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CONVENTIONAL AND MICROWAVE-ASSISTED SYNTHESIS AND CHARACTERIZATION of Ru(III)/Cu(II) COMPLEXES CONTAINING DICARBOXYLIC ACID GROUPS

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Abstract: In this study, microwave-assisted and conventional syntheses of Ru(III) and Cu(II) complexes with 2,4-pyridinedicarboxylic acid (L1), 3,5-pyridinedicarboxylic acid (L2), and 3,5-pyrazoledicarboxylic acid (L3) have been studied. A comparative study of microwave and conventional methods was performed to determine their differences in terms of reaction time, the amount of solvent, and reaction yield. The reaction time was reduced significantly from several hours to a few minutes, and high yields were obtained by microwave method while using considerably less amount of solvent. The synthesized complexes were characterized by FT-IR, UV-Vis, AAS, ^{1}H-NMR, elemental analyses, and magnetic susceptibility. These studies showed that copper and ruthenium complexes have square planar and octahedral geometries, respectively. The metal complexes of Cu(II) and Ru(III) were easily synthesized upon exposure to microwave irradiation.

Keywords: Microwave synthesis, Inorganic-organic hybrid, Ru(III)-Cu(II) complexes.

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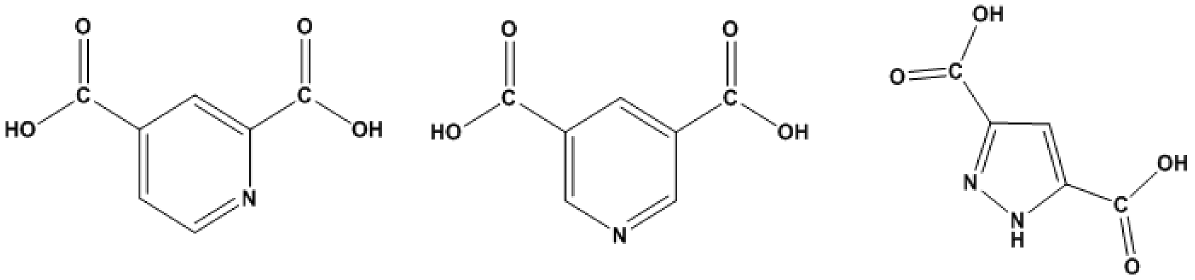
INTRODUCTION

Organic-inorganic hybrid materials attract considerable attention in recent years because of their interesting molecular topologies and crystal packing motifs along with potential applications in many areas, including gas storage, separation, catalysis, magnetism, optics, as well as electrical conductivity [1]. The functionality of such hybrid materials can be multiplied by the incorporation of organic and inorganic counterparts into one structural unit [2,3]. A microwave-assisted inorganic synthesis method is an important technique in green synthetic chemistry [4]. The technique offers several advantages over conventional synthesis, especially the synthesis of ruthenium complexes, which typically require many hours of refluxing in high-boiling solvents to affect a reaction. Similar reactions, when performed in a microwave reactor, can occur in a matter of minutes [5-7]. The main advantage of this reactor is the almost instantaneous 'in-core' heating of materials in a homogenous and selective manner [8]. Particularly, the reaction time and energy input are supposed to be mostly reduced in the reactions that are run for a long time at high temperatures under conventional conditions [9]. In this work, we present the syntheses of Cu(II) and Ru(III) having different stabilities as first and second row transition metal complexes with L1, L2 and L3 ligands (Scheme 1) because they have various side-bonding in their structures due to carboxylic moieties [10]. Both conventional and microwave methods were carried out and the obtained results were compared with each other. The complexes were characterized by analytical and spectroscopic methods.



Scheme 1. The ligands used in this study (L1, L2, L3).

MATERIALS AND METHODS

Materials

$CuCl_2.2H_2O$, $RuCl_3.xH_2O$, 2,4-pyridinedicarboxylic acid, 3,5-pyridinedicarboxylic acid, and 3,5-pyrazinedicarboxylic acid were purchased from Sigma Aldrich and used without further purification. All other chemicals and solvents were commercially available (Merck, Fluka).

Physical measurements

FT-IR spectra were recorded on a Perkin-Elmer Spectrum RX I FT-IR spectrometer as KBr pellets in the 4000-400 cm^{-1} range. The UV-Vis spectra was determined in DMSO solvent with a concentration of 1.0×10^{-3} M for the free ligands and their complexes using a Perkin Elmer Lambda 25 Spectrophotometer with 1 cm quartz cell, in the range 200-800 nm. AAS analyses were recorded on a Perkin Elmer Analyst 400 spectrometer. The DC magnetic susceptibilities of powdered samples were measured by a Sherwood Scientific magnetic susceptibility meter.

Synthesis of [Cu(L1)$_2$] by the Conventional Method (CM)

Copper(II) chloride dihydrate (0.335 g, 2.50 mmol) in MeOH (10 mL) was slowly added to a solution of L1 acid (0.417 g, 2.50 mmol) in MeOH (40 mL) at room temperature. The mixture was left for 144 h. The light green solid product which precipitated was filtered off and washed with acetonitrile (Yield: 48%). M.P.:315-316°C. [Cu(L1)$_2$]: ^{1}H-NMR (300 MHz, DMSO, 25°C): δ (ppm) = 13.10 (s, 1H, OH), 8.26 (d, 1H, CH), 8.70 (s, H, CH), 7.58 (d, H, CH). UV-Vis (DMSO, λ_{max}(nm)): L1: 279, L1-Cu: 446. AAS. Calculated (1:2): 15.90%; Found: 15.18%.

Synthesis of [Cu(L1)$_2$] by the Microwave Method (MM)

The ligand (0.022 g, 0.13 mmol) and the metal salt (0.017 g, 0.130 mmol) were mixed thoroughly in a porcelain capsule. Methanol (5 mL) was added to this mixture and stirred. The mixture was irradiated for 3 minutes in the microwave oven at 850 W power. The product was washed with methanol to dissolve any unreacted material, if any, and filtered. The product was repeatedly washed with methanol and finally dried on air (Yield: 89%). M.P.:315-316°C. [Cu(L1)$_2$]: ^{1}H-NMR (300 MHz, DMSO, 25°C): δ (ppm) = 13.10 (s, 1H, OH), 8.26 (d, 1H, CH), 8.70 (s, H, CH), 7.58 (d, H, CH). UV-Vis (DMSO, λ_{max}(nm)): L1: 279, L1-Cu: 446. AAS. Calculated (1:2): 15.90%; Found: 15.18%.

Synthesis of [Cu(L2)Cl$_2$] by the Conventional Method

Copper(II)chloride dihydrate (0.202 g, 1.50 mmol) in MeOH (8 mL) was slowly added at room temperature to a solution of L2 (0.251 g, 1.50 mmol) in MeOH (90 mL). The mixture was left at room temperature for 144 h. The turquoise solid product was precipitated in and washed with acetonitrile (Yield: 41%). M.P.:259-260°C. [Cu(L2)Cl$_2$]: ^{1}H-NMR (300 MHz, DMSO, 25°C): δ (ppm) = 12.14 (s, 1H, OH), 3.09 (m, 2H, CH$_2$), 2.33 (m, 1H, CH), 2.09 (m, 2H, CH$_2$). UV-Vis (DMSO, λ_{max}(nm)): L2: 254, L2-Cu: 654. AAS. Calculated (1:1): 21.05%; Found: 21.00%.

Synthesis of [Cu(L2)Cl$_2$] by the Microwave Method

The synthesis was similar to that described for [Cu(L1)$_2$]. It used the L2 ligand (0.022 g, 0.13 mmol) and a turquoise solid was obtained (Yield: 82%). M.P.:259-260°C. [Cu(L2)Cl$_2$]: ^{1}H-NMR (300 MHz, DMSO, 25°C): δ (ppm) = 12.14 (s, 1H, OH), 3.09 (m, 2H, CH$_2$), 2.33 (m, 1H, CH), 2.09 (m, 2H, CH$_2$). UV-Vis (DMSO, λ_{max}(nm)): L2: 254, L2-Cu: 654. AAS. Calculated (1:1): 21.05%; Found: 21.00%.

Synthesis of [Cu(L3)$_2$] by the Conventional Method

Copper(II) chloride dihydrate (0.135 g, 1.0 mmol) in MeOH (10 mL) was slowly added, at room temperature, to a solution of L3 (0.175 g, 1.0 mmol) in MeOH (15 mL). The mixture was left at room temperature for 144 h. The green solid precipitate was filtered off and washed with acetonitrile (Yield: 60%). M.P.:>300°C. [Cu(L3)$_2$]: ^{1}H-NMR (300 MHz, DMSO, 25°C): δ (ppm) = 13.70 (s, 1H, NH), 12.20 (s, 1H, OH), 6.30 (s, 1H, CH) ppm. UV-Vis (DMSO, λ_{max}(nm)): L3: 257, L3-Cu: 648. AAS. Calculated (1:2): 15.40%; Found: 17.30%.

Synthesis of $[Cu(L3)_2]$ by the Microwave Method

The synthesis was similar to that described for $[Cu(L1)_2]$. It used the L3 (0.023 g, 0.13 mmol) ligand and a green-colored solid were obtained (Yield: 86%). M.P.:>300°C. $[Cu(L3)_2]$: ^{1}H-NMR (300 MHz, DMSO, 25°C): δ (ppm) = 13.70 (s, 1H, NH), 12.20 (s, 1H, OH), 6.30 (s, 1H, CH). UV-Vis (DMSO, λ_{max}(nm)): L3: 257, L3-Cu: 648. AAS. Calculated (1:2): 15.40%; Found: 17.30%.

Synthesis of $[Ru(L1)_2(H_2O)Cl]$ by the Conventional Method

$RuCl_3.xH_2O$ (0.016 g, 0.08 mmol) in MeOH (12 mL) was slowly added at room temperature to a solution of L1 (0.013 g, 0.08 mmol) and NaOH (0.016 g, 0.04 mmol) in H_2O (10 mL). The mixture was left at room temperature for one month [11]. The green solid product which precipitated was filtered off and isolated from the methanolic solution (Yield: 62%). M.P.:310°C. $[Ru(L1)_2(H_2O)Cl]$: ^{1}H-NMR (300 MHz, DMSO, 25°C): δ (ppm) = 12.74 (s, 1H, OH), 9.24 (s, 1H, CH), 8.59 (s, 1H, CH). UV-Vis (DMSO, λ_{max}(nm)): L1: 279, L1-Ru: 447, AAS. Calculated (1:2): 20.74%; Found: 21.05%.

Synthesis of $[Ru(L1)_2(H_2O)Cl]$ by the Microwave Method

$RuCl_3.xH_2O$ (0.016 g, 0.08 mmol), L1 (0.013 g, 0.08 mmol) and ethylene glycol (2 mL) was mixed in a porcelain capsule, and they were dissolved in an ultrasonic mixer. The mixture was irradiated for 20 seconds in the microwave oven with a power of 850W. The capsule was cooled under tap water. Acetone (1.5 mL) was added into the solution and the mixture was stirred in 10 minutes. The solution was evaporated and the green product was recrystallized from ethanol (Yield: 76%). M.P.:310°C. $[Ru(L1)_2(H_2O)Cl]$: ^{1}H-NMR (300 MHz, DMSO, 25°C): δ (ppm) = 12.74 (s, 1H, OH), 9.24 (s, 1H, CH), 8.59 (s, 1H, CH). UV-Vis (DMSO, λ_{max}(nm)): L1: 279, L1-Ru: 447, AAS. Calculated (1:2): 20.74%; Found: 21.05%.

Synthesis of $[Ru(L2)_2(H_2O)Cl]$ by the Conventional Method

$RuCl_3.xH_2O$ (0.021 g, 0.10 mmol) in MeOH (15 mL) was slowly added, at room temperature, to a solution of L2 (0.017 g, 0.10 mmol) and NaOH (0.082 g, 2 mmol) in H_2O (10 mL). The mixture was left at room temperature for one month. The green solid product was filtered off and isolated from the methanolic solution (Yield: 65%). M.P.:>300°C. $[Ru(L2)_2(H_2O)Cl]$: ^{1}H-NMR (300 MHz, DMSO, 25°C): δ (ppm) = 12.74 (s, 1H, OH), 9.48 (d, 1H, CH), 8.93 (s, 1H, CH), 8.12 (d, 1, CH). UV-Vis (DMSO, λ_{max}(nm)): L2: 254, L2-Ru: 385, AAS. Calculated (1:2): 20.74%; Found: 19.82%.

Synthesis of $[Ru(L2)_2(H_2O)Cl]$ by the Microwave Method

$RuCl_3.xH_2O$ (0.021 g, 0.10 mmol), L2 (0.017 g, 0.10 mmol) and MeOH (15 mL) were added in a porcelain capsule, and they were dissolved in the ultrasonic mixer. The mixture was irradiated for 5 minutes in the microwave oven with a power of 850 W. The capsule was cooled under tap water. The solution was evaporated and the green product was washed with petroleum ether and recrystallized from acetone (Yield: 78%). M.P.:>300°C. $[Ru(L2)_2(H_2O)Cl]$: ^{1}H-NMR (300 MHz, DMSO, 25°C): δ (ppm) = 12.74 (s, 1H, OH), 9.48 (d, 1H, CH), 8.93 (s, 1H, CH), 8.12 (d, 1, CH). UV-Vis (DMSO, λ_{max}(nm)): L2: 254, L2-Ru: 385, AAS. Calculated (1:2): 20.74%; Found: 19.82%.

RESULTS AND DISCUSSION

The results of the elemental analyses and magnetic susceptibility values of the obtained compounds are given in Table 1. The complexes are air-stable, have higher melting points, and are insoluble in H_2O and most of the organic solvents except for DMSO and DMF. The elemental analysis and atomic absorption data of the complexes indicated a 1:2 metal: ligand ratio for all the complexes except for $[Cu(L2)Cl_2]$, (1:1). As shown in Table 1, elemental analyses and AAS results for both microwave and conventional methods are in agreement with theoretical data. Our proposed structural formulas are given in Schemes 2 and 3.

Fourier Transform Infrared Spectra

The main FT-IR data of the free ligands and their complexes are summarized in Table 2. All complexes containing H_2O or -OH groups exhibited characteristic absorption bands in the range 3390-3462 cm^{-1}. The FT-IR spectra of the ligands L1, L2, and L3 displayed absorption bands at 3092-3111 cm^{-1}, 1704-1721 cm^{-1}, and 1604-1702 cm^{-1} are assigned to υ(O-H), υ(C=O), and υ(C=N), respectively [12]. The spectra of the ligands exhibited broad medium intensity bands in the range 3092-3111 cm^{-1} which were assigned to the intramolecular H-bonding vibration (O-H…C). In the spectra of the complexes, these bands disappeared (Figs. 1 and 2), indicating the deprotonation of these groups on coordination with the metal atoms. In the ligands, the bands at 1704-1721 cm^{-1} and 1257-1277 cm^{-1} can be assigned to the υ(C=O) and υ(C-N) bond vibrations. In the metal complexes, these bands displaced variations in the frequencies because of coordination of oxygen and nitrogen to the metals.

In all the complexes, the bands at 682-693 cm^{-1}, 728-766 cm^{-1}, 408-475 cm^{-1} and 472-519 cm^{-1} can be attributed to the υ(Ru-O) and υ(Ru-N), υ(Cu-N) and υ(Cu-O) bonds respectively [13, 14]. In addition, the appearance of bands in the region of 395-486 cm^{-1} were due to υ(M-Cl) vibrations [15].

Magnetic Susceptibility Measurements

The magnetic susceptibility values of the ruthenium(III) and copper(II) complexes with L1, L2, and L3 ligands were measured at 298 K. Ruthenium(III) complexes were measured as antiferromagnetic while all other copper(II) complexes were paramagnetic for bearing unpaired electrons. The Ru(III) complexes displayed antiferromagnetic property, which involves σ interactions between the half-filled, e_g orbitals of Ru^{3+} ions [16,17]. The effective magnetic moments (μ_{eff}) derived from the Curie-law fit were 1.78, 1.83 and 1.96 B.M., respectively. These results agree well with the theoretical effective magnetic moment for Cu(II), 1.73 B.M. and they are comparable with the similar type of complexes in the literature [18,19].

Table 1. Analytical data and physical properties of Ru(III) and Cu(II) complexes.

Compounds	**Analytical Data Found % (Calculated %)**				
Conventional Method	**M**	**C**	**H**	**N**	**μ_{eff} (BM)**
[Cu(L1)$_2$]	15.18	37.17	2.93	5.91	1.78
	(15.90)	(35.97)	(2.39)	(5.99)	
[Cu(L2)Cl$_2$]	21.00	26.38	3.05	4.16	1.83
	(21.05)	(27.50)	(2.96)	(4.65)	
[Cu(L3)$_2$]	17.30	27.79	3.21	12.14	1.96
	(15.40)	(26.84)	(2.79)	(12.53)	
[Ru(L1)$_2$(H$_2$O)Cl]	21.05	24.11	2.99	4.23	N/A
	(20.74)	(25.19)	(2.10)	(4.20)	
[Ru(L2)$_2$(H$_2$O)Cl]	19.82	24.81	3.22	3.84	N/A
	(20.74)	(25.19)	(2.10)	(4.20)	
Microwave Method					
[Cu(L1)$_2$]	15.18	37.17	2.93	5.91	1.78
	(15.90)	(35.97)	(2.39)	(5.99)	
[Cu(L2)Cl$_2$]	21.00	26.38	3.05	4.16	1.83
	(21.05)	(27.50)	(2.96)	(4.65)	
[Cu(L3)$_2$]	17.30	27.79	3.21	12.14	1.96
	(15.40)	(26.84)	(2.79)	(12.53)	
[Ru(L1)$_2$(H$_2$O)Cl]	21.05	24.11	2.99	4.23	N/A
	(20.74)	(25.19)	(2.10)	(4.20)	
[Ru(L2)$_2$(H$_2$O)Cl]	19.82	24.81	3.22	3.84	N/A
	(20.74)	(25.19)	(2.10)	(4.20)	

UV-Visible Spectra

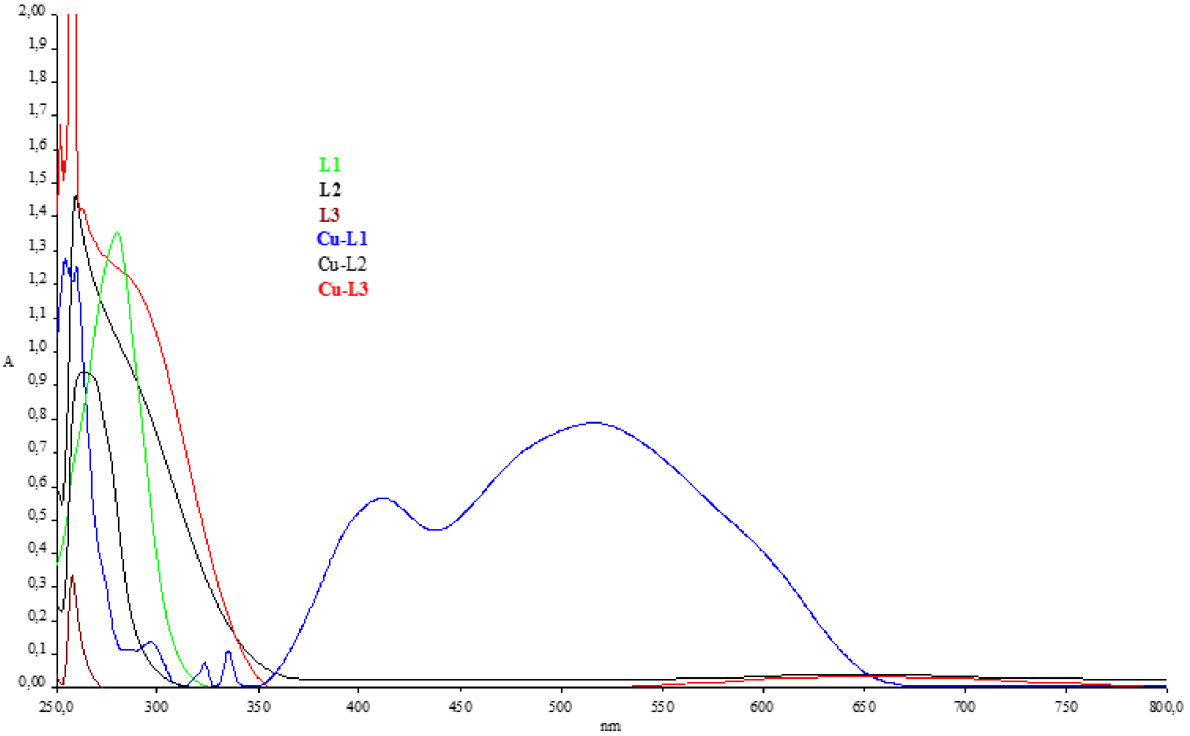
All the Ru(III) and Cu(II) complexes showed the characteristic $d_{\pi\text{-}\pi*}$ (L) MLCT bands in the region of 370-700 nm, in addition to the ligand π-π* (L) bands at 279 nm for L1, at 254 nm for L2 and at 257 nm for L3. The UV-Vis absorption spectra of Ru(III) complexes with L1, L2, and Cu(II) complexes with L1, L2 and L3 ligands were given in Figs. 3 and 4. All complexes showed the expected absorption bands at the main peaks appearing at λ_{max} = 446, 648 and 654 nm for Cu(II) [20,21], 379, 447 nm and 382, 385 nm for Ru(III), respectively [22]. These bands may be attributed for the metal to ligand charge transfer (MLCT) transitions.

Table 2. FT-IR spectral data of the ligands and their metal complexes (cm^{-1}).

Compounds	υ(OH)	υ(C=O)	υ(C=N)	υ(C-N)	υ(M-N)	υ(M-O)	υ(M-Cl)
L1	3105	1704	1611	1257	N/A	N/A	N/A
L2	3092	1721	1604	1267	N/A	N/A	N/A
L3	3111	1714	1702	1277	N/A	N/A	N/A
Microwave method							
$[Cu(L1)_2]$	3396	1725	1635	1257	422	472	N/A
$[Cu(L2)Cl_2]$	3390	1720	1640	1281	475	546	395
$[Cu(L3)_2]$	3462	1722	1648	1290	408	519	N/A
$[Ru(L1)_2(H_2O)Cl]$	3441	1729	1636	1248	766	690	473
$[Ru(L2)_2(H_2O)Cl]$	3429	1730	1652	1288	736	690	470
Conventional Method							
$[Cu(L2)Cl_2]$	3390	1725	1635	1257	422	472	N/A
$[Cu(L1)_2]$	3396	1720	1640	1281	475	546	395
$[Cu(L3)_2]$	3462	1722	1648	1290	408	519	N/A
$[Ru(L1)_2(H_2O)Cl]$	3441	1729	1636	1248	766	690	473
$[Ru(L2)_2(H_2O)Cl]$	3429	1730	1652	1288	736	690	470

Table 3. Comparison between conventional method (CM) and microwave method (MM).

Compounds	**Yield (%)**		**Solvent (mL)**		**Time**	
	CM	**MM**	**CM**	**MM**	**CM (days)**	**MM (min)**
$[Cu(L1)_2]$	48	89	50	5	6	3
$[Cu(L2)Cl_2]$	41	82	100	5	6	3
$[Cu(L3)_2]$	60	86	25	5	6	3
$[Ru(L1)_2(H_2O)Cl]$	62	76	25	2	30	1/3
$[Ru(L2)_2(H_2O)Cl]$	65	78	30	15	30	5



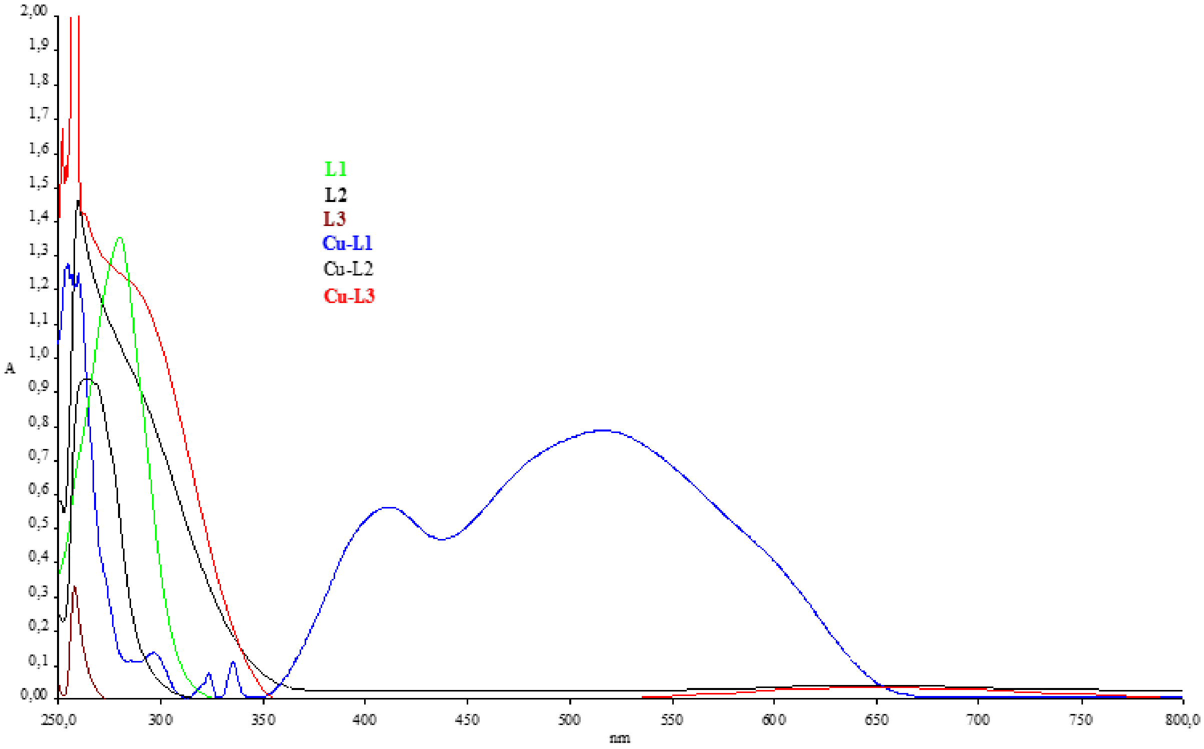


Figure 3. UV-Vis Spectra of compounds L1, L2, L3 and their Cu(II) complexes using microwave (top) and conventional methods (bottom).

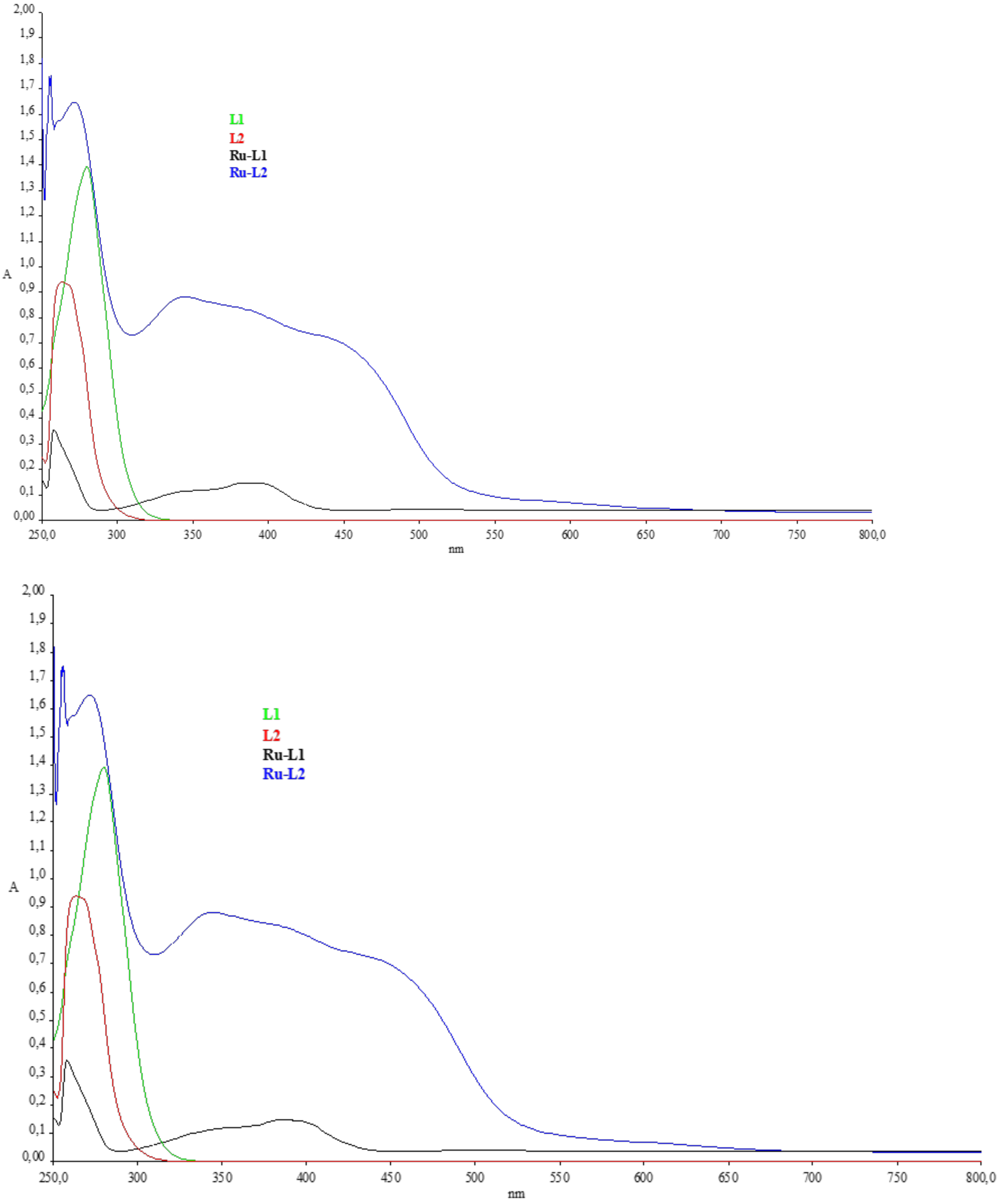


Figure 4. UV-Vis Spectra of compounds L1, L2, and their Ru(III) complexes using microwave (top) and conventional methods (bottom).

^{1}H-NMR and ^{13}C-NMR

^{1}H-NMR spectra were consistent with the proposed structures. The ^{1}H-NMR spectral data of the ligands and their corresponding Cu(II) and Ru(III) complexes were recorded in DMSO by employing TMS as an internal standard. The ^{1}H-NMR spectra of the ligands (L1, L2, and L3) exhibited aromatic signals at δ 8.13-9.30, δ 8.59-9.08 and δ 6.3 ppm, respectively. The protons of -OH groups of the ligands gave signals at δ 12.14-13.2 ppm. In the spectra of their metal complexes, these intension signals were reduced. The ^{1}H-NMR spectrum is shown in Fig. S1 (Supporting Information). These results showed that the chelation of the ligand moiety is via one of the carboxyl groups. In the spectra of the L3 ligand and its Cu(II) complex, the -NH proton signals appeared at δ 13.70 ppm, indicating the bonding of the other nitrogen atom [9]. ^{13}C-NMR spectral data for the complexes could not be obtained since they have paramagnetic character. Comparison of the microwave and conventional methods were given in Table 3. For the microwave assisted synthesis, 0-5 minutes were required for the reactions to complete. While using the conventional method, the reaction time was six days for the Cu(II) complexes and 30 days for Ru(III) complexes. The product yields were less in the conventional method as compared to that of the obtained complexes by the microwave synthesis. For the microwave synthesis, between 2-15 mL of solvent was consumed in the reactions, while this amount was 25-30 mL in the conventional method. Although $[Cu(L1)_2]$ was synthesized in 48% yield by the conventional method, the reaction occurred in a few minutes by 89% yield by microwave method.

CONCLUSION

Herein, ruthenium(III) and copper(II) complexes were obtained by both microwave and conventional methods and were characterized by UV-Visible, FT-IR, ^{1}H-NMR, AAS, elemental analysis, and magnetic susceptibility techniques. Single crystals of the synthesized compounds could not be isolated from any solution; thus no definite structure may be described. Assuming the analytical data and spectral studies, the ligands coordinated to the copper(II) and ruthenium(III) metals in a bidentate manner as square planar and octahedral geometry, respectively. We compared these methods in terms of the reaction time, amount of solvent, and reaction yield. The salient features of microwave method include the simple reaction set-up, mild reaction conditions, and short reaction times. Because of these advantages, the method is more efficient and environmentally friendly for the synthesis of the related metal complexes.

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DİKARBOKSİLİK ASİT GRUPLARI İÇEREN Cu(II)/Ru(III) KOMPLEKSLERİNİN KONVANSİYONEL VE MİKRODALGA DESTEKLİ SENTEZ VE KARAKTERİZASYONLARI

Öz: Bu çalışmada, 2,4-piridindikarboksilik asit (L1), 3,5- piridindikarboksilik asit (L2) ve 3,5-pirazoldikarboksilik asit (L3) ligandları kullanılarak konvansiyonel ve mikrodalga yöntemleri ile Ru(III) ve Cu(II) metal kompleksleri sentezlenmiştir. Mikrodalga ve konvansiyonel yöntemlerinin kıyaslanması için yapılan bu çalışmada yöntemlerin birbirlerine göre farklılıkları, tepkime süresi, çözücü miktarı ve verim açısından değerlendirilmiştir. Tepkime süresi uzun saatlerden birkaç dakikaya kadar önemli derecede azaltılmıştır. Mikrodalga yöntemi ile çok daha az çözücü kullanılması sonucunda yüksek verimlerde kompleksler elde edilmiştir. Sentezlenen komplekslerin yapıları FT-IR, UV-Vis, AAS, 1H-NMR, elementel analiz ve manyetik duyarlılık teknikleri ile karakterize edilmiştir. Analiz sonuçları bakır ve rutenyum komplekslerinin sırasıyla kare düzlem ve düzgün sekizyüzlü geometrilere sahip olduğunu göstermiştir. Cu(II) ve Ru(III) metal kompleksleri mikrodalga ışınına maruz bırakılarak kolay bir şekilde sentezlenmiştir.

Anahtar Kelimeler: Mikrodalga sentez, İnorganik-organik hibrit, Rutenyum(III) ve Bakır(II) kompleksleri.

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