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Water soluble (η^6 -arene) ruthenium(II) complexes incorporating marine derived bioligand: Synthesis, spectral and structural studies

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Abstract: A series of water soluble compounds of general formula [$\{\eta^6$ -arene)Ru(HMP)Cl], [η^6 -arene = η^6 -cymene (**1**), η^6 -HMB (**2**), η^6 -C₆H₆ (**3**); HMP = 5-hydroxy-2-(hydroxymethyl)-4-pyrone] have been prepared by the reaction of [$\{\eta^6$ -arene) RuCl₂}]₂ with HMP. The complexes **1** and **2** react with NaN₃ to give in excellent yield tetra-azido complexes [$\{\eta^6$ -arene)Ru(μ N₃)N₃}]₂ (arene = cymene **4**, HMB = **5**) but similar reaction of complex **3** with NaN₃ yielded di-azido complex [$\{\eta^6$ -C₆H₆)Ru(μ N₃)Cl}]₂ (**6**). Reaction of [$\{\eta^6$ -arene)Ru(μ N₃)Cl}]₂ with HMP in the presence of NaOMe resulted in the formation of azido complex [$\{\eta^6$ -arene)Ru(HMP)N₃]. Mono and dinuclear complexes [$\{\eta^6$ -arene)Ru(HMP)(L₁)]⁺ and [$\{\eta^6$ -arene)Ru(HMP)}₂(μ L₂)]²⁺ were also prepared by the reaction of complexes **1** and **2** with the appropriate ligand, L₁ or L₂ in the presence of AgBF₄ (L₁ = PyCN, DMAP; L₂ = 4,4'-bipy, pyrazine). The complexes are characterized on the basis of spectroscopic data and molecular structures of three representative compounds have been determined by single crystal X-ray diffraction study.

Keywords: Arene, azide, kojic acid, bioorganometallic, crystallography.

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1. Introduction

Arene ruthenium (II) complexes have been subject of current interest owing to their biological and catalytic properties [1-6]. Catalytic activities of these complexes ranges from hydrogen transfer [7] to ring closer metathesis [8]. Moreover, anti tumour [5,6,9], antiviral [10] and catalytic activities [11,12] exhibited by some of the water soluble (η^6 -arene) ruthenium(II) complexes has evoked interest in recent years. Recently, much attention has focussed on the development of bioorganometallic complexes. Some of these complexes have been reported to exhibit side-on intercalative into DNA [13,14]. There have been extensive studied on η^6 -arene ruthenium complexes bearing nitrogen ligands [15-19]. However, η^6 -arene ruthenium complexes bearing oxygen ligands are relatively less explore. In our previous communication, we have reported synthesis of (η^6 -arene) ruthenium(II) triazole compounds containing β -diketonate group by 1, 3-dipolar addition of terminal azido group with activated alkynes [20]. Our current interest on (η^6 -arene) ruthenium complexes containing oxygen ligand arises due to labile nature of oxygen ligand and possibility of forming water soluble compounds.

During the course of our study on bioactive compounds from marine organisms we isolated kojic acid from a marine fungus *Aspergillus* species. Kojic acid is one of the metabolite produced by various fungal or bacteria strains of genus *Aspergillus* and *Penicillium*. It has been used in many countries as skin whitening agent because of its tyrosinase inhibitory activity on melanin synthesis [21, 22]. Our current interest in η^6 -arene ruthenium(II) complexes bearing oxygen ligands [20] prompted us to study the synthesis of η^6 -arene ruthenium complexes containing kojic acid ligand keeping in mind their possible biological activities. In this paper, we would like to report synthesis of water soluble (η^6 -arene) ruthenium (II) complexes incorporating kojic acid ligand (HMP) of the type $[(\eta^6\text{-arene})\text{Ru}(\text{HMP})\text{X}]$ ($\text{X} = \text{Cl}, \text{N}_3$) and cationic complexes $[(\eta^6\text{-arene})\text{Ru}(\text{HMP})\text{L}_1]^+$ or $[\{(\eta^6\text{-arene})\text{Ru}(\text{HMP})\}_2 \text{L}_2]^{2+}$ (Where, $\text{L}_1, \text{L}_2 =$ Neutral ligands). We also disclosed the reaction of $[(\eta^6\text{-arene})\text{Ru}(\text{HMP})\text{Cl}]$ with sodium azide to yield azido dimeric complexes $[\{(\eta^6\text{-arene})\text{Ru}(\mu\text{N}_3)\text{N}_3\}_2]$ and $[\{(\eta^6\text{-arene})\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2]$. The complexes are fully characterized on the basis of FTIR and NMR spectroscopic data.

The molecular structures of three representative compounds viz. $[(\eta^6\text{-}p\text{-cymene}) \text{Ru}(\text{HMP})\text{Cl}]$ (**1**), $[\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{N}_3\}_2]$ (**4**) and $[(\eta^6\text{-HMB})\text{Ru}(\text{HMP})\text{N}_3]$ (**8**) were established by single crystal X-ray diffraction.

2. Experimental

2.1 *General Remarks:* Solvents were dried using appropriate drying agents and distilled prior to use. RuCl₃.3H₂O (Aurora Matthey), pyridine cyanide (PyCN), 4-(dimethyl amino) pyridine (DMAP), pyrazine (pz), sodium azide (Sigma Aldrich), 4,4-bipyridine (Merk) were used as received. NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at 300.13 (¹H), 75.47 MHz (¹³C) with SiMe₄ as internal references and coupling constants are given in hertz. Infra red spectra were recorded in a diffused reflection spectroscopy (DRS) assembly on a Shimadzu-8201PC spectrometer with sample prepared in KBr. The precursor complexes [$\{\{\eta^6\text{-}p\text{-cymene}\}\text{RuCl}_2\}_2$] [23, 24], [$\{\{\eta^6\text{-C}_6\text{Me}_6\}\text{RuCl}_2\}_2$] [25, 26], [$\{\{\eta^6\text{-C}_6\text{H}_6\}\text{RuCl}_2\}_2$] [23, 24], [$\{\{\eta^6\text{-}p\text{-cymene}\}\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2$] [27] and [$\{\{\eta^6\text{-HMB}\}\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2$] [28] were prepared according to literature procedures. Kojic acid (HMP) was obtained from a marine derived fungus *Aspergillus* sp. isolated from sea weeds.

2.2. Synthesis of compounds

2.2.1. Synthesis of [$\{\{\eta^6\text{-}p\text{-cymene}\}\text{Ru}(\text{HMP})\text{Cl}\}$] (**1**)

A mixture of kojic acid (0.05g, 0.35 mmol) and NaOMe (0.019g, 0.35 mmol) in dry methanol (40 ml) was stirred for 10 minutes. After which the complex [$\{\{\eta^6\text{-}p\text{-cymene}\}\text{RuCl}_2\}_2$] (0.1g, 0.163 mmol) was added to the mixture and stirring continued for additional 5 hrs. Solution was rotary evaporated to dryness and taken in dichloromethane to precipitate out sodium chloride. The solution was filtered and concentrated to ca 3 ml then excess diethyl ether was added. The yellow needle crystalline solid formed on leaving the solution for 2 hrs at room temperature was collected, washed with diethyl ether and dried in vacuum to afford 0.125g (93% yield) of the compound.

IR (KBr, cm⁻¹): 3300, 3043, 1602, 1562, 1502, 1469, 1288, 1247.

¹HNMR (CDCl₃, δ): 1.22 (dd, 6H, Me, CHMe₂, $J_{\text{H-H}} = 2.1$, $J_{\text{H-H}} = 4.8$), 2.30 (s, 3H, Me), 2.87 (sept, 1H, CHMe₂), 4.44 (s, 2H, CH₂-C₅H₂O₃), 5.30 (d, 2H, cymene ring, $J_{\text{H-H}} = 5.4$), 5.51 (d, 2H, cymene ring, $J_{\text{H-H}} = 5.1$), 6.63 (s, 1H), 7.66 (s, 1H). ¹³C{¹H} NMR(CDCl₃, δ): 15.25 (s, Me), 18.59 (s, Me, CMe), 22.31(d, Me, $J_{\text{C-H}} = 5.28$, CHMe₂), 31.08 (s, CH, CHMe₂), 60.73 (s, CH₂, CH₂OH), 77.43 (d, cymene ring), 78.61 (t, $J_{\text{H-H}} = 46.7$, cymene ring), 95.56 (s, C, CMe), 100.08 (s, C, CPrⁱ), 107.57 (s, CH, HMP), 141.07 (s, CH-O, HMP) 159.49 (s, C, C=CH, HMP), 167.44 (s, C-O), 185.80 (s, C=O).

2.2.2. Synthesis of $[\{\eta^6\text{-C}_6\text{Me}_6\}\text{Ru}(\text{HMP})\text{Cl}]$ (**2**)

This complex was prepared by following a similar procedure as described in the preparation of **1** using kojic acid (0.046 g, 0.32 mmol), NaOMe (0.018 g, 0.33 mmol) and complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$ (0.1g, 0.149 mmol).

Yield: 0.095g (72%).

FTIR (KBr, cm^{-1}): 3201, 1612, 1560, 1500, 1278, 1247.

^1H NMR (CDCl_3 , δ): 2.15 (s, 18H, HMB), 4.41 (s, 2H, HMP), 6.55 (s, 1H, HMP), 7.62 (s, 1H, HMP).

^{13}C (CDCl_3 , δ): 15.59 (s, Me, HMB), 60.90 (s, CH_2 , CH_2OH) 89.75 (s, C, HMB ring), 107.75 (s, CH, HMP) 140.72 (s, CH-O, HMP), 159.73 (s, C=CH, HMP), 166.08 (s, C-O), 185.69 (s, C=O).

2.2.3. Synthesis of $[\{\eta^6\text{-C}_6\text{H}_6\}\text{Ru}(\text{HMP})\text{Cl}]$ (**3**)

A mixture of HMP (0.06 g, 0.42 mmol) and NaOMe (0.023 g, 0.43 mmol) was stirred at room temperature for 30 min. To this stirring solution, complex $[\{\eta^6\text{-C}_6\text{H}_6\}\text{RuCl}_2]_2$ (0.1g, 0.19 mmol) was added and reaction further stirred for another 4 hrs. During this time the brown suspension became clear and bright orange solid precipitated out. The orange solid was collected washed with cold methanol (2 x10 ml) and diethyl ether (2x10 ml) then dried under vacuum. Additional compound was recovered by concentrating the mother solution.

Overall yield: 0.083g (98%).

FTIR (KBr, cm^{-1}): 3058, 1602, 1550, 1504.

^1H NMR ($\text{MeOD-}d_4$, δ): 4.42 (s, 2H, HMP) 5.77 (s, 6H, C_6H_6), 6.70 (s, 1H, HMP), 7.81 (s, 1H, HMP).

2.2.4. Synthesis of $[\{\eta^6\text{-}p\text{-cymene}\}\text{Ru}(\mu\text{N}_3)\text{N}_3]_2$ (**4**)

A mixture of complex **1** (0.1g, 0.229 mmol), NaN_3 (0.031g, 0.480 mmol) and EtOH (20 ml) was stirred for 3hrs at room temperature. After which the solvent was rotary evaporated and the residue was extracted with dichloromethane then filtered. The filtrate on concentration to ca 3 ml and addition of excess diethyl ether afforded red crystals of complex **4** after leaving overnight at room temperature.

Yield: 0.056g (54%).

IR (KBr, cm^{-1}): 2057 (νN_3), 2034, (νN_3).

^1H NMR (CDCl_3 , δ): 1.33 (d, 12H, $J_{\text{H-H}} = 6.9$), 2.29 (s, 6H), 2.87 (qt, 2H), 5.24 (d, 4H, $J_{\text{H-H}} = 5.1$), 5.49 (d, 4H, $J_{\text{H-H}} = 6.8$).

2.2.5. Synthesis of $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\mu\text{N}_3)\text{N}_3]_2$ (**5**)

This complex was synthesised by following a similar method as described for complex **4** using complex **2** (0.04 g, 0.09 mmol) and NaN_3 (0.012 g, 0.18 mmol).

Yield: 0.025 g (81%).

IR (KBr, cm^{-1}): 2061 (νN_3), 2025, (νN_3).

^1H NMR (CDCl_3 , δ): 2.07 (s, 36H, HMB).

2.2.6. Synthesis of $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu\text{N}_3)\text{Cl}]_2$ (**6**)

A mixture of $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{HMP})\text{Cl}]$ (0.04g, 0.084 mmol) and NaN_3 (0.016 g, 0.17 mmol) were stirred in 30 ml of ethanol for 5 hrs. The colour of the solution turned into dark red as the reaction progress. After stirring for 5 hrs, the solvent was rotary evaporated and the brown solid was washed with methanol then hexane (2x10 ml) and dried under vacuum.

IR (KBr, cm^{-1}): 2056 cm^{-1} .

^1H NMR ($\text{DMSO-}d_6$, δ): 5.78 (s, 12H, C_6H_6).

2.2.7. Synthesis of $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{HMP})\text{N}_3]$ (**7**)

A mixture of HMP (0.024 g, 0.169 mmol), NaOMe (0.01g, 0.185 mmol) and methanol (20 ml) were stirred at room temperature for 10 minutes. To this solution complex $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{Cl}]_2$ (0.052 g, 0.083 mmol) was added then the reaction mixture was stirred at room temperature for 6 hrs. Initially orange suspension turned bright red in colour as the reaction progress. The solution was rotary-evaporated and the residue was dissolved in CH_2Cl_2 then filtered through a silica gel bed. The filtrate was concentrated to ca 3 ml and excess diethyl ether was added. The red crystal of complex **7** was separated when the solution allowed to kept overnight under fridge. The crystal was collected, washed with hexane (2x10 ml) and dried under vacuum.

Yield: 0.0512g (74%).

IR (KBr, cm^{-1}): 3292, 2032, (νN_3); 1602 (C-O), 1560, 1500 (C=O).

^1H NMR (CDCl_3 , δ): 1.33 (d, 6H, CHMe_2 , $J_{\text{H-H}} = 6.9$), 2.29 (s, 3H, Me), 2.87 (qt, 1H, CH, CHMe_2), 4.46 (s, 2H, $-\text{CH}_2\text{OH}$), 5.52 (d, 2H, cymene ring), 5.49 (d, 2H, cymene ring), 6.62 (s, 1H), 7.68 (s, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR: 17.92 (s, Me), 22.30 (s, Me, CHMe_2) 30.95 (d, CH, CHMe_2), 60.86 (s, CH_2 , HMP), 78.58 (s, C, cymene ring), 80.11 (d, C, cymene ring), 95.07 (s, C, CMe), 99.46 (s, C, CPr^i), 107.66 (s, CH, HMP), 141.32 (s, CH-O, HMP), 159.36 (s, C=CH, HMP), 167.32 (s, C-O, HMP), 185.71 (s, C=O, HMP).

2.2.8. Synthesis of $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{HMP})\text{N}_3]$ (**8**)

To a suspension of HMP (0.048g, 0.34 mmol) and NaOMe (0.02g, 0.34 mmol) was added complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\mu\text{N}_3)\text{Cl}]_2$ (0.1g, 0.15 mmol). The mixture was stirred at room temperature for 6 hrs. As the reaction proceed the yellow orange solution turned into a red and suspension became clear. The solution was evaporated to dryness and residue dissolved in Dichloromethane and filtered. The filtrate on subsequent concentration to ca 3 ml and addition of diethyl ether gave red crystals of complex.

Yield: 0.09g (66%).

IR (KBr, cm^{-1}): 2036, 1604, 1556, 1508, 1471, 1272.

^1H NMR (CDCl_3 , δ): 2.09 (m, 18H, Me), 4.39 (s, 2H), 6.27 (m, 1H), 6.61 (m, 1H).

2.2.9. Synthesis of $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{HMP})\text{N}_3]$ (**9**)

A mixture of kojic acid (0.023 g, 0.2 mmol), NaOMe (0.011g, 0.2 mmol) and $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu\text{N}_3)\text{Cl}]_2$ (0.05 g, 0.097 mmol) were stirred in MeOH (40 ml) for 10 hrs at room temperature. During the course of reaction the brown solid dissolved completely and solution turned into yellow orange colour. The solution was filtered to remove insoluble materials and volume was reduced to ca 3 ml under reduce pressure. Addition of excess diethyl ether to this solution causes precipitation of yellow solid. The yellow solid was centrifuged, washed with diethyl ether (2x10ml) and dried in vacuum.

Yield: 0.036g (51%).

FTIR (KBr, cm^{-1}): 2038, 1645, 1556, 1523, 1485.

^1H NMR (DMSO- d_6 , δ): 4.38 (s, 2H), 5.73 (s, 6H, C_6H_6), 6.85 (s, 1H, OH), 7.35 (s, 1H), 7.82 (s, 1H).

2.2.10. Synthesis of $[\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{HMP})\text{L}_1\}]^+ \{L_1 = \text{PyCN} (\mathbf{10a}), \text{DMAP} (\mathbf{10b})\}$

A mixture of complex **1** (0.05 g, 0.12 mmol) and AgBF_4 (0.030 g, 0.15mmol) suspended in acetone (30 ml) was stirred for 20 minutes and then filtered to remove the white precipitate of silver chloride. To this filtrate, ligand L_1 (0.24 mmol) was added and the mixture was stirred for 3 hrs then insoluble material was filtered off. The solvent was evaporated to dryness under reduce pressure and residue was dissolved in dichloromethane then filtered through a short alumina bed. The filtrate on concentration to *ca* 3 ml and addition of excess hexane afforded a yellow solid. The yellow solid was washed with hexane (2x10 ml) and dried under vacuum.

Compound **10a**: Yield (0.036 g, 52%).

IR (KBr, cm^{-1}): 2239, 1685, 1602, 1548, 1060.

^1H NMR (DMSO- d_6 , δ): 1.32 (d, 6H, $J_{\text{H-H}} = 4.2$), 2.12 (s, 3H), 2.85 (sept., 1H), 4.36 (s, 2H), 5.64 (d, 2H, $J_{\text{H-H}} = 6.6$), 5.85 (d, 2H, $J_{\text{H-H}} = 5.8$), 6.72 (s, 1H), 7.87 (d, 2H, $J_{\text{H-H}} = 5.9$), 7.93 (s, 1H), 8.80 (d, 2H, $J_{\text{H-H}} = 6.6$).

Compound **10b**: Yield (0.042 g, 59%).

1.26 (s, 6H, CHMe_2 , cymene), 2.09 (s, 3H, CHMe , cymene), 2.83 (m, 1H), 3.03 (s, 6H, NMe_2 , DMAP), 4.47 (s, 2H, CH_2OH , HMP), 5.37 (s, 1H, OH), 5.52 (d, 2H, $J_{\text{H-H}} = 5.4$), 5.57 (d, 2H, $J_{\text{H-H}} = 5.7$), 5.79 (d, 1H, $J_{\text{H-H}} = 5.7$, DMAP), 6.50 (s, 1H, HMP), 6.74 (s, 1H, HMP), 7.63 (s, 1H, HMP), 7.81 (d, 1H, $J_{\text{H-H}} = 6.6$, DMAP), 8.39 (d, 1H, $J_{\text{H-H}} = 6.9$, DMAP).

2.2.11. Synthesis of $[\{(\eta^6\text{-HMB})\text{Ru}(\text{HMP})\text{L}_1\}]^+ \{L_1 = \text{PyCN} (\mathbf{11a}), \text{DAMP} (\mathbf{11b})\}$

These complexes were prepared by following a similar method described above using complex **2** (0.05 g, 0.11mmol), AgBF_4 (0.022 g, 0.11mmol) and ligand L (0.22 mmol).

Complex **11a**: Yield (0.048 g, 71%).

¹HNMR (CDCl₃, δ): 2.09 (s, 18H, HMB), 4.39 (s, 2H, HMP), 6.73 (s, 1H, HMP), 7.63 (s, 1H, HMP), 7.75 (d, 2H, PyCN, *J*_{H-H} = 6.3), 8.53 (d, 2H, PyCN, *J*_{H-H} = 5.4).

Complex **11b**: Yield (0.063 g, 91%).

¹HNMR (CDCl₃, δ): 2.07 (s, 18H, HMB), 3.04 (s, 6H, NMe₂), 4.41 (s, 2H, HMP), 6.49 (d, 2H, *J*_{H-H} = 6.9, DMAP), 6.69 (s, 1H, HMP), 7.57 (s, 1H, HMP), 7.60 (d, 1H, *J*_{H-H} = 6.9, DMAP), 8.33 (d, 1H, *J*_{H-H} = 7.2, DMAP).

2.2.12. Synthesis of [$\{\{\eta^6\text{-}p\text{-cymene}\}\text{Ru}(\text{HMP})\}_2(\mu\text{-}L_2)]^{2+}$ $\{L_2 = 4,4\text{-bipy} (\mathbf{12a}), \text{pyrazine} (\mathbf{12b})\}$

A mixture of complex **1** (0.025g, 0.057 mmol) and AgBF₄ (0.022 g, 0.114 mmol) in acetone (20 ml) was stirred for 30 min. The white precipitate of AgCl formed was filtered off and then the mixture was stirred for 10 hrs after adding the appropriate ligand, L₂ (0.025 mmol). The solvent was rotary-evaporated and the residue was dissolved in dichloromethane then filtered through a short silica gel bed. Addition of excess diethyl ether to this filtrate afforded a yellow solid that was washed with hexane (2x10ml) and dried under vacuum.

Compound **12a**: Yield (0.022 g, 68%).

¹HNMR (DMSO-d₆, δ): 1.24 (t, 12H, *J*_{H-H} = 4.2, Me), 2.03 (s, 6H, Me), 2.83 (m, 2H), 4.24 (s, 4H), 5.7 (br, 2H, OH), 5.93 (d, 4H, *J*_{H-H} = 5.7), 5.98 (d, 4H, *J*_{H-H} = 5.7), 6.65 (s, 2H), 8.00 (s, 2H), 8.10 (s, 4H), 8.61 (d, 4H, *J*_{H-H} = 6).

Compound **12b**: Yield (16 mg, 53%).

¹HNMR (CDCl₃, δ): 1.27 (m, 12H, Me), 2.12 (s, 6H, Me), 2.84 (m, 2H), 4.39 (s, 4H), 5.53 (m, 4H), 5.64 (m, 4H), 6.76 (s, 2H), 6.84 (s, 2H), 7.65 (s, 2H), 8.50 (s, 2H).

2.2.13. Synthesis of [$\{\{\eta^6\text{-HMB}\}\text{Ru}(\text{HMP})\}_2(\mu\text{-}L_2)]^{2+}$ $\{L_2 = 4,4\text{-bipy} (\mathbf{13a}), \text{pyrazine} (\mathbf{13b})\}$

These complexes were prepared by following similar method described above using complex **2** (0.057g, 0.13 mmol) and AgBF₄ (0.026g, 0.13 mmol).

Compound **13a**: Yield (0.041g, 56%).

IR(KBr, cm⁻¹): 1602, 1550, 1492, 1473, 1080.

¹HNMR (MeOD-*d*₄, δ): 2.13 (d, 36H, HMB, *J*_{H-H} = 11), 4.32 (s, 4H), 6.66 (s, 2H), 7.83 (s, 2H), 7.92 (s, 4H), 8.51 (d, 4H, *J*_{H-H} = 4.2).

Compound **13b**: Yield (0.035 g, 51%).

¹HNMR (CDCl₃, δ): 2.07 (s, 36H, HMB), 4.35 (s, 4H, HMP), 6.75 (s, 2H, HMP), 7.69 (s, 2H, HMP), 8.25 (d, 2H, *pz*, *J*_{HH} = 4.6), 8.50 (br, 2H, *pz*).

Caution: (η⁶-benzene)ruthenium azide dimer is highly explosive in dried condition. Preparation of this complex on large scale should be avoided.

3. Structure analysis and refinement

The X-ray intensity data were measured at 293(2)° K on a Bruker Apex II CCD area detector employing graphite monochromator using Mo-Kα radiation (λ=0.71073 Å). An empirical absorption correction was made by modeling a transmission surface by spherical harmonics employing equivalent reflections with $I > 2\sigma(I)$ (program **SADBAS**) [29]. The structures were solved by direct methods (**SHELXS 97**) [30] and refined by full matrix least squares base on F^2 using (**SHELXL-97**) [31] softwares. The weighting scheme used was $W=1/[\sigma^2(F_0^2)+ 0.0311P^2 + 3.5016 P]$ where $P = (F_0^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a “riding” model. Refinement converged at a final $R = 0.0385$, 0.0315 and 0.0583 (for complexes **1**, **4** and **8** respectively, for observed data F^2), and $wR_2 = 0.0427$, 0.0430 and 0.1267 (for complexes **1**, **4** and **8** respectively, for unique data F^2). Molecular structures of the compounds are shown in Figures 1-3. Selected bond lengths and angles are tabulated in Tables 1-3. Details of crystallographic data collection parameters and refinement are summarized in Table 4.

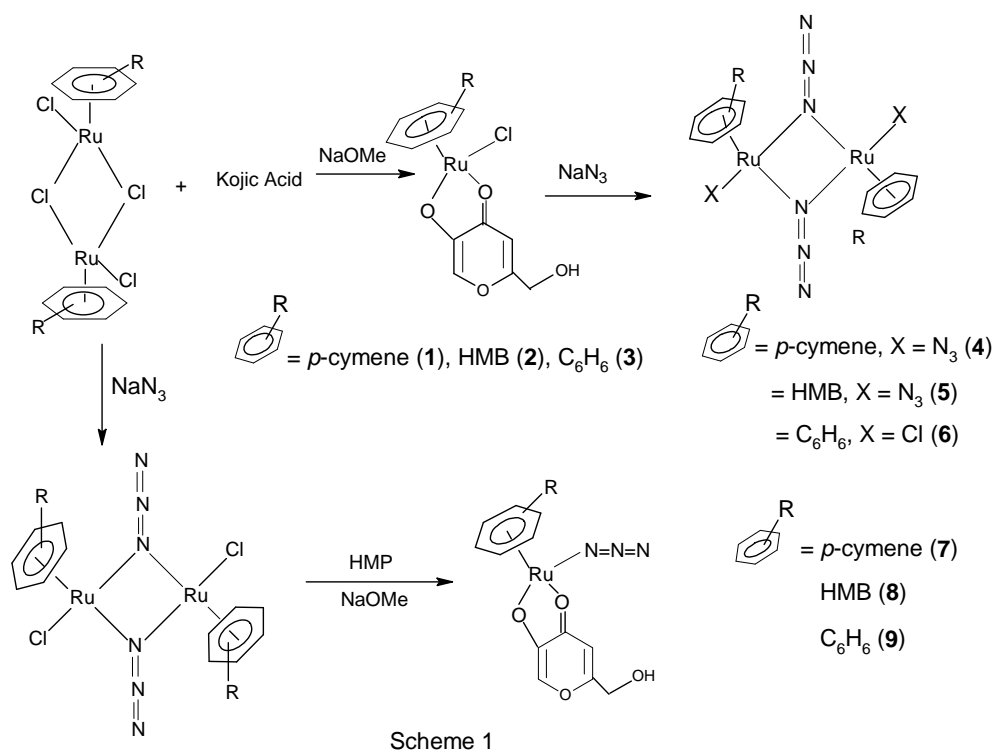
4. Results and discussion

4.1. Neutral complexes

The reaction of [$\{(\eta^6\text{-arene})\text{RuCl}_2\}_2$] with two equivalents of HMP in the presence of NaOMe yielded a series of water soluble complexes of formulation [$\{(\eta^6\text{-arene})\text{Ru}(\text{HMP})\text{Cl}\}(\eta^6\text{-$

arene = *p*-cymene, **1**; HMB, **2**; C₆H₆, **3**) in good yield (Scheme 1). The complexes were characterized on the basis of FTIR, ¹H and partly by ¹³C NMR spectroscopic data. ¹H NMR spectrum of complex **1** exhibited resonance for isopropyl proton as two doublets at δ 1.31 which could be due to loss of planarity. In addition to the *p*-cymene ring protons at δ 5.30 and 5.51, the spectrum also displayed two singlets at δ 6.63 and 7.66 due to alkene protons of HMP ligand. The methylene proton (-CH₂OH) of HMP appeared as a single resonance at δ 4.41. In the case of complexes **2** and **3** a singlet resonance were observed at δ 2.15 and 5.77 assignable to the protons of HMB and C₆H₆ groups, respectively. The ¹³C {¹H} NMR spectrum of **1** displayed fourteen distinct signals with olefinic quaternary carbon appeared at δ 159.4 while oxy-quaternary carbon (C-O) and C=O appeared at δ 167.4 and 185.8, respectively. The IR spectrum of these complexes showed absorption band due to C=O stretching frequency at around 1602 cm⁻¹. In addition to C=O stretching frequencies, the IR spectra also showed a pair of strong bands in the region 1502-1562 cm⁻¹ assignable to coupled C=O + C=C mode of vibrations [32, 33]. Complex **1** was finally characterized by X-ray crystallography, it crystallises in *P21/c* space group in monoclinic unit cell and consists of 8 molecules per unit cell of which two independent molecules are shown in figure 1. The distance between centroid of the ring and ruthenium for molecule A is 1.641 Å while for molecule B is 1.648 Å. The structure showed shorter bond distance of C16-O2 (1.261 Å) as compared to C11-O1 (1.324 Å) suggesting significant localization of double bond electron at C16-O2. This indicates that double bond is localised at C16-O2 and there is no extent of delocalisation of double bond to C11-O1.

We have recently synthesized azide complex such as [[{(η^6 -*p*-cymene)Ru(O,O'-diketonate)N₃}] by reacting the complex [{(η^6 -*p*-cymene)Ru(O,O-diketonate)Cl}] with NaN₃ [20]. However, in this present work, treatment of [{(η^6 -arene)Ru(HMP)Cl}] with NaN₃ did not yield complex [{(η^6 -arene)Ru(HMP)N₃}] instead, an unexpected azido ruthenium complexes [{(η^6 -arene)Ru(μ N₃)N₃}₂] (η^6 -arene = *p*-cymene (**4**), HMB (**5**)) were obtained while the analogous benzene complex invariably yielded only disubstituted azido complex [{(η^6 -C₆H₆)Ru(μ N₃)Cl}]₂ (**6**) [34] (Scheme 1).



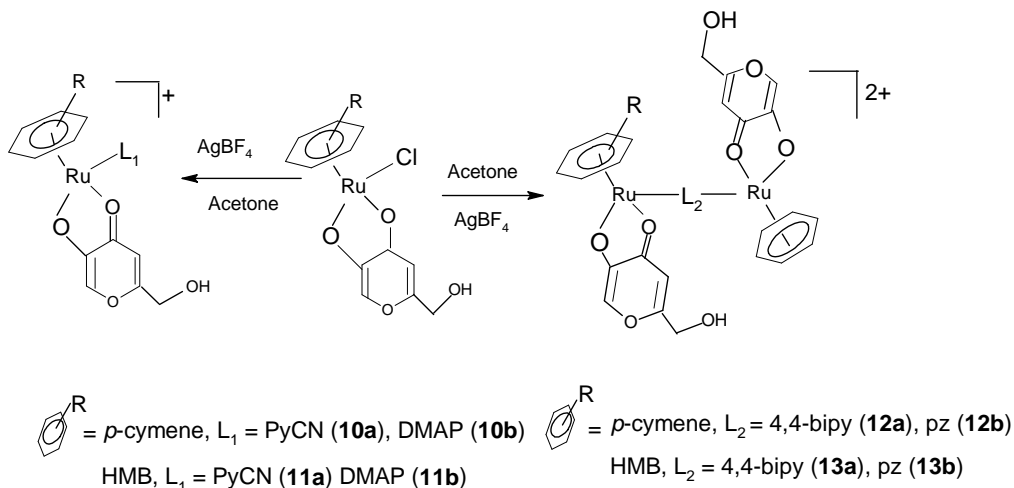
It is noteworthy that the reaction of $[\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2\}_2]$ with NaN_3 or SiMeN_3 afforded compound of the type $[\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\mu\text{N}_3)(\text{Cl})\}_2]$ irrespective of the stoichiometric ratio of the azide ligand used [27,28] but did not yield the complex $[\{(p\text{-cymene})\text{Ru}(\mu\text{N}_3)(\text{N}_3)\}_2]$ (**4**). However, under similar reaction condition analogous $[\{(\eta^6\text{-HMB})\text{RuCl}_2\}_2]$ yielded both $[\{(\eta^6\text{-HMB})\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2]$ and $[\{(\eta^6\text{-HMB})\text{Ru}(\mu\text{N}_3)\text{N}_3\}_2]$ (**5**) depending on the stoichiometric ratio of the sodium azide used [28]. We believed that, complexes **4** and **5** were resulted by displacement of HMP with azide and HMP regenerated as its sodium salt. The formation of complexes **4** and **5** were supported by the appearance of absorption bands at 2034 cm^{-1} and 2057 cm^{-1} for complex **4** and 2025 cm^{-1} and 2061 cm^{-1} for complex **5** in their IR spectrum corresponding to absorption band for terminal and bridged azide groups, respectively. This leads to confirmation of molecular composition $[\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{N}_3\}_2]$ (**4**) and $[\{(\eta^6\text{-HMB})\text{Ru}(\mu\text{N}_3)\text{N}_3\}_2]$ (**5**) having both terminal and bridged azide ligands. The IR spectrum of complex **6** showed a strong absorption band at 2056 cm^{-1} due to bridge νN_3 group but no absorption band corresponding to terminal azide group, consistent with molecular composition $[\{(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2]$. To the best of our knowledge complex **4** represent the first example of tetra-azido *p*-cymene ruthenium (II) complex. Solid state structure of complex **4** has been determined by single X-ray analysis (figure 2). The complex crystallizes in *P1* space group in a

triclinic crystal system. The distance between centroid of *p*-cymene ring and ruthenium are 1.562 Å and 1.759 Å, respectively. The molecule adopt the well known piano stool structure where the bond angle N11-RuA1- N11A around the ruthenium atom is 85.4(3)°, which is a little higher than the analogous HMB compound [28]. The Ru-N bond distances of 2.128 (7) Å for RuA1-N11A and 2.214 (6) Å for RuA1-N21 are comparable with the reported Ru-N bond distances [35]. The N-N bond distances in terminal azide are N11A-N12A (1.219(10)Å) and N12A-N13A (1.062(11)Å), respectively which is slightly shorter than the bridging N-N azide bond distances, N11-N12 (1.244(8)Å) and N12-N13 (1.159(10) Å).

We have been interested on the synthesis of terminal azide complex of formulation [$\{(\eta^6\text{-arene})\text{Ru}(\text{HMP})(\text{N}_3)\}$]. Preparation of these complexes were achieved by azide bridged cleavage reaction of [$\{(\eta^6\text{-arene})\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2$] with HMP ligand. Thus, reaction of [$\{(\eta^6\text{-arene})\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2$] with two folds excess of HMP in the presence of NaOMe afforded the desire complexes [$(\eta^6\text{-arene})\text{Ru}(\text{HMP})\text{N}_3$] { $\eta^6\text{-arene}$ = cymene (**7**), HMB (**8**), C₆H₆ (**9**)} in high yield (Scheme 1). However, in the absence of NaOMe the reaction did not undergo even by allowing a longer reaction time. The complexes were isolated as red crystalline solid, soluble in water and stable at room temperature. Formation of these complexes follows from the lack of absorption bands at 2057, 2068 and 2056 cm⁻¹ corresponding to bridging azide group for the starting $\eta^6\text{-p-cymene}$, $\eta^6\text{-HMB}$ or $\eta^6\text{-C}_6\text{H}_6$ azide complexes, respectively and appearance of bands at 2032, 2036 and 2038 cm⁻¹ for complexes **7**, **8** and **9** respectively, corresponding to terminal νN_3 . The ¹H NMR spectrum of complexes **7-9** showed two singlets in the region of δ 6.62-7.68 due to methine proton of HMP ligand, whereas methylene proton of HMP ligand appeared at around δ 4.46. Notably, the presence of HMP ligand provides versatile water soluble properties to these complexes. We observed that coordination of HMP ligand to ($\eta^6\text{-arene}$) ruthenium complexes makes the compound water soluble irrespective of the arene moiety present. The azide complexes **7-9** were characterized with spectroscopic data and the solid state structure of complex **8** has been determined by X-ray crystallography (figure 3). Complex **8** crystallizes in *P-1* space group in a triclinic crystal system. The geometry around the ruthenium atom can be regarded as octahedral, in which three coordination sites were occupied by $\eta^6\text{-HMB}$, two by the HMP ligand and one by azide ligand (figure 3). The complex adopted the well known piano stool structure where the bond angle O1-Ru-O2 around the Ru is 79.5(2)°. The Ru1-N1 bond distance (2.113 (4) Å) is comparable to that of Ru-N bond length of complex **4** and the values fall within the usual range of Ru-N bond length [35].

4.2. Cationic complexes

The reaction of complexes **1** and **2** with monodentate neutral ligand in the presence of halide scavengers such as AgBF_4 afforded mono-nuclear complexes **10-11** (Scheme 2). Similarly, dinuclear compounds **12-13** were prepared by treating complexes **1** and **2** with the corresponding ligand (Scheme 2). The complexes were soluble in water and isolated as their tetrafluoroborate salts in moderate to high yield. The spectroscopic data are in agreement with the formulation of these complexes. ^1H NMR spectrum of complexes (**10a-10b**) displayed two singlets at δ 7.57 and 6.69 attributed to the olefinic methine (CH) of HMP while methylene group of HMP ligand appeared as singlet at δ 4.41. In the case of complex (**10a**), a resonance was observed in the aromatic region in the range of δ 8.33-7.81 attributed to the DMAP ligand while methyl protons of DMAP attached to the nitrogen was appeared as singlet at δ 3.04. The *p*-cymene signals are well resolved and exhibit only H-H coupling. The *p*-cymene ring protons appeared as two sets of doublet at around δ 5.6 and 5.8 while a septet is observed for H-CMe_2 at δ 2.83 as observed in other *p*-cymene complexes.



Scheme 2

^1H NMR spectrum of **12a** & **13a** showed single resonances at δ 4.24, 6.65 and 8.00 due to the HMP ligand. In the case of complex **12a** a singlet is also observed at δ 5.70 assignable to the OH group of HMP ligand.

Table 1: Selected bond lengths (Å) and bond angles (°) for complex **1** with estimated standard deviations (esd's) in parenthesis.

	Molecule A	Molecule B
<i>Bond lengths (Å)</i>		
Ru-Cent	1.641	1.648
Ru-Cl	2.412 (3)	2.418 (3)
Ru-O1	2.118 (7)	2.173 (7)
Ru-O2	2.124 (8)	2.129 (7)
C17-O3	1.363 (12)	1.435 (11)
C14-O13	1.3900	1.3900
C16-O2	1.261(8)	1.277(8)
C11-O1	1.324(8)	1.339(8)
<i>Bond angles (°)</i>		
O1-Ru-O2	79.1 (3)	78.7 (3)
O1-Ru-Cl	85.8 (2)	85.5 (2)
Ru-O2-C16	111.6 (5)	110.9 (5)
Ru-O1-C11	107.6 (5)	108.7 (5)

Table 2: Selected bond lengths (Å) and bond angles (°) for complex **4** with estimated standard deviations (esd's) in parenthesis.

<i>Bond lengths (Å)</i>			
Ru1-Cent	1.562	Ru2-Cent	1.729
N11-N12	1.244 (8)	N12-N13	1.159 (10)
N11B-N12B	1.144 (10)	N12B-N13B	1.260 (11)
Ru1A-N21	2.214 (6)	Ru1B-N21	2.164 (6)
Ru1A-N11	2.123 (5)	Ru1B-N11	2.113 (5)
<i>Bond angles (°)</i>			
Ru1A-N21-Ru1B	102.4 (3)	Ru1B-N11-Ru1A	107.3 (2)
N21-Ru1A-N11	83.9 (3)	N11-Ru1B-N21	75.8 (2)

Table 3: Selected bond lengths (Å) and bond angles (°) for complex **8** with estimated standard deviations (esd's) in parenthesis.

<i>Bond lengths (Å)</i>			
Ru1-Cent	1.644		
Ru1-N1	2.113 (5)	N1-N2	1.176 (7)
N2-N3	1.163 (7)	C18-O4	1.300 (14)
Ru1-O1	2.105 (5)	Ru1-O2	2.108 (4)
<i>Bond angles (°)</i>			
O1-Ru1-O2	79.5 (2)	O1-Ru1-N1	85.9 (2)
N1-Ru1-O2	85.70 (18)	C17-C18-O4	113.2 (8)

Table 4: Summary of crystal structure determination and refinement parameters for complexes **1**, **4** and **8**.

	1	4	8
Empirical formula	C ₁₆ H ₁₉ ClO ₄ Ru	C ₂₀ H ₂₈ N ₁₂ Ru ₂	C ₁₈ H ₂₃ N ₃ O ₄ Ru
Formula weight	411.83	638.68	446.46
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Triclinic	Triclinic
Space group	<i>P21/c</i>	<i>P1</i>	<i>P-1</i>
<i>Unit cell dimensions</i>			
a (Å)	10.872(2)	8.2082(9)	9.0285(10)
b (Å)	14.255(3)	8.2204(8)	9.5758(11)
c (Å)	23.107(5)	10.0122(11)	12.0705(15)
α (°)	90	83.216(9)	76.176(9)
β (°)	113.08(3)	82.420(9)	76.975(9)
γ (°)	90	77.217(8)	67.634(9)
Volume (Å ³)	3294.2(12)	650.30(12)	926.53(19)
Z	8	1	2
Density (calculated) (Mg/m ³)	1.661	1.631	1.600
Absorption coefficient (mm ⁻¹)	1.128	1.194	0.874
F(000)	1664	320	456
Crystal size (mm ³)	0.08 x 0.10 x 0.22	0.20 x 0.28 x 0.39	0.30 x 0.24 x 0.15
θ range for data collection (°)	1.72 to 24.64	2.06 to 29.11	1.76 to 29.19
Index ranges	$-12 \leq h \leq 12$ $-16 \leq k \leq 16$ $-27 \leq \ell \leq 27$	$-11 \leq h \leq 11$ $-11 \leq k \leq 11$ $-13 \leq \ell \leq 13$	$-12 \leq h \leq 12$ $-13 \leq k \leq 13$ $-16 \leq \ell \leq 16$
Reflections collected	32007	12035	16451
Independent reflections [R _{int}]	5530 [0.1895]	6519 [0.0363]	4937 [0.0748]
Completeness to θ (%)	24.64 - 99.5	29.11-99.6	29.19-98.2

Absorption correction	Numerical		
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/ parameters	5530 / 0 / 363	6519 / 3 / 289	4937 / 0 / 230
Goodness-of-fit on F^2	0.534	0.769	0.887
Final R indices	$R_1 = 0.0385$	$R_1 = 0.0315$	0.0583
$[I > 2\sigma(I)]$	$wR_2 = 0.0427$	$wR_2 = 0.0430$	$wR_2 = 0.1267$
R indices (all data)	$R_1 = 0.1907$ $wR_2 = 0.0631$	$R_1 = 0.0669$ $wR_2 = 0.0469$	$R_1 = 0.1152$ $wR_2 = 0.1438$
Largest diff. peak and hole ($e \text{ \AA}^{-3}$)	0.717 and -0.479	0.779 and -0.718	1.470 and -1.187

5. Concluding remarks

This paper described, synthesis of a series of water soluble (η^6 -arene) ruthenium (II) complexes containing marine derived bio-ligand. Reaction of [$\{(\eta^6\text{-arene})\text{RuCl}\}_2$] with HMP gave complexes **1-3** while reaction of HMP with [$\{(\eta^6\text{-arene})\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2$] afforded azido complexes **7-9**. We also described, reaction of [$(\eta^6\text{-arene})\text{Ru}(\text{HMP})\text{Cl}$] ($\eta^6\text{-arene} = \eta^6\text{-cymene}$, **1**; $\eta^6\text{-HMB}$, **2**; $\eta^6\text{-C}_6\text{H}_6$, **3**) with sodium azide. The former two yielded tetra azido dimeric complexes **4& 5** while the later gives only di-azido dimeric complex **6**. The complexes **1** and **2** undergo substitution reaction with mono- or bidentate ligands to yield monomeric (**10a-11b**) and dimeric complexes (**12a-13b**). Whereas the azido complex [$(\eta^6\text{-arene})\text{Ru}(\text{HMP})(\text{N}_3)$] undergo 1,3-dipolar cycloaddition reaction with acetylenes to yield η^6 -arene ruthenium triazole complexes. This work is currently under progress in our laboratory.

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Supplementary Materials

CCDC 702211, 702212 and 716745 contain the supplementary Crystallographic data for complexes **1**, **4** and **8**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk> or email: deposit@ccdc.cam.ac.uk.

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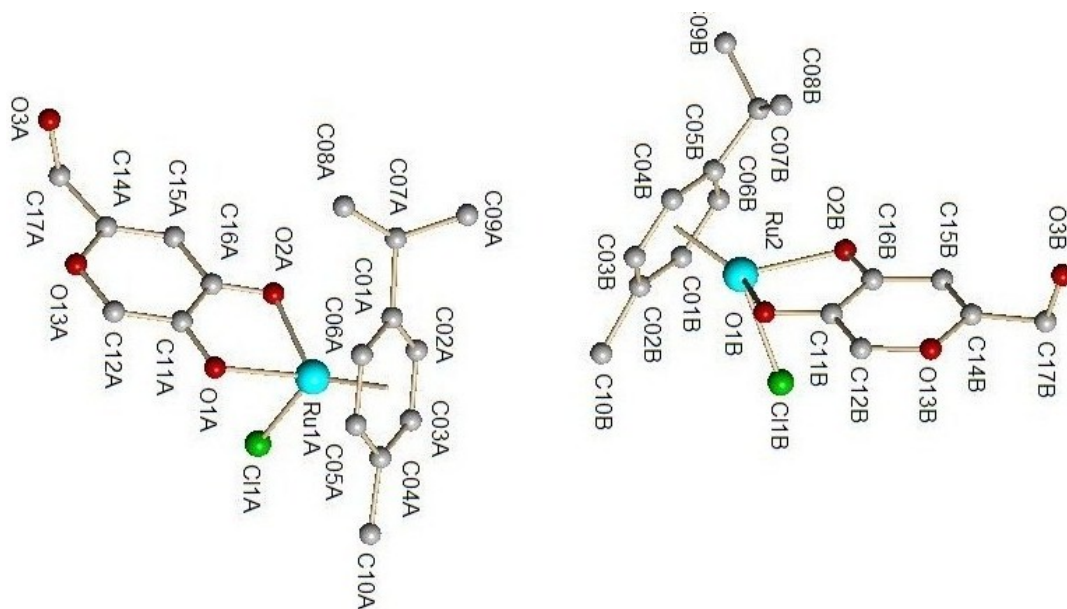


Figure 1. Molecular structure of complex **1** showing two independent molecule A and molecule B. All hydrogen atoms have been omitted for clarity.

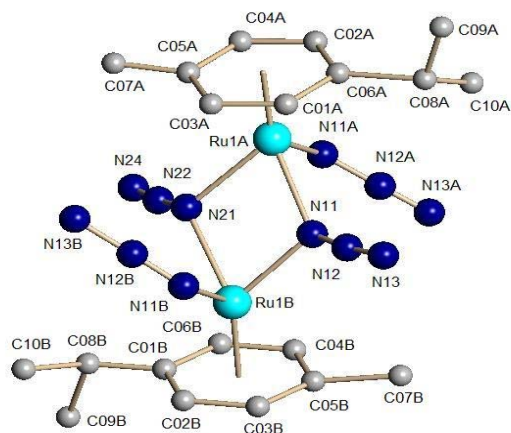


Figure 2: Molecular structure of complex **4**. All hydrogen atoms have been omitted for clarity.

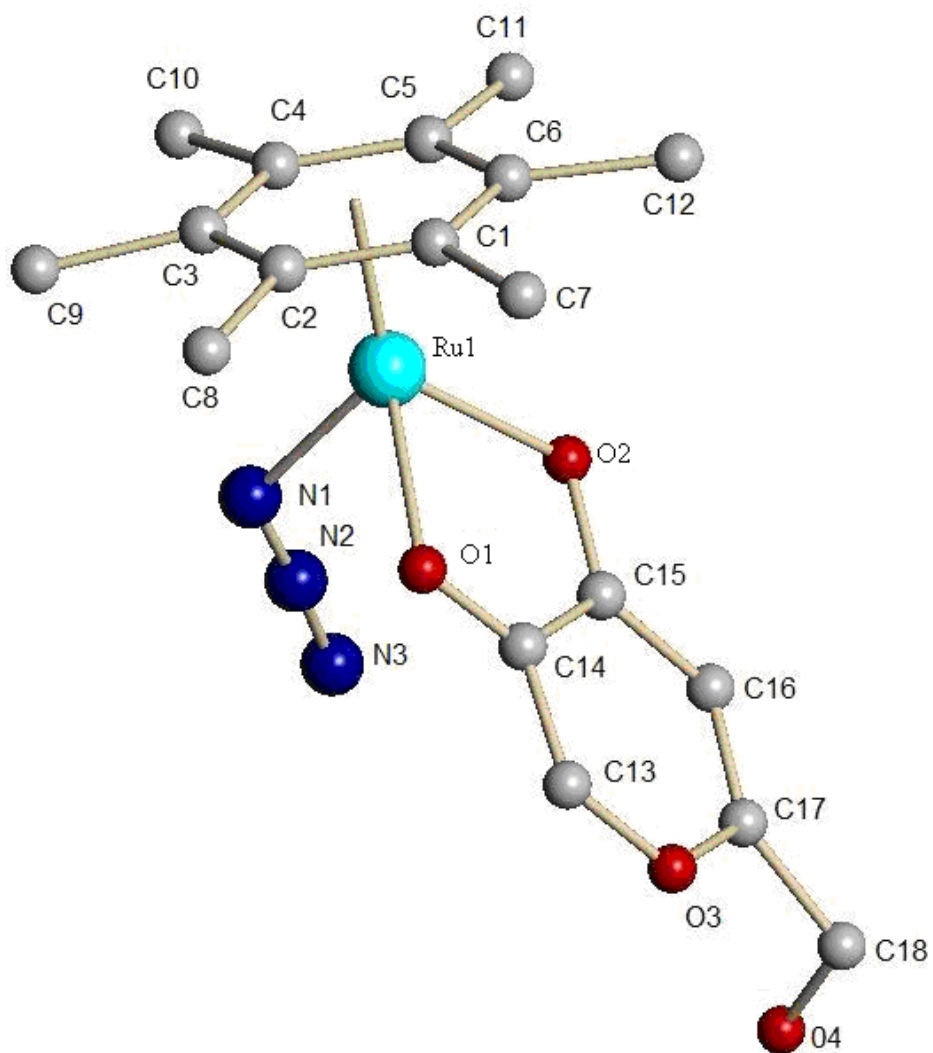


Figure 3: Molecular structure of complex **8**. All hydrogen atoms have been omitted for clarity.