Synthesis and Characterization of Novel Oxime-Imine Ligands and their Heteronuclear Ruthenium(III) Complexes¹

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Abstract—Vicinal carbonyl oxime (HL¹) and oxime-imine (H₂L²) ligands and their mononuclear Ru(III) and Cu(II), heterodinuclear Ru(III)—Mn(II), Ru(III)—Ni(II), Ru(III)—Cu(II), and heterotrinuclear Ru(III)—Cu(II)—Ru(III) chelates were synthesized and characterized by elemental analysis, molar conductivity, IR, ESR, ICP-OES, magnetic moment measurements, and thermal analyses studies. The free ligands were also characterized by ¹H NMR spectra. The carbonyl-oxime ligand coordinates through the oxygen of =N–OH to form a six-membered chelate ring. The quadridentate tetraaza ligand (H₂L²) obtained by condensing of the bidentate ligand 1-*p*-diphenylmethane-2-hydrox-yimino-2-(1-naphthylamino)-1-ethanone (HL¹) with 1,2-phenylenediamine coordinates with Ru(III) through its nitrogen donors in the equatorial position with the loss of one of the oxime protons and concomitant formation of an intramolecular hydrogen bond. Stoichiometric and spectral results of the metal complexes indicated that the metal : ligand ratios in the mononuclear complexes of the ligand (HL¹) were found to be 1 : 2, while these ratios were 1 : 1 in the mononuclear complexes of the ligand (H₂L²). The metal : ligand ratios of the dinuclear complexes were found to be 2 : 1, and this ratio was 3 : 2 in the trinuclear complex.

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INTRODUCTION

Oximes and Schiff bases are two important classes of compounds owing to their wide applications in industry, medicine, detection, and determination of various metal ions. These compounds have a number of potential bonding sites, such as azomethine and imine nitrogens and oxime oxygen. Therefore, Schiff bases and oximes, as well as their coordination compounds, have been studied extensively [1–8].

Ruthenium is well known for its ability to cover a wide range of oxidation states (-2 to +8) and to adopt various coordination geometries. Therefore, ruthenium complexes exhibit versatile electron-transfer properties. A large number of ruthenium complexes have been studied for their interesting and important properties, such as artificial photosynthesis, photomolecular devices, studies on biological macromolecules, catalytic oxidation of water and organic substrates, and organic synthesis. Because of such a broad range of applications, there is a continuous interest to synthesize new complexes of ruthenium with different types of ligands [9–12].

The ruthenium complexes of diimine ligands is an area of significant current interest, particularly with regard to the photophysical and photochemical properties exhibited by such complexes [13–15]. Schiff base and oxime complexes having O and N donor atoms

have shown an exponential increase, as inorganic catalytic processes, such as hydrogenation, isomerization, decarbonylation, reductive elimination, oxidative addition, and C–C bond formation [16–21].

In previous studies, we investigated the synthesis and characterization of the mono- and trinuclear copper(II) complexes of novel tetradentate Schiff bases [22, 23]. In the present work, we report the synthesis and characterization of the mononuclear Ru(III) (I) and Cu(II) (II) chelates with the bidentate ligand, 1-*p*-diphenylmethane–2-hydrox-yimino–2-(1-naphthylamino)–1-ethanone (HL¹), mononuclear Ru(III) (III), heterodinuclear Ru(III)–Mn(II) (IV), Ru(III)–Ni(II) (V), Ru(III)–Cu(II) (VI), and heterotrinuclear Ru(III)–Cu(II)–Ru(III) (VII) chelates with the quadridentate ligand, N,N'-*o*-bis[1-*p*-diphenylmethane–2-hydroxyimino–2-(1-naphthylamino)–1-ethylidene]-phenylenediamine (H₂L²).

EXPERIMENTAL

Physical measurements. All solvents, 1-naphthylamine and metal salts (RuCl₃ · H₂O, Cu(ClO₄)₂ · 6H₂O, Mn(OAc)₂ · 4H₂O, Ni(OAc)₂ · 4H₂O) used for the synthesis and physical measurements were purchased from Aldrich, J.T. Baker, and Merck and used as received. ¹H NMR spectra of the ligands were recorded in CDCl₃ solutions with TMS as internal standard at the NMR Laboratory at Hacettepe University-Ankara-Turkey. IR spectra (4000–400 cm⁻¹) were recorded on a Shimadzu

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IRPrestige–21 FT-IR spectrophotometer as KBr pellets. The thermogravimetric analysis (TG and DTG) of the complexes were measured at the Central Laboratory at METU-Ankara-Turkey. The C, H, and N contents were determined microanalytically on a LECO 932 CHNS analyzer. The Ru, Mn, Ni, and Cu contents were measured on a Perkin Elmer Optima 5300 DV ICP-OES spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MX1) at room temperature. The X-band ESR spectra of the complexes were recorded at room temperature on a Bruker Elexsys E580 spectrometer. The conductance measurements were carried out using an Optic Ivymen System conductivity meter. Melting point determinations were performed with a digital melting point instrument (Electrothermal model IA 9100).

Synthesis of ligands HL^1 and H_2L^2 was carried out in a few steps according following eqs:



At first 4-chloroacetyldiphenylmethane (**DMK**) was prepared according to the literature method [24] from chloroacetylchloride and diphenylmethane in the presence of AlCl₃ as catalyst in the Friedel-Crafts reaction according Eq. (1). Then 1-*p*-diphenylmethane–2hydroxyimino–2-chloro–1-ethanone (**HL**) was prepared according to previously published procedures [22] according Eq. (2). DMK (2.45 g, 10 mmol) was dissolved in 20 ml of chloroform with cooling, then passing HCl gas into the solution for half an hour, and then butyl nitrite (1.40 ml, 11 mmol) was added dropwise to the mixture with stirring and passing HCl gas into the mixture. The mixture was left overnight at room temperature to form a precipitate. The precipitate was filtered off and recrystallized from an ether-hexane (1:1) mixture. The crystallized product was filtered, washed with hexane, and dried over P_2O_5 .

The bidentate ligand HL¹ was conveniently prepared as reported in the literature [23] according Eq. (3). A solution of 1-naphthylamine (2.86 g, 20 mmol) was added dropwise to a solution of HL (10 mmol) in ethanol (20 ml) for 30 min at 0°C. The reaction mixture was stirred for 2 h at the same temperature. Then it was allowed to stir at ambient temperature for 2 h. The powder resulting from the reaction is insoluble in ethanol and, thus, was filtered off, washed with aqueous sodium bicarbonate (1%), distilled water, and ethanol, and dried over P₂O₅.

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The quadridentate ligand H_2L^2 was conveniently prepared as reported in the literature [23] according Eq. (4). 1,2-Phenylenediamine (0.53 g, 5 mmol) and HL¹ (10 mmol) were mixed in absolute EtOH. The content was stirred magnetically at room temperature for 1 h. After the addition of distilled water to the reaction mixture, the yellow powder product was seperated, collected by filtration, washed several times with aqueous sodium bicarbonate (1%), distilled water, and ethanol, and dried over P₂O₅.

Synthesis mononuclear complexes of $[Ru(L^1)_2Cl(H_2O)]$ (I) and $[Ru(HL^2)Cl_2]$ (III) were carried out as reported in similar literature [25]. A stoichiometric amount of $RuCl_3 \cdot H_2O(10 \text{ mmol})$ in EtOH was added to a hot solution of the desired ligand (20 mmol in the case of HL^1 ; 10 mmol in the case of H_2L^2) in absolute EtOH, and the reaction mixture was boiled under reflux with stirring for 2 h. On slow evaporation of EtOH the desired complex was obtained as powder. In some cases, complete precipitation was achieved by the addition of Et₂O to the cold reaction mixture. The deeply colored precipitates were separated by filtration, washed with cold EtOH followed by Et₂O, and dried over P₂O₅.

Synthesis of mononuclear complex $[Cu(L^1)_2(H_2O)_2]$ (II) was carried out as reported in similar literature [25]. A stoichiometric amount of $Cu(CH_3COO)_2 \cdot H_2O$ (0.20 g, 1 mmol) in EtOH was added to a hot solution of the bidentate ligand (2 mmol) in absolute EtOH, and the reaction mixture was boiled under reflux with stirring for 2 h. On slow evaporation of EtOH the desired complex was obtained as powder. The deeply colored precipitate was separated by filtration, washed with cold EtOH followed by Et₂O, and finally dried over P₂O₅.

Synthesis of binuclear complex [Ru(L²)Cl₂Mn(Phen)₂]ClO₄ (IV) was carried out asreported in similar literature [23]. The complex III (1 mmol) was mixed with Et_3N (1 mmol) in MeOH (20 ml) and stirred for 0.5 h. Separated solutions of $Mn(OAc)_2 \cdot 4H_2O$ (245 mg, 1 mmol) in MeOH (10 ml) and 1,10-phenanthroline monohydrate (400 mg, 2 mmol) in MeOH (10 ml) were successively added to the resulting solution. A stoichiometric amount of $NaClO_4 \cdot H_2O$ (140 mg, 1 mmol) was then added to the resulting mixture, which was boiled under reflux for 24 h. The product was filtered off, washed with H_2O , MeOH, and Et_2O , and dried over P_2O_5 .

Synthesis of binuclear complex $[\operatorname{Ru}(L^2)\operatorname{Cl}_2\operatorname{Ni}(\operatorname{Phen})_2]\operatorname{ClO}_4$ (V). The complex III (1 mmol) was mixed with Et₃N (1 mmol) in MeOH (20 ml) and stirred for 0.5 h. Separated solutions of Ni(OAc)₂ · 4H₂O (245 mg, 1 mmol) in MeOH (10 ml) and 1,10-phenanthroline monohydrate (400 mg, 2 mmol) in MeOH (10 ml) were successively added to the resulting solution. A stoichiometric amount of NaClO₄ · H₂O (140 mg, 1 mmol) was then added to the resulting mixture, which was boiled under reflux for

24 h. The product was filtered off, washed with H_2O , MeOH, and Et_2O , and dried over P_2O_5 .

Synthesis of binuclear complex $[\mathbf{Ru}(\mathbf{L}^2)\mathbf{Cl}_2\mathbf{Cu}(\mathbf{Phen})]\mathbf{ClO}_4$ (VI). The mononuclear ruthenium complex III (1 mmol) was added to Et₃N (1mmol) in Me₂CO (20 ml) and the mixture was stirred for 0.5 h. Separated solutions of Cu(ClO₄)₂ · 6H₂O (370 mg, 1 mmol) in Me₂CO (10 ml) and 1,10-phenan-throline monohydrate (200 mg, 1 mmol) were successively added to the resulting mixture, which was boiled under reflux for 3 h. The product was filtered off, washed with H₂O, MeOH, and Et₂O, and dried over P₂O₅.

Synthesis of trinuclear complex $[\mathbf{Ru}_2(\mathbf{L}^2)\mathbf{Cl}_4\mathbf{Cu}]$ (VII) was carried out as reported in similar literature [23]. A mixture of III (1 mmol), $\mathbf{Cu}(\mathbf{ClO}_4)_2 \cdot 6\mathbf{H}_2\mathbf{O}$ (185 mg, 0.5 mmol), and $\mathbf{Et}_3\mathbf{N}$ (0.1 g, 1 mmol) in Me₂CO (20 ml) was refluxed for 2 h. The resulting solution was filtered while hot and concentrated slowly. As the solution cooled, a black powder product precipitated. It was isolated by filtration, washed with $\mathbf{Et}_2\mathbf{O}$, and dried in air.

RESULTS AND DISCUSSION

As a result of conducted reactions we have gotten the following complexes. The mononuclear Ru(III) and Cu(II) complexes of HL^1 [25]:



where M = Ru(III), Cu(II); $X_1 = H_2O$, $X_2 = Cl$ in Ru(III)complex and $X_1 = X_2 = H_2O$ in Cu(II) complex.

The mononuclear ruthenium(III) complex of H_2L^2 [23]:



Heterodinuclear Ru(III)–Mn(II) and Ru(III)–Ni(II) complexes of H_2L^2 (M = Mn(II), Ni(II)) [23]:



Heterodinuclear Ru(III)–Cu(II) complex of H_2L^2 [23]:



Heterotrinuclear Ru(III)–Cu(II)–Ru(III) complex of H_2L^2 [23]:



The powdered complexes are soluble in DMF and DMSO and slightly soluble in chloroform and acetone. The resulting solids are intensely colored, and stable in air. Attempts to isolate crystals suitable for X-ray diffraction were unsuccessful. Therefore, elemental analysis, spectroscopic tecniques, conductivity, thermal and magnetic susceptibility techniques were employed in order to determine the structural characteristics of the complexes. The analytical and physical data for the ligands and their complexes are given in Table 1.

The ¹H NMR spectra of the starting compounds HL and the ligands HL¹, H₂L² exhibited a broad singlet peak at 8.85 and 8.11 ppm for the OH protons of the oxime groups. The chemical shifts in a region of 7.10–8.10 ppm were assigned to hydrogen of the aromatic ring. Furthermore, the singlets in a range of 3.99– 4.20 ppm were assigned to protons of the methylene groups of the diphenylmethane. The other obtained values for ¹H NMR chemical shifts of these compounds are given in Table 2. The total number of protons present in the compounds exhibited signals of the protons in their expected regions, and these data are in good agreement with those previously reported for similar compounds [23, 26].

The IR spectra of the free ligands and their complexes represented in Table 3. The IR spectra of the starting compounds HL and the ligands HL^1 , H_2L^2 showed medium-to-strong bands in the 3232- 3271 cm^{-1} range, assignable to v(OH) of oxime groups; the broad nature of these bands and their low wavenumbers suggested the presence of hydrogen bonding [27]. The spectrum of the ligands exhibited fairly strong bands at 3369 (HL¹) and 3379 (H₂L²) cm⁻¹ attributable to the v(NH) vibration of the aromatic amine groups. The medium, sharp band at 1226 cm⁻¹ was due to the N–O stretching vibration [1, 2]. In the IR spectra of the ligand H_2L^2 , the stretching vibrations of $C = N_{imine}$ and $C = N_{\text{oxime}}$ were observed at 1635 and 1596 cm⁻¹, respectively. The band observed at 1596 cm⁻¹ in ligand HL¹ also was assigned to the C=N groups. The C=O vibrations for the compounds HL and HL¹ were observed as medium bands at 1655 and 1675 cm⁻¹, respectively. The spectrum of the ligand H_2L^2 did not show absorption characteristic of the C=O function owing to the formation of the imine [1, 2].

The characteristic absorption bands of the ligands HL^1 , H_2L^2 were shifted on complex formation, and new vibrational bands characteristic of the complex appeared. The broad stretching bands due to the –OH groups of the free ligands did not appear in the IR spectra of the complexes (except for the mononuclear ruthenium complex III) indicating the deprotonation of the –OH groups and the formation of M–O bonds. This was supported by the appearance of a new band in the region 507–581 cm⁻¹ assigned to v(M–O) [1, 2]. In the IR spectrum of the complex III a broad weak band was observed at 1766 cm⁻¹ due to O–H···O intramolecular hydrogen bonds [1, 2].

Except for the heteronuclear Ru–Mn (IV) and Ru– Ni (V) complexes, all of the complexes showed a broad band in the 3436–3447 cm⁻¹ region, which confirms the presence of water molecules hydrated to the metal ion [6]. In the spectrum of the heteronuclear Ru–Cu complex (VII), a broad band is in the 3236 cm⁻¹, indicating that the complex has coordination water. In the complexes I, II, C=O group bands became extinct, indicating coordination through the C=O group. Vibrational evidence for the coordination of the oximato group in the complexes is provided by the higher frequency band of N–O at ~1266–1296 cm⁻¹ [3]. The appearance of a new band at 419–433 cm⁻¹ was assigned to v(M–N) [6, 28].

The binuclear complexes IV-VI have a medium band in a region of 1108–1123 cm⁻¹ and a weak band at the 1019–1020 cm⁻¹ range, featuring typical characteristics of uncoordinated perchlorates [1, 2]. Thus, the IR spectra of the ligands and their metal complexes give strong evidence for the complexation of the potentially multidentate ligands.

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Compound	μ_{eff}, μ_B	Color	$\stackrel{\Lambda_m,}{Ohm^{-1}cm^2mol^{-1}}$	M. p., °C	Yield, %	Content (found/calcd), %				
						С	Н	Ν	Cu, Ni, or Mn	Ru
[C ₁₅ H ₁₃ OCl] (DMK)		Light yellow		55	27	73.21/ 73.62	5.07/ 5.35			
$[C_{15}H_{12}NO_2Cl]$ (HL)		Yellow		108	79	65.34/ 65.82	4.18/ 4.42	4.99/ 5.12		
$[C_{25}H_{20}N_2O_2](HL^1)$		Light yellow		148	95	78.76/ 78.93	5.03/ 5.29	7.25/ 7.36		
$[C_{50}H_{40}N_4O_5ClRu](I)$	1.62	Black	32	247	26	65.37/ 65.75	4.14/ 4.41	6.02/ 6.13		10.84/ 11.07
$[C_{50}H_{42}N_4O_6Cu](II)$	1.23	Dark brown	18	205	34	69.57/ 69.96	4.58/ 4.93	6.51/ 6.53	7.11/ 7.40 (Cu)	
$[C_{56}H_{44}N_6O_2]H_2L^2$		Light yellow		170	38	80.39/ 80.75	5.26/ 5.32	9.70/ 10.09		
$[C_{56}H_{47}N_6O_4Cl_2Ru](III)$	1.70	Black	21	225	76	64.55/ 64.67	4.17/ 4.56	7.87/ 8.08		9.54/ 9.72
$[C_{80}H_{58}N_{10}O_6Cl_3RuMn]~({\rm IV})$	4.14	Black	86	195*	61	63.07/ 63.31	3.52/ 3.85	8.88/ 9.23	3.29/ 3.62 (Mn)	6.24/ 6.66
$[C_{80}H_{58}N_{10}O_6Cl_3RuNi](V)$	2.23	Black	78	225*	55	62.76/ 63.15	3.65/ 3.84	8.92/ 9.21	3.22/ 3.86 (Ni)	6.31/ 6.64
[C ₆₈ H ₅₄ N ₈ O ₈ Cl ₃ RuCu] (VI)	1.26	Black	92	245	88	58.82/ 59.09	3.51/ 3.93	7.93/ 8.11	4.26/ 4.60 (Cu)	7.08/ 7.31
[C ₁₁₂ H ₈₈ N ₁₂ O ₆ Cl ₄ Ru ₂ Cu] (VII)	0.97	Black	23	250*	40	63.87/ 63.89	3.79/ 4.21	7.86/ 7.98	2.96/ 3.02 (Cu)	9.27/ 9.60

Table 1. Elemental analysis data and some physical properties of the ligands and their complexes

* Decomposition point.

 Table 2. ¹H NMR data (ppm) of the starting compounds and the ligands

Compound	OH _{oxime}	C–H _{arom}	N–H	-CH _{DFM}	-CH _{aliph}
DMK		7.90–7.10 (m., 9H)		4.00 (s., 2H)	4.50 (s., 2H)
HL	8.85 (s., 1H)	8.10–7.10 (m., 9H)		4.20 (s., 2H)	
HL^{1}	8.11 (s., 1H)	7.99–7.20 (m., 16H)	6.96 (s., 1H)	3.99 (s., 1H)	
H_2L^2	8.11 (s., 2H)	7.98–7.11 (m., 36H)	6.96 (s., 2H)	3.99 (s., 2H)	

The molar conductance of the complexes was an aid for proposing their formulas. Conductivity measurements were carried out in 10^{-3} mol dm⁻³ N,N-dimethylformamide solutions at 20°C. The binuclear complexes **IV–VI** exhibited various conductances between the 78– 92 Ohm⁻¹ cm² mol⁻¹ range, and other complexes (**I**, **II**, **III**, **VII**) exhibited conductances between the 18– 32 Ohm⁻¹ cm² mol⁻¹ range (Table 1). The molar conductances of the binuclear complexes **IV–VI** in DMF indicated that these complexes contain perchlorate ions behave as 1 : 1 electrolytes [1, 2]. However, the other complexes (**I**, **II**, **III**, **VII**) are non electrolytes [27]. The room temperature magnetic moments of the complexes showed that all of the complexes are paramagnetic (Table 1). The measured magnetic moments of the mononuclear ruthenium(III) complexes are 1.62 and 1.70 μ_B for I and III, respectively. Magnetic susceptibility measurements showed that these complexes are one-electron paramagnetics ($\mu_{eff} = 1.62-1.70 \ \mu_B$), which corresponds to the +3 oxidation state of ruthenium (low-spin d^5 , S = 1/2) in these complexes [1, 2]. The magnetic moment of the mononuclear copper(II) complex II is 1.23 μ_B and the magnetic moment of trinuclear Ru(III)–Cu(II)–Ru(III) complex is 0.97 μ_B . The

C	ν , cm ⁻¹										
Compound	N–H	(OH)	C=O	C=N	C–N	(NO)	ClO_4^-	M–N	М–О	Ru–N	
HL		3232 s	1655 s	1601 s		1290 s					
HL^1	3379 m	3271 b	1675 s	1596 s	1404 m	1226 s					
Ι	3310 b	3436 b		1601 s	1399 m	1276 m			581 w	700 m	
Π	3360 b	3447 b	1650 w	1601 w	1394 m	1271 w			517 w		
H_2L^2	3369 s	3271 m		1596 s 1635 m	1404 m	1226 s					
III	3320 b	3261 b 1766 b		1601 s	1399 w	1275 w				670 s	
IV	3367 b			1601 m	1399 w	1295 m	1123 m 1019 w	419 m	517 m	670 s	
V	3330 b			1601 s 1621 w	1394 w	1275 w	1108 m 1019 w	433 w	512 w	700 m	
VI	3320 b	3447 b		1597 s	1394 w	1296 m	1123 m 1020 w	428 w	507 w	670 w	
VII	3320 b	3236 b		1601 s	1394 w	1266 m		424 w	513 m	670 w	

 Table 3. IR spectra of the ligands and their metal complexes

magnetic moments of the dinuclear complexes are 4.14, 2.23, and 1.26 μ_B for IV, V and VI, respectively. It can be observed that these magnetic moment values of the ruthenium(III) complexes are slightly lower than those expected for the binuclear ruthenium(III) complexes and the theoretical value of 1.73 $\mu_{\rm B}$ for one low-spin d^5 ruthenium ion. The strong antiferromagnetic coupling that was found for bi (IV-VI) and trinuclear ruthenium(III) (VII) complexes is explained as the oximato group have good superexchange properties [29]. These abnormal magnetic moment values of the binuclear complexes may be explained by the weak antiferromagnetic intramolecular interaction, since this situation can occur when two equivalent metal ions are coupled via an exchange interaction in a polynuclear complex [26, 30].

The room temperature solid-state EPR spectrum of the mononuclear Ru(III) complex (**III**) was recorded at X-band frequencies. The low-spin d^5 configuration is a good probe of molecular structure and bonding, since the observed g values are very sensitive to small changes in structure and to the metal-ligand covalency. The EPR spectra of the complexes exhibit a characteristic of an axially symmetric system with g_{\perp} of 2.599 and g_{\parallel} of 1.998. The presence of two different g values $(g_x = g_y \neq g_z)$ indicates an octahedral field with tetragonal or square pyramidal distortion. Overally, the position of lines and nature of the EPR spectra of the complexes are characteristic of low-spin ruthenium(III) octahedral complexes [31]. The thermal behavior of all the complexes was almost the same. In thermogravimetry (TG) the change in weight of a complex was recorded as a function of temperature during heating. The TG curve was also supported by the derivative thermogravimetry (DTG) curves.

It is noted from the TG analysis that the monouclear Ru(III) complex (I) of HL¹ lost 85.90% (calculated mass loss = 86.31%) of its original mass between 185 and 535°C and the residue was Ru₂O₃. The sample decomposed in three stages. The first decomposition occurred between 185 and 288°C with 6.10% estimated mass loss (calculated mass loss = 5.85%), the second and third decompositions occurred between 288 and 535°C with 79.80% estimated mass loss (calculated mass loss = 80.46%) corresponding to the loss of the ligand molecules.

The mononuclear Cu(II) complex (II) of HL¹ showed the decomposition pattern of five stages. The first four steps with an estimated mass loss of 37.50% (calculated mass loss = 37.46%) were found within the temperature range 115–550°C corresponding to the loss of two H₂O molecules and 1-naphthylamine molecule. The last stage did not finish completely at 900°C.

The ligand H_2L^2 showed a decomposition pattern of four stages. The first three stages with an estimated mass loss of 38.40% (calculated mass loss = 38.22%) were found within the temperature range 120–340°C corresponding to the loss of one OH and 1-naphthy-

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Compound	TC range °C	DTG °C	Estimated	(calcd), %	Assignment	Matallia rasidua
Compound	TO fallge, C	DIO _{max} , C	mass loss	total mass loss	Assignment	Wietanie Tesidue
Ι	185–288	249	6.10 (5.85)		Loss of one Cl and one H ₂ O molecule	
	288–535	400, 495	79.80 (80.46)	85.90 (86.31)	Loss of ligand molecules	Ru ₂ O ₃ /2
II	115–550	220, 330, 360, 410	37.50 (37.46)		Loss of two H ₂ O and 1- naphthylamine molecules	
	550–900	590			Loss of the other groups	Decomposition is in progress
H_2L^2	120–340	160, 210, 280	38.40 (38.22)		Loss of 1-naphthylamine and OH molecules	
	340–900	460			Loss of the other groups	Decomposition is in progress
III	35-102	69	2.95 (3.46)		Loss of two H ₂ O molecules	
	102–280	235	7.10 (6.78)		Loss of two Cl atom	
	280–635	412	77.40 (77.74)	87.45 (87.98)	Loss of ligand molecules	Ru ₂ O ₃ /2
IV	50–515	390	43.40 (44.01)		Loss of ClO ₄ , two Cl, two phenanthroline and diphe- nylmethane molecules	
	515–900	560			Loss of the other groups	Decomposition is in progress
V	50–555	310	33.40 (33.05)		Loss of ClO ₄ , two Cl and two phenanthroline mole- cules	
	555–900	635			Loss of the other groups	Decomposition is in progress
VI	40–120	65	2.40 (2.61)		Loss of two H ₂ O molecules	
	120–350	245	12.60 (12.63)		Loss of ClO ₄ and two Cl atoms	
	350–560	487	13.10 (13.04)		Loss of phenanthroline mol- ecule	
	560–945	687	24.50 (24.20)	52.60 (52.48)	Loss of diphenylmethane molecules	Decomposition is in progress
VII	35–110	60	2.10 (1.71)		Loss of two H ₂ O molecules	
	110–675	290, 450, 620	39.00 (38.51)		Loss of four Cl and diphe- nylmethane molecules	
	675–980	772			Loss of the other groups	Decomposition is in progress

Table 4. Thermoanalytical results (TG, DTG) of the metal complexes

lamine molecules. The last stage did not finish completely at 900°C.

It was found from TG analysis that the mononuclear Ru(III) complex (III) of H_2L^2 starts losing mass at 35°C and ends at 635°C after losing 87.45% (calculated mass loss = 87.98%) of its mass with a Ru₂O₃ residue which corresponds to 12.65% of the total mass. The examination of the TG curve showed that the complex decomposes in three stages. The sample lost 2.95% of mass between 35 and 102°C, 7.10% of the mass between 102 and 280°C, and 77.40% between 280 and 635°C. These decomposition stages corresponded to the loss of two H₂O molecules, two Cl atoms, and ligand molecules and calculated mass losses were 3.46, 6.78, and 77.74, respectively.

The binuclear Ru(III)–Mn(II) complex (**IV**) exhibited the first mass loss in the temperature range 50–515°C with a maximum at 390°C in the DTG curve. It may be attributed to the liberation of ClO_4 , two Cl, two phenanthroline and diphenylmethane molecules. The second mass loss at 515–900°C with a maximum at 560°C was due to the liberation of the other groups. However, the decomposition did not finish at 900°C completely.

The binuclear Ru(III)–Ni(II) complex (V) decomposed in two stages. In the first stage the estimated mass loss was 33.40% (calculated mass loss = 33.05%). The temperature range of this decomposition was found to be 50–555°C corresponding to the loss of ClO₄, two Cl, and two phenanthroline molecules. The second stage did not finish completely at 1000°C.

The binuclear Ru(III)–Cu(II) complex (VI) showed the decomposition pattern of four stages. The first stage with an estimated mass loss of 2.40% (calculated mass loss = 2.61%) was found within the temperature range 40–120°C corresponding to the loss of two H₂O molecules. The second stage with an estimated mass loss of 12.60% (calculated mass loss = 12.63%) was found within the temperature range 120-350°C and the third stage with an estimated mass loss of 13.10% (calculated mass loss = 13.04%) was found within the temperature range 350-560°C corresponding to the loss of perchlorate, two Cl, and phenanthroline groups. The last stage with an estimated mass loss of 24.50% (calculated mass loss = 24.20%) was found within the temperature range 565–945°C corresponding to the loss of diphenylmethane groups.

The trinuclear Ru(III)–Cu(II)–Ru(III) complex (VII) showed a decomposition pattern of four stages. The first stage with an estimated mass loss of 2.10% (calculated mass loss = 1.71%) was found within the temperature range $35-110^{\circ}$ C corresponding to the loss of two H₂O molecules. The other three stages with an estimated mass loss of 39.00% (calculated mass loss = 38.51%) were found within the temperature range $110-675^{\circ}$ C corresponding to loss of four Cl and diphenylmethane groups. The last stage did not finish completely at 1000° C.

The theoretical and experimental percent mass losses obtained from these decomposition stages are in good agreement. The critical data and values deduced from the present study are summarized in Table 4.

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