisangela F. PimentelAline R. BuzinTainã Z. VieiraWanderson RomãoLilian V. ToseDominik LenzTadeu U. de AndradeMarcio FronzaTamara P. KondratyukDenise C. Endringer, *Rev. bras. farmacogn.*26 (6) Nov-Dec 2016
- [4] P. Parvekar, J. Palaskar, S. Metgud, R. Maria and S. Dutta, *Biomaterial Investigations in Dentistry* (7) 2020
- [5] W. H. Hegazy and I. H. Al-Motawaa, A. Hameed, M. Al-Rashida, M. Uroos, S. Abid Ali, K. M. Khan, Expert opinion on therapeutic patents 27 (1) (2017) 63-79.
- [6] K. T. Tadele, T. W. Tsega, Formerly Current Medicinal Chemistry-Anti-Cancer Agents, 19 (15) (2019) 1786-1795.
- [7] N. Uddin, F. Rashid, S. Ali, S. A. Tirmizi, I. Ahmad, S. Zaib, M. Zubair, P. L. Diaconescu, M. N. Tahir, J. Iqbal, *Journal of Biomolecular Structure and Dynamics* 38 (11) (2020) 3246-3259.
- [8] O. A. Ali., *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 121 (2014) 188-195.
- [9] C. Çelik, M. Tümer, S. Serin, *Synthesis and reactivity in inorganic and metal-organic chemistry* 32 (10) (2002) 1839-1854.
- [10] S. Kasselouri, A. Garoufis, G. Kalkanis, S. P. Perlepes, N. Hadjiliadis,, *Transition Metal Chemistry* 18 (5) (1993) 531-536.
- [11] A. A. Saleh, *Journal of Coordination Chemistry* 58 (3) (2005) 255-270.
- [12] *New Journal of Chemistry* 42 (23) (2018) 19294-19304.
- [13] S. Celedon, T. Roisnel, V. Artigas, M. Fuentealba, D. Carrillo, I. Ledoux-Rak, J.-R. Hamon, C. Manzur, *New Journal of Chemistry* 44 (22) (2020) 9190-9201.
- [14] X. Liu, C. Manzur, N. Novoa, S. Celedón, D. Carrillo, J.-R. Hamon, *Coordination Chemistry Reviews* 357 (2018) 144-172.
- [15] *New Journal of Chemistry* 43 (28) (2019) 11391-11407.
- [16] P. Parvekar, J. Palaskar, S. Metgud, R. Maria and S. Dutta, *Biomaterial Investigations in Dentistry* (7) 2020
- [17] B. Sarkar, G. Bocelli, A. Cantoni, and A. Ghosh, *Polyhedron* (27) 2008, 693-700
- [18] K. Mohammadi, and M. Rastegari, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, (97) 2012, 711-716
- [19] A. A. Saleh, *Journal of Coordination Chemistry*, 58 (3) (2005) 255-270.
- [20] C. Perez, M. Pauli, and P. Bazerque. *J. Acta Bio. Med. Exper*, 15 (1990), 113-115