

# Synthesis, characterization and properties of heteronuclear ruthenium(III) complexes of *N,N'*-*o*-bis[1-*p*-diphenylmethane-2-(arylamino)-1-ethyliden]-phenylenediamine quadridentate ligands

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**Abstract** In this study, we synthesized the amine compounds (1-*p*-diphenylmethane-2-hydroxyimino-2-(1-arylamino)-1-ethanones) [HL<sup>1</sup> (**2**) and HL<sup>2</sup> (**9**)] as the starting material, and then we prepared the quadridentate tetraaza Schiff base ligands [H<sub>2</sub>L<sup>3</sup> (**3**) and H<sub>2</sub>L<sup>4</sup> (**10**)] from the reactions of the amine compounds with 1,2-phenylenediamine. A new series of mononuclear Ru(III) (**4**), (**11**), heterodinuclear Ru(III)–Mn(II) (**8**), (**15**), Ru(III)–Ni(II) (**7**), (**14**), Ru(III)–Cu(II) (**5**), (**12**) and heterotrinary Ru(III)–Cu(II)–Ru(III) (**6**), (**13**) complexes have been synthesized using the quadridentate oxime-imine ligands, 1,10-phenanthroline monohydrate, ruthenium(III) and a second metal salts. The complexes were characterized by elemental analysis, molar conductivity, IR, ESR, ICP-OES, magnetic moment measurements and thermal analyses studies. The free ligands were also characterized by <sup>1</sup>H-NMR spectra. The quadridentate tetraaza ligands coordinates with Ru(III) through its nitrogen donors in the equatorial position with loss of one of the oxime protons and concomitant formation of an intra-molecular hydrogen bond. Stoichiometric and spectral results of the metal complexes indicated that the metal: ligand ratios of the mononuclear complexes were found to be 1:1 while ratios 2:1 in the dinuclear complexes and 3:2 in the trinuclear complexes.

**Keywords** Schiff bases · Oxime-imine · Heteronuclear · Ruthenium complexes

## Introduction

Oximes and Schiff bases are the 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, imine nitrogen and oxime oxygen or nitrogen. Therefore, Schiff bases and oximes as ligands have been playing an important role in the development of coordination chemistry as a whole and these compounds have been studied extensively [1–9]. Schiff base and oxime complexes having O and N donor atoms have shown an exponential increase in inorganic catalytic processes such as hydrogenation, isomerisation, decarbonylation, reductive elimination, oxidative addition and in making C–C bonds [10–15].

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, photophysical and photochemical properties 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 [16–18]. In spite of the considerable growth in the literature on transition metal Schiff base complexes, little attention has been given to their ruthenium analogues [19, 20].

In previous studies we investigated the synthesis and characterization of mono- and trinuclear copper(II) complexes of novel tetradentate Schiff bases [21, 22]. The

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present study deals with the synthesis and characterization of *N,N'*-*o*-bis[1-*p*-diphenylmethane-2-hydroxyimino-2-(1-arylamino)-1-ethyliden]-phenylenediamine quadridentate ligands and their mononuclear Ru(III), heterodinuclear Ru(III)–Mn(II), Ru(III)–Ni(II), Ru(III)–Cu(II), heterotri-nuclear Ru(III)–Cu(II)–Ru(III) chelates.

## Experimental

All solvents, *p*-toluidine, *p*-chloroaniline, 1,2-phenylenediamine, 1,10-phenanthroline monohydrate, diphenylmethane, chloroacetyl chloride, aluminium chloride, isopentyl nitrite, metal salts [RuCl<sub>3</sub> · H<sub>2</sub>O, Cu(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O, Mn(OAc)<sub>2</sub> · 4H<sub>2</sub>O, Ni(OAc)<sub>2</sub> · 4H<sub>2</sub>O] and other chemicals used for the synthesis and physical measurements were purchased from Aldrich, J.T. Baker, Acros and Merck and used as received. <sup>1</sup>H NMR spectra of the ligands were recorded from CDCl<sub>3</sub> solutions with TMS as internal standard at the NMR Laboratory at Hacettepe University-Ankara-Turkey. The FT-IR spectra were recorded in the 4,000–400 cm<sup>-1</sup> range on a Shimadzu IRPrestige-21 FT-IR Spectrophotometer as KBr pellets. The thermal analyses studies of the complexes were performed on a Perkin-Elmer Diamond TGA Thermal System under nitrogen atmosphere at a heating rate of 10 °C/min in temperature range 25–900 °C. C, H and N content were determined microanalytically on a LECO 932 CHNS analyzer. Ru, Mn, Ni and Cu contents were measured on Perkin Elmer Optima 5300 DV ICP-OES Spectrometer. Room temperature magnetic susceptibility measurements were done on a Sherwood Scientific Magnetic Susceptibility Balance (Model MX1). The X-band ESR spectra of the complexes were recorded at room temperature on a Bruker Elexsys E580 spectrometer. Molar conductances of the complexes in DMF (1 × 10<sup>-3</sup> M) solution were measured with an Optic Ivymen System conductivity meter. Melting points were measured on an Electrothermal model IA 9100.

### Synthesis of the ligands [H<sub>2</sub>L<sup>3</sup> (3) and H<sub>2</sub>L<sup>4</sup> (10)]

1-*p*-Diphenylmethane-2-chloro-1-ethanon (DMK) was prepared according to the literature method [23] from chloroacetyl chloride and diphenylmethane in the presence of AlCl<sub>3</sub> as catalyst in a Friedel–Crafts reaction. Light yellow, m.p. 55 °C, was isolated in 27% yield; Anal. Calcd. for C<sub>15</sub>H<sub>13</sub>OCl: C, 73.62; H, 5.35. Found: C, 73.21; H, 5.07.

### Synthesis of 1-*p*-diphenylmethane-2-hydroxyimino-2-chloro-1-ethanone (1)

The compound was prepared according to previously published procedures [22, 24, 25]. A quantity of 2.45 g

(10 mmol) 1-*p*-diphenylmethane-2-chloro-1-ethanon was dissolved in 20 cm<sup>3</sup> chloroform with cooling, then passing HCl gas into the solution for half an hour and then 1.40 cm<sup>3</sup> (11 mmol) isopentyl nitrite 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 and recrystallized from ether: hexane (1:1). The crystallized product was filtered, washed with hexane and dried over P<sub>2</sub>O<sub>5</sub>. Yellow, m.p. 108 °C, was isolated in 79% yield; Anal. Calcd. for C<sub>15</sub>H<sub>12</sub>NO<sub>2</sub>Cl: C, 65.82; H, 4.42; N, 5.12. Found: C, 65.34; H, 4.18; N, 4.99.

### Synthesis of 1-*p*-diphenylmethane-2-hydroxyimino-2-(1-arylamino)-1-ethanones [HL<sup>1</sup>](2) and [HL<sup>2</sup>](9)

The compounds were prepared according to the modified method described earlier [22, 26, 27]. A solution of *p*-toluidine or *p*-chloroaniline (20 mmol) was added dropwise to a solution of 2.72 g (10 mmol) 1-*p*-diphenylmethane-2-hydroxyimino-2-chloro-1-ethanon in ethanol (20 cm<sup>3</sup>) for 30 min at 0 °C. The reaction mixtures were stirred for 2 h at the same temperature. Then they were allowed to stir at ambient temperature for 2 h. The powders resulting from the reaction are insoluble in ethanol and thus were filtered off, washed with aqueous sodium bicarbonate (1%), distilled water, and ethanol, and dried over P<sub>2</sub>O<sub>5</sub>.

[HL<sup>1</sup>](2): Light cream, m.p. 116 °C, was isolated in 97% yield; Anal. Calcd. for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>Cl: C, 69.14; H, 4.69; N, 7.68. Found: C, 69.04; H, 4.37; N, 7.59.

[HL<sup>2</sup>](9): Light yellow, m.p. 121 °C, was isolated in 93% yield; Anal. Calcd. for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 76.73; H, 5.85; N, 8.13. Found: C, 76.46; H, 5.52; N, 7.89.

### Synthesis of *N,N'*-*o*-bis[1-*p*-diphenylmethane-2-(1-arylamino)-1-ethyliden]-phenylenediamine quadridentate ligands [H<sub>2</sub>L<sup>3</sup> (3) and H<sub>2</sub>L<sup>4</sup> (10)]

The quadridentate ligands were conveniently prepared as reported in the literature [3, 21, 22, 28]. 1,2-Phenylenediamine (5 mmol, 0.53 g) and 1-*p*-diphenylmethane-2-hydroxyimino-2-(1-arylamino)-1-ethanones (10 mmol) were mixed in absolute EtOH. The contents were stirred magnetically at room temperature for 1 h. Addition of distilled water to the reaction mixtures, the yellow powder products separated, collected by filtration, washed several times with aqueous sodium bicarbonate (1%), distilled water, and ethanol, and dried over P<sub>2</sub>O<sub>5</sub>.

[H<sub>2</sub>L<sup>3</sup>](3): Light yellow, m.p. 203 °C, was isolated in 28% yield; Anal. Calcd. for C<sub>48</sub>H<sub>38</sub>N<sub>6</sub>O<sub>2</sub>Cl<sub>2</sub>: C, 71.91; H, 4.77; N, 10.48. Found: C, 71.87; H, 4.76; N, 10.03.

[H<sub>2</sub>L<sup>4</sup>] (**10**): Dark yellow, m.p. 165 °C, was isolated in 40% yield; Anal. Calcd. for C<sub>50</sub>H<sub>44</sub>N<sub>6</sub>O<sub>2</sub>: C, 78.93; H, 5.82; N, 11.05. Found: C, 78.52; H, 5.74; N, 10.81.

### Synthesis of complexes

*Synthesis of mononuclear Ru(III) complexes:*  
[Ru(HL<sup>3</sup>)Cl<sub>2</sub>] (**4**) and [Ru(HL<sup>4</sup>)Cl<sub>2</sub>] (**11**)

The complexes were prepared as reported in similar literature [22, 28]. To the hot solution of the desired ligand (10 mmol) in absolute EtOH was added RuCl<sub>3</sub> · H<sub>2</sub>O (10 mmol) dissolved in EtOH. The mixtures were heated at reflux temperature for 2 h. On slow evaporation of EtOH the desired complex was obtained as powder. The deeply coloured precipitates were separated by filtration, washed with cold EtOH followed by Et<sub>2</sub>O and dried over P<sub>2</sub>O<sub>5</sub>.

[Ru(HL<sup>3</sup>)Cl<sub>2</sub>] (**4**): Dark brown, m.p. 290 °C, was isolated in 26% yield; molar conductivity (Λ<sub>m</sub>): 33 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>; μ<sub>eff</sub> = 1.79 B.M.; Anal. Calcd. for C<sub>48</sub>H<sub>39</sub>N<sub>6</sub>O<sub>3</sub>Cl<sub>4</sub>Ru: C, 58.19; H, 3.97; N, 8.48; Ru, 10.20. Found: C, 58.37; H, 4.14; N, 8.02; Ru, 9.92.

[Ru(HL<sup>4</sup>)Cl<sub>2</sub>] (**11**): Black, m.p. 246 °C, was isolated in 27% yield; molar conductivity (Λ<sub>m</sub>): 25 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>; μ<sub>eff</sub> = 1.68 B.M.; Anal. Calcd. for C<sub>50</sub>H<sub>43</sub>N<sub>6</sub>O<sub>2</sub>Cl<sub>2</sub>Ru: C, 64.45; H, 4.65; N, 9.02; Ru, 10.85. Found: C, 64.06; H, 4.42; N, 8.84; Ru, 10.47.

*Synthesis of dinuclear Ru(III)–Mn(II) complexes:*  
[Ru(L<sup>3</sup>)Cl<sub>2</sub>Mn(phen)<sub>2</sub>]ClO<sub>4</sub> (**8**), [Ru(L<sup>4</sup>)Cl<sub>2</sub>Mn(phen)<sub>2</sub>]ClO<sub>4</sub> (**15**)

All the heterodinuclear Ru(III) complexes were prepared [3, 22] by similar methods. The mononuclear complexes (**4**) and (**11**) (1 mmol) were mixed Et<sub>3</sub>N (1 mmol) in MeOH (20 cm<sup>3</sup>) and stirred for 0.5 h. Separated solutions of Mn(OAc)<sub>2</sub> · 4H<sub>2</sub>O (1 mmol, 245 mg) in MeOH (10 cm<sup>3</sup>) and 1,10-phenanthroline monohydrate (2 mmol, 400 mg) in MeOH (10 cm<sup>3</sup>) were successively added to the resulting solution. A stoichiometric amount of NaClO<sub>4</sub> · H<sub>2</sub>O (140 mg, 1 mmol) was then added to the resulting mixtures which were boiled under reflux for 24 h. These precipitates were filtered off, washed with H<sub>2</sub>O, MeOH and Et<sub>2</sub>O and dried over P<sub>2</sub>O<sub>5</sub>.

[Ru(L<sup>3</sup>)Cl<sub>2</sub>Mn(phen)<sub>2</sub>]ClO<sub>4</sub> (**8**): Dark brown, m.p. 308 °C, was isolated in 30% yield; molar conductivity (Λ<sub>m</sub>): 84 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>; μ<sub>eff</sub> = 1.98 B.M.; Anal. Calcd. for C<sub>72</sub>H<sub>52</sub>N<sub>10</sub>O<sub>6</sub>Cl<sub>5</sub>RuMn: C, 58.17; H, 3.53; N, 9.42; Ru, 6.80; Mn, 3.70. Found: C, 57.97; H, 3.36; N, 9.13; Ru, 6.57; Mn, 3.65.

[Ru(L<sup>4</sup>)Cl<sub>2</sub>Mn(phen)<sub>2</sub>]ClO<sub>4</sub> (**15**): Black, m.p. 233 °C, was isolated in 50% yield; molar conductivity (Λ<sub>m</sub>): 88 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>; μ<sub>eff</sub> = 2.59 B.M.; Anal. Calcd. for

C<sub>74</sub>H<sub>60</sub>N<sub>10</sub>O<sub>7</sub>Cl<sub>3</sub>RuMn: C, 60.72; H, 4.13; N, 9.57; Ru, 6.91; Mn, 3.75. Found: C, 61.12; H, 3.67; N, 9.23; Ru, 6.58; Mn, 3.68.

*Synthesis of dinuclear Ru(III)–Ni(II) complexes:*  
[Ru(L<sup>3</sup>)Cl<sub>2</sub>Ni(phen)<sub>2</sub>]ClO<sub>4</sub> (**7**) and [Ru(L<sup>4</sup>)Cl<sub>2</sub>Ni(phen)<sub>2</sub>]ClO<sub>4</sub> (**14**)

The mononuclear complexes (**4**) and (**11**) (1 mmol) were mixed Et<sub>3</sub>N (1 mmol) in MeOH (20 cm<sup>3</sup>) and stirred for 0.5 h. Separated solutions of Ni(OAc)<sub>2</sub> · 4H<sub>2</sub>O (1 mmol, 245 mg) in MeOH (10 cm<sup>3</sup>) and 1,10-phenanthroline monohydrate (2 mmol, 400 mg) in MeOH (10 cm<sup>3</sup>) were successively added to the resulting solution. A stoichiometric amount of NaClO<sub>4</sub> · H<sub>2</sub>O (140 mg, 1 mmol) was then added to the resulting mixtures which were boiled under reflux for 24 h. The final products were filtered off, washed with H<sub>2</sub>O, MeOH and Et<sub>2</sub>O and dried over P<sub>2</sub>O<sub>5</sub>.

[Ru(L<sup>3</sup>)Cl<sub>2</sub>Ni(phen)<sub>2</sub>]ClO<sub>4</sub> (**7**): Dark brown, m.p. 345 °C, was isolated in 39% yield; molar conductivity (Λ<sub>m</sub>): 85 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>; μ<sub>eff</sub> = 2.39 B.M.; Anal. Calcd. for C<sub>72</sub>H<sub>56</sub>N<sub>10</sub>O<sub>8</sub>Cl<sub>5</sub>RuNi: C, 56.66; H, 3.70; N, 9.18; Ru, 6.62; Ni, 3.85. Found: C, 56.58; H, 3.29; N, 9.11; Ru, 6.31; Ni, 3.47.

[Ru(L<sup>4</sup>)Cl<sub>2</sub>Ni(phen)<sub>2</sub>]ClO<sub>4</sub> (**14**): Dark brown, m.p. 210 °C, was isolated in 47% yield; molar conductivity (Λ<sub>m</sub>): 91 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>; μ<sub>eff</sub> = 2.18 B.M.; Anal. Calcd. for C<sub>74</sub>H<sub>58</sub>N<sub>10</sub>O<sub>6</sub>Cl<sub>3</sub>RuNi: C, 61.32; H, 4.03; N, 9.66; Ru, 6.97; Ni, 4.05. Found: C, 61.13; H, 3.60; N, 9.42; Ru, 6.54; Ni, 3.89.

*Synthesis of dinuclear Ru(III)–Cu(II) complexes:*  
[Ru(L<sup>3</sup>)Cl<sub>2</sub>Cu(phen)]ClO<sub>4</sub> (**5**) and [Ru(L<sup>4</sup>)Cl<sub>2</sub>Cu(phen)]ClO<sub>4</sub> (**12**)

The mononuclear complexes (**4**) and (**11**) (1 mmol) were added to Et<sub>3</sub>N (1 mmol) in Me<sub>2</sub>CO (20 cm<sup>3</sup>) and the mixtures were stirred for 0.5 h. Separated solutions of Cu(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O (1 mmol, 370 mg) in Me<sub>2</sub>CO (10 cm<sup>3</sup>) and 1,10-phenanthroline monohydrate (1 mmol, 200 mg) were successively added to the resulting mixtures, which were boiled under reflux for 3 h. The products were filtered off, washed with H<sub>2</sub>O, MeOH and Et<sub>2</sub>O and dried over P<sub>2</sub>O<sub>5</sub>.

[Ru(L<sup>3</sup>)Cl<sub>2</sub>Cu(phen)]ClO<sub>4</sub> (**5**): Black, m.p. 300 °C, was isolated in 37% yield; molar conductivity (Λ<sub>m</sub>): 77 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>; μ<sub>eff</sub> = 1.45 B.M.; Anal. Calcd. for C<sub>60</sub>H<sub>48</sub>N<sub>8</sub>O<sub>8</sub>Cl<sub>5</sub>RuCu: C, 53.34; H, 3.58; N, 8.29; Ru, 7.48; Cu, 4.70. Found: C, 53.70; H, 3.13; N, 8.16; Ru, 7.68; Cu, 4.36.

[Ru(L<sup>4</sup>)Cl<sub>2</sub>Cu(phen)]ClO<sub>4</sub> (**12**): Dark brown, m.p. 250 °C, was isolated in 22% yield; molar conductivity (Λ<sub>m</sub>): 75 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>; μ<sub>eff</sub> = 1.39 B.M.; Anal. Calcd. for

for  $C_{62}H_{50}N_8O_6Cl_3RuCu$ : C, 58.45; H, 3.95; N, 8.80; Ru, 7.93; Cu, 4.99. Found: C, 58.13; H, 3.66; N, 8.49; Ru, 7.83; Cu, 4.60.

*Synthesis of trinuclear Ru(III)–Cu(II)–Ru(III) complexes:  $[Ru_2(L^3)Cl_4Cu]$  (**6**) and  $[Ru_2(L^4)Cl_4Cu]$  (**13**)*

The complexes were prepared as reported in similar literature. [3, 22] A mixture the mononuclear complexes (**4**) and (**11**) (1 mmol),  $Cu(ClO_4)_2 \cdot 6H_2O$  (0.5 mmol, 185 mg) and  $Et_3N$  (100 mg, 1 mmol) in  $Me_2CO$  (20  $cm^3$ ) was refluxed for 2 h. The resulting solutions were filtered while hot and concentrated slowly. As the solutions cooled black powder products precipitated. The products were isolated by filtration, washed with  $Et_2O$ , and dried in air.

$[Ru_2(L^3)Cl_4Cu]$  (**6**): Black, m.p. 180 °C, was isolated in 24% yield; molar conductivity ( $\Lambda_m$ ): 44  $\Omega^{-1}cm^2 mol^{-1}$ ;  $\mu_{eff} = 1.61$  B.M.; Anal. Calcd. for  $C_{96}H_{72}N_{12}O_4Cl_8Ru_2Cu$ : C, 57.45; H, 3.61; N, 8.38; Ru, 10.07; Cu, 3.17. Found: C, 57.28; H, 3.12; N, 7.89; Ru, 9.86; Cu, 2.78.

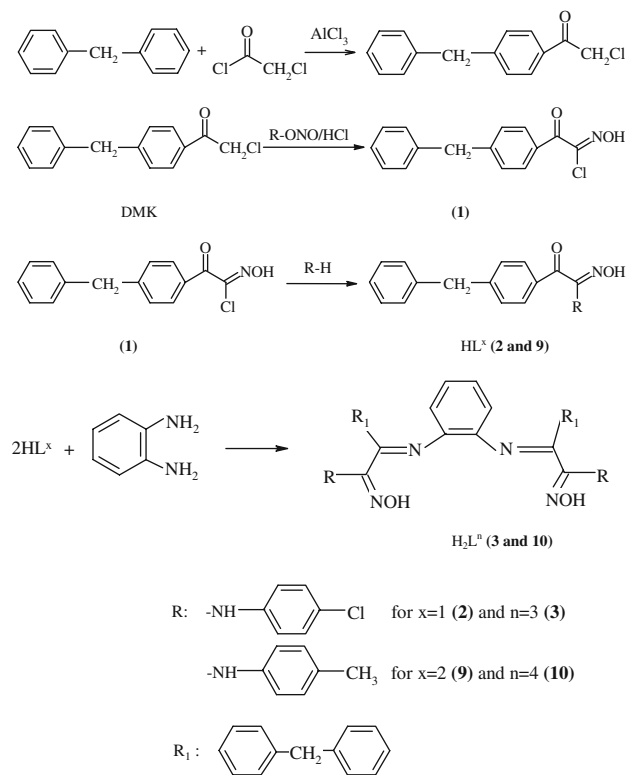
$[Ru_2(L^4)Cl_4Cu]$  (**13**): Dark brown, m.p. 200 °C, was isolated in 29% yield; molar conductivity ( $\Lambda_m$ ): 31  $\Omega^{-1} cm^2 mol^{-1}$ ;  $\mu_{eff} = 1.53$  B.M.; Anal. Calcd. for  $C_{100}H_{84}N_{12}O_4Cl_4Ru_2Cu$ : C, 62.39; H, 4.39; N, 8.73; Ru, 10.50; Cu, 3.30. Found: C, 62.10; H, 4.07; N, 8.24; Ru, 10.24; Cu, 3.06.

## Results and discussion

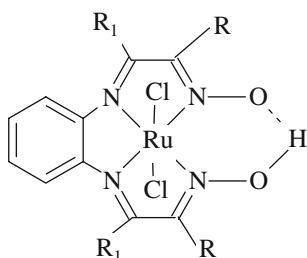
The quadridentate ligands,  $N,N'$ -bis[1-*p*-diphenylmethane-2-hydroxyimino-2-(1-arylamino)-1-ethyliden]-phenylenediamines were prepared from diphenylmethane as shown in Scheme 1. Firstly 1-*p*-diphenylmethane-2-chloro-1-ethanon was synthesized according to the literature [23]. 1-*p*-Diphenylmethane-2-hydroxyimino-2-chloro-1-ethanon was obtained by reacting 1-*p*-diphenylmethane-2-chloro-1-ethanon with isopentyl nitrite [22, 24, 25]. 1-*p*-Diphenylmethane-2-hydroxyimino-2-(1-arylamino)-1-ethanones were prepared by reaction of 1-*p*-diphenylmethane-2-hydroxyimino-2-chloro-1-ethanon with *p*-toluidine or *p*-chloroaniline [22, 26, 27]. Condensation of the 1-*p*-diphenylmethane-2-hydroxyimino-2-(1-arylamino)-1-ethanones with 1,2-phenylenediamine gives to the quadridentate ligands [3, 21, 22, 28], which were identified by their IR, elemental and thermal analysis,  $^1H$  NMR spectra. Reaction of the ligands with Ru(III) chloride led to the isolation of mononuclear Ru(III) [28] (Fig. 1) complexes. Further reaction with 1 equiv. of the appropriate divalent metal ions, 1,10-phenanthroline and triethylamine gave the heterodinuclear [3, 22] Ru(III)–Mn(II), Ru(III)–Ni(II), Ru(III)–Cu(II) (Figs. 2, 3) complexes. And reaction of 2 equiv. of the mononuclear Ru(III) complexes with 1

equiv. of  $Cu(ClO_4)_2 \cdot 6H_2O$  and 2 equiv. of  $Et_3N$  led to the isolation of heterotrimeric Ru(III)–Cu(II)–Ru(III) [3, 22] (Fig. 4) complexes. The resulting solids are intensely coloured, and stable in air. Attempts to isolate crystals suitable for X-ray diffraction were unsuccessful. Therefore, elemental analysis spectroscopic techniques, 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 in well agreement with the expected values.

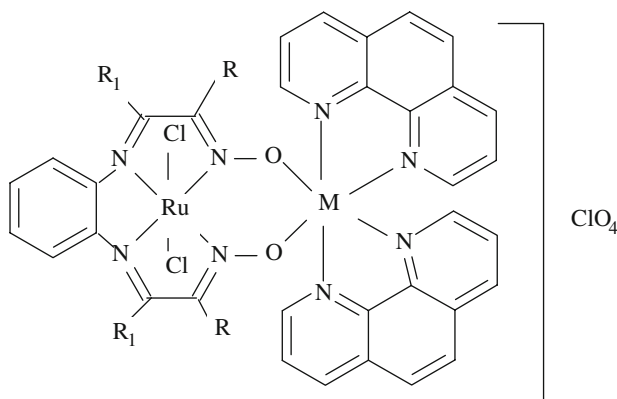
The  $^1H$ -NMR spectra of the starting compounds and the free ligands were recorded in  $CDCl_3$ . The chemical shifts, expressed in ppm downfield from TMS, are given in Table 1. The  $^1H$ -NMR spectra of the starting compounds and the ligands exhibited a broad singlet peak at 7.94–8.85 ppm for the OH protons of the oxime groups. The peaks observed at range 6.98–8.10 ppm are assignable to the protons of the aromatic rings as multiplet peaks. Furthermore the singlets in the range of 4.00–4.22 ppm have been 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 Schiff bases exhibited signals of the protons in their expected regions and these data are in good agreement with that previously reported for similar compounds [22, 27, 29].



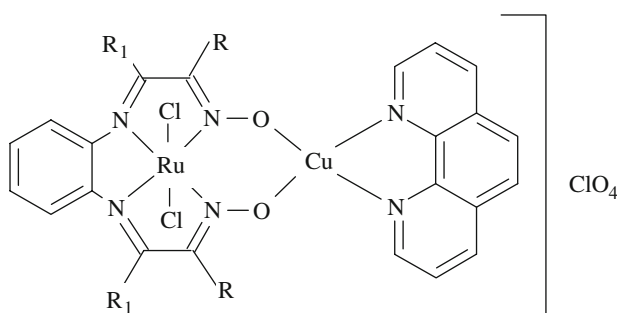
**Scheme 1** Preparation of the ligands



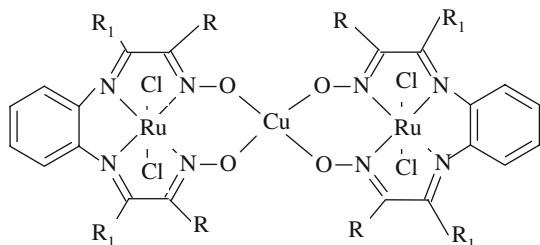
**Fig. 1** Mononuclear ruthenium(III) complexes of the ligands



**Fig. 2** Heterodinuclear Ru(III)–Mn(II) and Ru(III)–Ni(II) complexes of the ligands [M=Mn(II), Ni(II)]



**Fig. 3** Heterodinuclear Ru(III)–Cu(II) complexes of the ligands



**Fig. 4** Heterotrimeric Ru(III)–Cu(II)–Ru(III) complexes of the ligands

The important IR spectral data of the free ligands and their mono- and heteropolynuclear ruthenium(III) complexes are presented in Table 2. In the IR spectra of the

**Table 1**  $^1\text{H}$  NMR data of the starting compounds and the ligands

Bileşikler	OH <sub>oxime</sub>	C-H <sub>arom</sub>	N–H	-CH <sub>(DFM)</sub>	-CH <sub>aliph</sub>
DMK	–	7.90–7.10 (m, 9H)	–	4.00 (s, 2H)	4.50 (s, 2H)
(1)	8.85 (s, 1H)	8.10–7.10 (m, 9H)	–	4.20 (s, 2H)	–
(2)	8.65 (s, 1H)	7.92–7.16 (m, 13H)	6.85 (s, 1H)	4.22 (s, 2H)	–
(3)	7.94 (s, 2H)	7.32–7.12 (m, 30H)	6.76 (s, 2H)	4.03 (s, 4H)	–
(9)	8.01 (s, 1H)	7.37–7.01 (m, 13H)	6.76 (s, 1H)	4.04 (s, 2H)	2.25 (s, 3H)
(10)	7.97 (s, 2H)	7.31–6.98 (m, 30H)	6.77 (s, 2H)	4.05 (s, 4H)	2.25 (s, 6H)

*s* singlet, *m* multiplet

starting compounds and the ligands, medium-to-strong bands in the 3231–3261  $\text{cm}^{-1}$  range can be attributed to  $\nu(\text{OH})$  vibrations of oxime groups; the broad nature of these bands and their low wavenumbers suggest the presence of hydrogen bonding [28]. In the IR spectral data of the (3) and (10), fairly strong bands at 3,369 and 3,399  $\text{cm}^{-1}$  belong to the  $\nu(\text{N–H})$  vibration of the aromatic amine groups. The medium, sharp band at 1,221 and 1,242  $\text{cm}^{-1}$  is due to the N–O stretching vibrations [3, 30]. In the IR spectra of the ligand (3), the stretching vibrations of the  $\text{C}=\text{N}_{\text{imine}}$  and  $\text{C}=\text{N}_{\text{oxime}}$  are observed at 1,645 and 1,601  $\text{cm}^{-1}$ , respectively. The bands observed at 1636 and 1601  $\text{cm}^{-1}$  in other ligand (10) also are assignable to the same groups. The C=O bands for the compounds (2) and (9) are observed as a medium band at 1,680 and 1,675  $\text{cm}^{-1}$ , respectively. The spectra of the ligands do not show absorptions characteristic of the C=O function owing to the formation of the imine [3, 11, 18].

The characteristic absorption bands of the ligands are shifted on complex formation and new vibrational bands characteristic of the complex appear. In the metal complexes, the bands due to the OH modes are no longer observed, denoting that all the hydroxyl protons are displaced by metal ions leading to covalent (M–O) bonding with the ligands. This is supported by the appearance of a band in the region 503–522  $\text{cm}^{-1}$  assigned to  $\nu(\text{M–O})$  [31–33].

The heteronuclear Ru–Ni complex of  $\text{H}_2\text{L}^3$  (7) showed a broad band in the 3,441  $\text{cm}^{-1}$ , which confirms the presence of water molecules hydrated to the metal ion [29]. Vibrational evidence for coordination of the oximate groups in the complexes is provided by the higher frequency bands of N–O at ca. 1251–1340  $\text{cm}^{-1}$  [3]. The appearance of a new bands at 419–456  $\text{cm}^{-1}$  assigned to  $\nu(\text{M–N})$  [29, 34].

The dinuclear complexes have a medium bands in the region of 1,104–1,182  $\text{cm}^{-1}$  and a weak bands at 1,020–



**Table 2** IR spectra (4,000–400 cm<sup>-1</sup>) of the ligands and their metal complexes

Compound	N–H	$\nu(\text{OH})$	C=N	C–N	$\nu(\text{NO})$	$\text{ClO}_4^-$	M–N	M–O	Ru–N
(1)	–	3232 s	1601 s	–	1290 s	–	–	–	–
(2)	3370 m	3241 b	1601 s	1371 s	1246 s	–	–	–	–
(3)	3369 s	3231 b	1601 s	1369 s	1221 s	–	–	–	–
(4)	3380 b	–	1601 s	1404 s	1340 w	–	–	–	670 s
(5)	3309 b	–	1600 m	1397 w	1315 w	1177 m	428 m	503 w	670 m
(6)	3339 w	–	1600 m	1400 w	1281 m	–	456 w	503 w	669 m
(7)	3383 b	3441 b	1601 m	1414 m	1320 b	1182 m	423 w	518 w	699 m
(8)	3320 b	–	1601 w	1417 m	1340 m	1177 m	423 m	515 w	669 s
(9)	3389 s	3242 b	1601 s	1399 m	1242 s	–	–	–	–
(10)	3399 s	3261 b	1601 s	1399 m	1242 s	–	–	–	–
(11)	3330 b	–	1601 s	1418 m	1290 w	–	–	–	670 s
(12)	3335 b	–	1601 s	1419 m	1251 w	1182 m	431 w	518 w	670 m
(13)	3336 b	–	1601 m	1418 w	1276 w	–	419 m	513 w	670 s
(14)	3320 b	–	1601 m	1413 m	1280 w	1123 m	434 m	518 m	670 m
(15)	3369 b	–	1601 m	1423 w	1285 w	1104 s	433 s	522 m	669 w

*s* strong, *m* medium, *w* weak, *b* broad

1,093 cm<sup>-1</sup> range featuring typical characteristics of uncoordinated perchlorates [35, 36]. Thus the IR-spectra of ligands and their metal complexes gives strong evidence for the complexation of the potentially multidentate ligands.

The room temperature molar conductivity measurements of the complexes were carried out in 10<sup>-3</sup> mol.dm<sup>-3</sup> *N,N*-dimethylformamide solutions. The molar conductance of the complexes was an aid for proposing their formulas. The dinuclear complexes exhibit various conductances between 75 and 91  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> range and other complexes (**4**, **6**, **11**, **13**) exhibit conductances between 25 and 44  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> range. The molar conductances of the dinuclear complexes in DMF indicated that these complexes behave as 1:1 electrolytes [37]. A perchlorate ion is outside the coordination sphere. The low conductivity values of the other complexes indicate that the complexes are nonelectrolytes [28].

The magnetic moments (as B.M.) of the solid state complexes were measured at room temperature. The magnetic moments of the complexes show that all of the

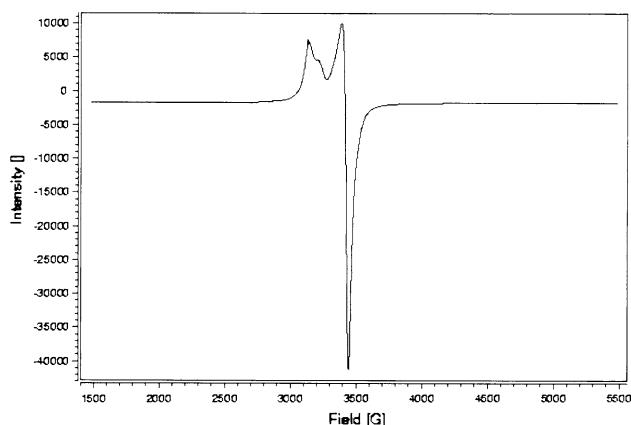
complexes are paramagnetic. The measured magnetic moments of the mononuclear ruthenium(III) complexes are 1.79 and 1.68 B.M. for (**4**) and (**11**), respectively. Magnetic susceptibility measurements show that these complexes are one-electron paramagnetic, which corresponds to the +3 oxidation state of ruthenium (low-spin d<sup>5</sup>,  $S = 1/2$ ) in these complexes. The magnetic moment of the trinuclear Ru(III)–Cu(II)–Ru(III) complexes 1.61 and 1.53 B.M. for (**6**) and (**13**), respectively. The magnetic moments of the dinuclear complexes are 1.45–1.39, 2.39–2.18 and 1.98–2.59 B.M. for Ru(III)–Cu(II), Ru(III)–Ni(II) and Ru(III)–Mn(II) complexes, respectively. It can be observed that these magnetic moment values of ruthenium(III) complexes are slightly lower than expected for dinuclear ruthenium(III) complexes than the total of the theoretical value of 1.73 B.M. for one low spin d<sup>5</sup> ruthenium ion and the theoretical magnetic moment values of the other ions. The strong antiferromagnetic coupling that was found for di- and trinuclear ruthenium(III) complexes is explained as the oximate group have good superexchange properties [38]. These subnormal magnetic moment values of the

dinuclear complexes may be explained by antiferromagnetic intramolecular interaction since this situation can occur when two equivalent metal ions are coupled via an exchange interaction in a polynuclear complex [27, 39].

The room temperature solid-state EPR spectrum of mononuclear Ru(III) complex (**4**) 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 complex exhibit a characteristic of an axially symmetric system with  $g_{\perp}$  is 2.239 and  $g_{\parallel}$  is 2.071. The EPR spectra of the complexes exhibit a characteristic of an axially symmetric system with  $g_{\perp}$  around 2.14–2.49 and  $g_{\parallel}$  around 1.82–2.14. For an octahedral field with tetragonal distortion  $g_x = g_y \neq g_z$ , these observations indicate tetragonal distortion in the complex. A representative spectrum for the complex (**4**) is shown in Fig. 5. Overall, the position of lines and nature of the EPR spectra of the complexes are characteristic of low spin ruthenium(III) octahedral complexes [15, 40].

In order to give more insight into the structure of the complexes, the thermal studies of the complexes have been carried out using thermogravimetry (TG-DTG) techniques. The thermogravimetric analyses for the ligands and metal complexes were carried out within the temperature range from ambient temperature up to 900 °C (Table 3). The thermal behaviour of all the complexes was almost the same.

The ligand (**3**) with the molecular formula  $[C_{48}H_{38}N_6O_2Cl_2]$  is thermally decomposed in three successive decomposition steps. The estimated mass loss of 85.00% (calculated mass loss = 84.02%) within the temperature range 150–610 °C may be attributed to the loss of two 4-chloroaniline, two OH, diphenylmethane and two CN groups leaving  $R(CN)_2$  as residue.



**Fig. 5** The EPR spectrum of the mononuclear ruthenium(III) complex (**4**)

It was found from TG analysis that the mononuclear Ru(III) complex (**4**) of  $H_2L^3$  starts losing mass at 30 °C and ends at 540 °C after losing 35.00% (calculated mass loss = 34.69%), but the decomposition did not finish completely at this temperature. The examination of TG curve showed that the complex decomposes in four stages. The sample loses 1.50% of mass between 30 and 125 °C and 33.50% of the mass between 125 and 540 °C. These decomposition steps correspond to loss of one  $H_2O$  molecule, two Cl atoms and two chloroaniline molecules and calculated mass losses 1.82 and 32.87, respectively.

The dinuclear Ru(III)–Cu(II) complex (**5**) of  $H_2L^3$  shows decomposition pattern of six stages. The first step with estimated mass loss of 2.50% (calculated mass loss = 2.67%), found within the temperature range 30–110 °C corresponding to loss of two  $H_2O$  molecules. Other three steps with estimated mass loss of 45.40% (calculated mass loss = 44.82%), found within the temperature range 110–695 °C corresponding to loss of perchlorate, two Cl, two chloroaniline and phenanthroline groups. Fourth step did not finish completely within the temperature range 695–900 °C.

It is noted from the TG analysis that the dinuclear Ru(III)–Ni(II) complex (**7**) of  $H_2L^3$  loses 86.00% (calculated mass loss = 86.74%) of its original mass between 40 and 950 °C and the residues are  $Ru_2O_3$  and NiO. The sample decomposes in four stages. The first decomposition occurs between 40 and 110 °C with 2.10% estimated mass loss (calculated mass loss = 2.36%), the second and third decompositions occurs between 110–420 and 420–630 °C with 30.05 and 27.10% estimated mass loss (calculated mass loss = 30.13% and 26.56%), respectively, corresponding to loss of two  $H_2O$  molecule,  $ClO_4$ , two phenanthroline molecules, diphenylmethane and two Cl groups. The last step occurs between 630 and 950 °C with 26.75% estimated mass loss (calculated mass loss = 27.69%).

The thermal decomposition of the other ligand (**10**) with the molecular formula  $[C_{50}H_{44}N_6O_2]$  proceeds with three main degradation steps. The first step occurs within the temperature range 165–250 °C with an estimated mass loss 27.60% (calculated mass loss = 27.90%) which is reasonably accounted for the loss of toluidine groups. The second step occurs within the temperature range 250–520 °C with an estimated mass loss 50.45% (calculated mass loss = 50.79%), which is reasonably accounted for the loss of diphenylmethane and  $(CN)_2$  groups. The last step occurs between 520 and 890 °C corresponding to loss of the other groups. Total estimated mass loss is 100.00%.

The trinuclear Ru(III)–Cu(II)–Ru(III) complex (**13**) of  $H_2L^4$  shows decomposition pattern of two stages. The first step with estimated mass loss of 7.80% (calculated mass loss = 7.37%), found within the temperature range 110–245 °C corresponding to loss of four Cl atoms. The second

**Table 3** Thermoanalytical results (TG, DTG) of the ligands and their metal complexes

Compound	TG range (°C)	DTG <sub>max</sub> (°C)	Estimated (%), calculated)		Assignment	Metallic residue
			Mass loss	Total mass loss		
(3)	150–610	210, 280, 350	85.00 (84.02)	85.00 (84.02)	Loss of chloroaniline, OH, diphenylmethane and (CN) <sub>2</sub> groups	Ar(CN) <sub>2</sub>
(4)	30–125	67	1.50 (1.82)	–	Loss of an H <sub>2</sub> O molecule	–
	125–540	232, 436	33.50 (32.87)	–	Loss of two chloroaniline and two Cl groups	–
	540–900	660	–	–	Loss of the other groups	Decomposition is in progress
(5)	30–110	55	2.50 (2.67)	–	Loss of two H <sub>2</sub> O molecule	–
	110–695	263, 330, 393, 615	45.40 (44.82)	–	Loss of two Cl ClO <sub>4</sub> , chloroaniline and phenanthroline groups	–
	695–900	–	–	–	Loss of the other groups	Decomposition is in progress
(7)	40–110	75	2.10 (2.36)	–	Loss of two H <sub>2</sub> O molecule	–
	110–420	360	30.05 (30.13)	–	Loss of ClO <sub>4</sub> and two phenanthroline molecules	–
	420–630	490	27.10 (26.56)	–	Loss of diphenylmethane and two Cl groups	–
	630–950	900	26.75 (27.69)	86.00 (86.74)	Loss of the other groups	Ru <sub>2</sub> O <sub>3</sub> /2 and NiO
(10)	165–250	198	27.60 (27.90)	–	Loss of toluidine groups	–
	250–520	280	50.45 (50.79)	–	Loss of diphenylmethane and (CN) <sub>2</sub> groups	–
	520–890	673	21.95 (21.31)	100.00 (100.00)	Loss of the other groups	–
(13)	110–245	202	7.80 (7.37)	–	Loss of four Cl atoms	–
	245–580	392	74.90 (75.51)	82.70 (82.88)	Loss of the ligand molecules	Ru <sub>2</sub> O <sub>3</sub> and CuO
(15)	40–100	45	1.80 (1.23)	–	Loss of an H <sub>2</sub> O molecule	–
	100–240	189	12.30 (11.61)	–	Loss of ClO <sub>4</sub> and two Cl groups	–
	240–500	315	25.20 (24.62)	–	Loss of two phenanthroline molecules	–
	500–900	600	–	–	Loss of the other groups	Decomposition is in progress

steps with estimated mass loss of 74.90% (calculated mass loss = 75.51%), found within the temperature range 245–580 °C corresponding to loss of ligand molecules leaving Ru<sub>2</sub>O<sub>3</sub> and CuO as residue.

The dinuclear Ru(III)–Mn(II) complex (**15**) of H<sub>2</sub>L<sup>4</sup> exhibits the first mass loss in the temperature range 40–100 °C, with a maximum at 45 °C in the DTG curve. The second mass loss at 100–240 °C, with a maximum at 189 °C is due to the liberation of ClO<sub>4</sub> and two Cl groups. The third step with estimated mass loss of 25.20 (calculated mass loss = 24.62%). The temperature range of this decomposition is found to be 240–500 °C corresponding to loss of two phenanthroline molecules. The last step did not finish completely at 900 °C.

The theoretical and the experimental per cent mass losses obtained from these decomposition stages are in good agreement. The critical data and values deduced from the present study were summarized in Table 3.

## Conclusion

*N,N'*-*o*-bis[1-*p*-diphenylmethane-2-(1-arylamine)-1-ethylidene]-phenylenediamine quadridentate ligands and their mononuclear ruthenium(III) and heterodinuclear ruthenium(III)–manganese(II), ruthenium(III)–nickel(II), ruthenium(III)–copper(II) and heterotrinary ruthenium(III)–copper(II)–ruthenium(III) complexes were synthesized and characterized by elemental, thermal analyses, ICP-OES, ESR, magnetic susceptibility, conductivity measurements, FT-IR and <sup>1</sup>H NMR. From the elemental analyses, stoichiometric and spectroscopic studies discussed above, the ligands have been shown to act as a quadridentate which coordinates through the nitrogen atoms of the oxime and imine groups. These data indicated that in the dinuclear complexes, in which the Ru(III) ions were complexed with nitrogen atoms of the oxime and imine groups, the second ions [Cu(II), Mn(II), Ni(II)] are ligated with dianionic



oxygen atoms of the oxime groups and are linked to the 1,10-phenanthroline nitrogen atoms. The trinuclear Ru(III)–Cu(II)–Ru(III) complexes were formed by coordination of the Cu(II) ion with dianionic oxygen atoms of each of two molecules of the mononuclear Ru(III) complexes. Moreover dinuclear complexes of the diimine-dioxime ligands have a 2:1, trinuclear complexes of the diimine-dioxime ligands have a 3:2 metal:ligand ratio. The thermal analyses data of these chelates shows that the complexes were generally thermally decomposed in 4–5 successive decomposition steps.

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