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Study of η^6- cyclic π-perimeter hydrocarbon ruthenium complexes bearing functionalized pyridyl diketones: Isolation of complexes with κ^2-N∩O and κ^4-N∩O bonding modes of ligands

SAPHIDABHA L NONGBRI[a], BABULAL DAS[b] and MOHAN RAO KOLLIPARA[a,*]

[a]Department of Chemistry, North Eastern Hill University, Shillong 793 022, India
[b]Department of Chemistry, Indian Institute of Technology, Guwahati 781 039, India
e-mail: mohanrao59@gmail.com

Abstract. Chelating mono- and di-pyridyl functionalized β-diketones, viz. 1-phenyl-3-(2-pyridyl) propane-1,3-dione (*pppdH*) and 1,3-di(2-pyridyl)propane-1,3-dione (*dppdH*) ligands yielded new water soluble η^6-arene ruthenium(II) complexes of the formulation $[(\eta^6\text{-arene})Ru(\kappa^2\text{-N-O-}pppdH)Cl]^+$ (arene = C_6H_6 **1**, p-^{i}PrC_6H_4Me **2**, C_6Me_6 **3**) and $[(\eta^6\text{-arene})_2Ru_2(\kappa^4\text{-N-O-}dppd)Cl_2]^+$ (arene = C_6H_6 **4**, *p*-^{i}PrC_6H_4Me **5**, C_6Me_6 **6**), as their (complexes **1**–**4**, **6**) PF_6 salt or (complex **5**) BF_4 salt. The complexes were obtained by treatment of respective precursors, $[(\eta^6\text{-arene})Ru(\mu\text{-Cl})Cl]_2$ (arene = C_6H_6, p-^{i}PrC_6H_4Me, C_6Me_6) in 1:2 and 1:1 molar ratio with *pppdH* and *dppdH* in the presence of NH_4PF_6/NH_4BF_4. All the complexes have been characterized on the basis of FT-IR and NMR spectroscopic data as well as by elemental analysis. Molecular structures of representative complexes **2**, **5** and **6** have been confirmed by single crystal X-ray diffraction studies. The '*O*–*C*–*C*–*C*–*O*' fragment of the coordinated ligand (*pppdH*) is neutral in complexes **1**–**3** and that of the *dppdH* ligand existed as a neutral as well as concomitantly uninegative fashion in complexes **4**–**6** due to the delocalization of π-electrons.

Keywords. 1-Phenyl-3-(2-pyridyl)propane-1,3-dione; 1,3-di(2-pyridyl)propane-1,3-dione; ruthenium; arene.

1. Introduction

Within the large family of η^5- and η^6-cyclic-hydrocarbon metal complexes, piano stool complexes of ruthenium are undeniably the most studied classes of complexes. In particular, η^6-arene metal complexes have emerged as versatile intermediates in organic synthesis as a consequence of the ease with which the arene ligand can be functionalized.[1,2] The applications of half-sandwich η^6-arene ruthenium complexes are extensive, particularly in synthetic organic chemistry. These purely inorganic materials are extraordinarily robust and therefore well-suited as homogenous catalysts under mild conditions;[3] their catalytic activities range from hydrogen transfer[4] to ring closer metathesis.[5] They are also used as anti-cancer drugs,[6–8] and recently as building blocks in supramolecular chemistry.[9] The chemistry of half-sandwich η^5- and η^6-cyclichydrocarbon metal complexes containing N∩O ligands have been developed; a series of arene ruthenium(II) oxinato complexes,[10,11] mononuclear and dinuclear pyrazine carboxylate complexes incorporating [Cp*M(III)] (M = Ir, Rh) or $(\eta^6$-arene)Ru(II) fragments[12] and arene ruthenium triazole complexes containing N∩O-bidentate ligand as the auxiliary ligand have been reported.[13] Extensive biological studies,[14,15] catalytic activities[11] and development of structural designs[16–20] have been carried out with arene ruthenium complexes of pyrazine carboxylate and 8-hydroxy quinoline ligands. The η^5- and η^6-cyclichydrocarbon metal complexes, in particular water-soluble complexes possessing N∩O ligand are reported to possess antitumour and anti-cancer activities[14] and also have been explored in biological studies[21] and catalytic hydrogenation.[11]

However, arene ruthenium(II) complexes bearing N, O- pyridyl functionalized diketones have not been reported so far to the best of our knowledge. The pyridine containing β-diketones were known in organic chemistry for a long time,[22] but hardly any report of their metal complexes in coordination chemistry[23–28] exists. Recently, Tamburini and co-workers[29] reviewed a series of metal complexes of functionalized β-diketones as ligands. The pyridine containing β-diketones evolved recently as ligands with the potential of exhibiting serendipitously a multitude of structural designs[30] arising from the delocalization of π-electrons and the presence of hetero donor atoms. Therefore, keeping in mind the potential of the pyridyl

*For correspondence

functionalized diketone ligand, we aim at synthesizing new η^6- cyclic hydrocarbon ruthenium complexes. The pyridyl β-diketones viz. 1-phenyl-3-(2-pyridyl) propane-1,3-dione (*pppdH*), 1,3-di(2-pyridyl)propane-1,3-dione (*dppdH*) ligand are used in this synthesis.

These new ruthenium N∩O pyridyl diketone complexes are interesting in their own rights from a synthetic and structural point of view. In addition, the complexes reported here are water soluble, which is an important criterion to study anticancer, antibiotic, antiviral, catalytic activities and also for biological research and applications.[11,14,15,21]

In this communication, we established the formation of new monomeric and dimeric N∩O bonded half-sandwich η^6-arene ruthenium complexes, and the interesting aspects of bonding, incorporated through the chelated mixed functional ligands. The successful synthetic application of this ligand and continuing research in these systems, the results demonstrate the utility and serendipitous nature of bonding attributed by the delocalization of π-electrons of the pyridyl diketone ligand when coordinated to half-sandwich η^6-arene ruthenium complexes.

2. Experimental

2.1 *Physical measurements*

All reactions were carried out under aerobic conditions using dried solvents. All solvents were dried using appropriate drying reagents and distilled. $RuCl_3.3H_2O$ purchased from Arora Mathey Ltd. and used as received. The ligands 1-phenyl-3-(2-pyridyl) propane-1,3-dione (*pppdH*)[31] and 1,3-di(2-pyridyl)propane-1,3-dione (*dppdH*)[32] were prepared using literature protocols. The NMR spectra were obtained using Bruker Avance II 400 spectrometer in acetone-d_6 at room temperature. Chemical shifts were reported as parts per million (ppm, δ) and ^{1}H chemical shifts referenced to TMS as an internal standard. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 983 spectrophotometer. Elemental analyses were performed in Perkin-Elmer-2400 CHNS analyzer.

2.2 *Single crystal X-ray structure analyses*

Crystals suitable for X-ray diffraction study for compounds **2**, **5** and **6** were obtained at room temperature by slow diffusion of non-polar solvent over dichloromethane solution of the corresponding complexes. Crystals of complexes $[(\eta^6\text{-}p\text{-}^i PrC_6H_4Me)Ru(\kappa^2\text{-N-O-}pppdH)Cl]$ **2**, $[(\eta^6\text{-}p\text{-}^i PrC_6H_4Me)_2Ru_2(\kappa^4\text{-N-O-}dppd)Cl_2]$ **5** and $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\kappa^4\text{-N-O-}dppd)Cl_2]$ **6** were mounted. X-ray intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo-Kα graphite monochromatic radiation at 296(2) K, with a 0.3° ω scan mode at a scan speed of 3 s/frame. The SMART[33] software was used for data acquisition. Data integration and reduction were undertaken with the SAINT[34] software. Structures were solved by direct methods using SHELXS-97[34] and refined with full-matrix least squares on F2 using SHELXL-97.[35] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3[36] for Windows. The data collection parameters are presented in table 1. Figures 1, 2 and 3 are the ORTEP representation of the molecules with 35% probability thermal ellipsoids displayed.

2.3 *Synthesis of complexes **1–3***

To a solution of 1 equivalent of the ligand *pppdH* (~ 0.06 mmol) in dry methanol, ½ equivalent of the corresponding starting dimer complexes $[(\eta^5\text{-arene})Ru(\mu\text{-}Cl)_2Cl_2]$ (arene = C_6H_6, $p-^i PrC_6H_4Me$, C_6Me_6) were added in the presence of NH_4PF_6. The resulting solution was stirred whereby compound started precipitating after ½ h, stirring was continued further to complete the reaction. The precipitate was centrifuged and was washed with hexane (2 × 2 ml) and diethyl ether. The filtrate was dried by rotary evaporator, the residue dissolved in dichloromethane (10 ml) and the solution filtered to remove ammonium chloride and excess ammonium salt. The solution was concentrated to 2 ml, whereupon addition of excess diethyl ether precipitated the additional complex, which was separated and dried under vacuum as crude product.

2.3a *Complex $[(\eta^6\text{-}C_6H_6)Ru(\kappa^2\text{-N-O-}pppdH)Cl]PF_6$ **1***: Colour: dark orange; Yield = 89 mg (81%). IR (KBr, cm^{-1}): 3423 $\nu_{(O-H)}$, 1613 $\nu_{(C=O)}$, 1573 $\nu_{(C-O)}$, 1460 $\nu_{(C-N\ aromatic)}$, 844 $\nu_{(P-F)}$. Elemental anal. (%) Calc. for $C_{20}H_{17}NO_2ClPF_6Ru$: C 41.07; H 2.93; N 2.39; found: C 41.13; H 2.85; N 2.41. ^{1}H NMR (Acetone d_6, δ in ppm): 6.24 (s, 6H, C_6H_6), 7.22 (s, 1H, α-CH), 7.57 (t,

Table 1. Crystallographic and structure refinement parameters for complexes, **2, 5** and **6**.

	2	**5**	**6**
Chemical formula	$C_{24}H_{25}NO_2ClPF_6Ru$	$C_{33}H_{37}N_2O_2Cl_2BF_4Ru_2$	$C_{37}H_{45}N_2O_2Cl_2PF_6Ru_2$
Formula weight	640.94	853.50	986.76
T (K)	296(2)	296(2)	296(2)
Λ (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n	$P2(1)/c$
Crystal colour and shape	Dark red block	Red block	Red plates
Crystal size (mm^3)	0.28 × 0.20 × 0.14	0.35 × 0.26 × 0.17	0.22 × 0.14 × 0.08
a (Å)	8.0712(2)	11.7622(6)	16.8576(5)
b (Å)	16.7797(4)	12.0629(6)	15.3785(5)
c (Å)	18.8626(4)	24.8443(13)	16.3180(5)
α (°)	90	90	90
β (°)	92.5360(10)	98.907(3)	110.336(2)
γ (°)	90	90	90
V ($Å^3$)	3482.6(3)	3482.6(3)	3966.7(2)
Z	4	4	4
D_c ($Mg.m^{-3}$)	1.668	1.628	1.652
μ (mm^{-1})	0.848	1.075	1.005
F(000)	1288	1712	1988
Scan range (°)	$1.62 < \theta < 28.38$	$1.66 < \theta < 25.00$	$1.85 < \theta < 25.00$
Index ranges	−10 <= h <= 10	−13 <= h <= 13	−20 <= h <= 19
	−22 <= k <= 19	−14 <= k <= 14	−15 <= k <= 18
	−25 <= l <= 25	−29 <= l <= 29	−19 <= l <= 19
Reflections collected	37261	45066	34437
Independent reflections (R_{int})	6346 (0.0623)	6114(0.0231)	6955 (0.0980)
Completeness to θ (%)	28.38–99.2	25.00–100.0	25.00–99.7
Absorption correction	None	None	None
Refinement method	Full-matrix least square on F^2	Full-matrix least square on F^2	Full-matrix least square on F^2
Data/restraints/parameters	6346/0/330	6114/0/421	6955/0/490
Goodness-of-fit on F^2	0.925	1.045	0.915
Final R indices [I>2σ(I)][a]	R1 = 0.0342	R1 = 0.0366	R1 = 0.0575
	wR2 = 0.0805	wR2 = 0.0996	wR2 = 0.1372
R indices (all data)	R1 = 0.0537	R1 = 0.0405	R1 = 0.1189
	wR2 = 0.0862	wR2 = 0.1031	wR2 = 0.1710
Max, Min Δρ/e ($Å^{-3}$)	0.569 and −0.735	1.034 and −0.795	0.679 and −0.633

[a]Structures were refined on F_0^2: $wR_2 = \left[\sum\left[w\left(F_0^2 - F_c^2\right)^2\right]/\sum w\left(F_0^2\right)^2\right]^{1/2}$, where $w^{-1} = \left[\sum\left(F_0^2\right) + (aP)^2 + bP\right]$ and $P = \left[\max\left(F_0^2,\ 0\right) + 2F_c^2\right]/3$

2H, H12,H14-pppdH), 7.67 (t, 1H, H13-pppdH), 7.91 (t, 1H, H5-pppdH), 8.14 (d, 2H, $J_{H-H} = 7.6$, H11, H15-pppdH), 8.29 (t, 1H, H4-pppdH), 8.71 (d, 2H, $J_{H-H} = 8$, H3-pppdH), 9.73 (d, 2H, $J_{H-H} = 5.2$, H6-pppdH).

2.3b *Complex [(η⁶-p-^{i}PrC$_6$H$_4$Me)Ru(κ²-N-O-pppdH)Cl]PF$_6$* **2**: Colour: orange; Yield = 95 mg (79%). IR (KBr, cm^{-1}): 3423 $\nu_{(O-H)}$, 1639 $\nu_{(C=O)}$, 1566 $\nu_{(C-O)}$, 1474 $\nu_{(C-N\ aromatic)}$, 850 $\nu_{(P-F)}$. Elemental Anal.(%) Calc. for $C_{24}H_{27}NO_2ClPF_6Ru$: C 44.83; H 4.23; N 2.18; found: C 44.78; H 4.28; N 2.20. ^{1}H NMR (Acetone d_6, δ in ppm): 1.31 (t, 6H, $J_{H-H} = 6.8$, CH(*Me*)$_2$), 2.37 (s, 3H, CH_3), 3.01 (m, 1H, C*H*(Me)$_2$), 5.99 (q, 2H, C_6H_{4cym}), 6.27 (q, 2H, C_6H_{4cym}), 7.53 (s, 1H, α-CH), 7.62 (t, 2H, H12,H14-pppdH), 7.73 (t, 1H, H13-pppdH), 7.98 (t,1H, H5-pppdH), 8.22 (d, 2H, $J_{H-H} = 7.6$, H11, H15-pppdH), 8.35 (t, 1H, H4-pppdH), 8.82 (d, 2H, $J_{H-H} = 8$, H3-pppdH), 9.67 (d, 2H, $J_{H-H} = 5.2$, H6-pppdH).

2.3c *Complex [(η⁶-C$_6$Me$_6$)Ru(κ²-N-O-pppdH)Cl]PF$_6$* **3**: Colour: red; Yield = 98 mg (77%). IR (KBr, cm^{-1}): 3462 $\nu_{(O-H)}$, 1620 $\nu_{(C=O)}$, 1541 $\nu_{(C-O)}$, 1456 $\nu_{(C-Naromatic)}$, 853 $\nu_{(P-F)}$. Elemental Anal. (%) Calc. for $C_{25}H_{35}NO_2ClPF_6Ru$: C 45.29; H 5.32; N 2.11; found:

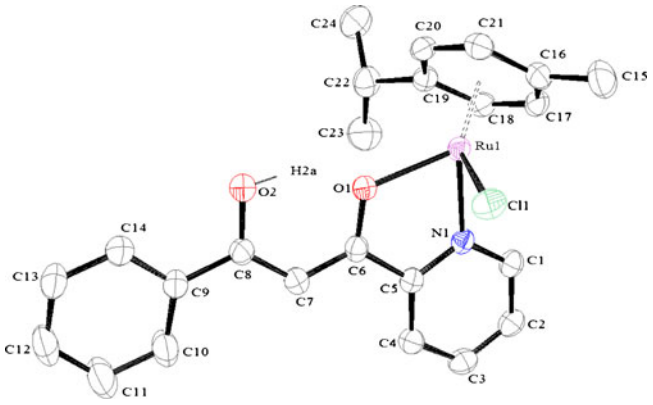


Figure 1. Molecular structure of complex $[(\eta^6\text{-}p\text{-}{}^{i}PrC_6H_4Me)Ru(\kappa^2\text{-N-O-}pppdH)Cl]^+$ **2** with atom numbering scheme. Thermal ellipsoids are depicted with 35% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1-cent 1.665, Ru1-O1 2.1131(16), C6-O1 1.275(3), C8-O2 1.322(3), C5-C6 1.483(3), C6-C7 1.404(3), C8-C7 1.369(3), C5-N1 1.361(3), Ru1-N1 2.093(2), O2-H2A 0.820, N1-C5-C6 113.1(2), O1-C6-C5 116.4(2), O1-C6-C7 121.1(2), C6-C7-C8 123.2(4), O2-C8-C7 121.8(2) C5-N1-Ru1 116.6(15), C6-O1-Ru1 117.4(15), O1-Ru1-N1 75.8(7), C8-O2-H2A 109.5

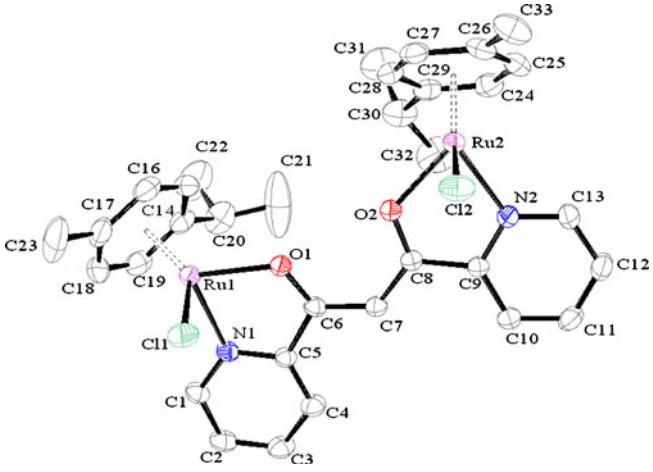


Figure 2. Molecular structure of complex $[(\eta^6\text{-}p\text{-}{}^{i}PrC_6H_4Me)_2Ru_2(\kappa^4\text{-N-O-}dppd)Cl_2]^+$ **5** with atom numbering scheme. Thermal ellipsoids are depicted with 35% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1-cent 1.673, Ru2-cent 1.663, Ru1-O1 2.084(3), Ru2-O2 2.087(3), C6-O1 1.267(5), C5-C6 1.497(5), C8-O2 1.272(4), C6-C7 1.396(5), C8-C7 1.397(5), Ru1-N1 2.088(3), Ru2-N2 2.084(3) N1-C5-C6 113.3(3), O1-C6-C5 115.8(3), O1-C6-C7 124.3(3), C6-C7-C8 126.2(3), O2-C8-C7 124.4(3), O2-C8-C9 115.8(3), N2-C9-C8 113.5(3), C5-N1-Ru1 116.2(2), C9-N2-Ru2 116.2(2), C6-O1-Ru1, 118.2(2), C8-O2-Ru2 117.9(2), O1-Ru1-N1 76.5(11), O2-Ru2-N2 76.5(11).

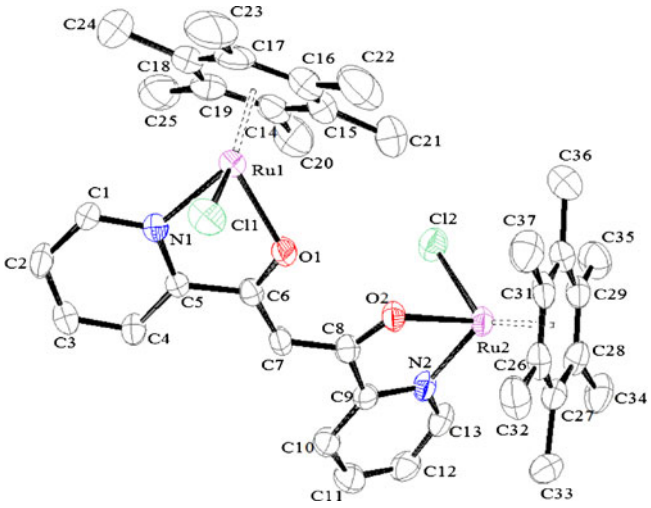


Figure 3. Molecular structure of complex $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\kappa^4\text{-N-O-}dppd)Cl_2]^+$ **6** with atom numbering scheme. Thermal ellipsoids are depicted with 35% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1-cent 1.661, Ru2-cent 1.681, Ru1-O1 2.095(5), Ru2-O2 2.107(5), C6-O1 1.263(8), C5-C6 1.487(9), C8-O2 1.268(8), C6-C7 1.396(10), C8-C7 1.403(9), Ru1-N1 2.094(6), Ru2-N2 2.080(6), N1-C5-C6 112.4(6), O1-C6-C5 116.9(6), O1-C6-C7 123.1(6), C6-C7-C8 127.0(7), O2-C8-C7 125.4(7), O2-C8-C9 116.9(6), N2-C9-C8 112.0(9), C5-N1-Ru1 116.0(4), C9-N2-Ru2, 116.7(5), C6-O1-Ru1 116.7(4), C8-O2-Ru2 117.0(4), O1-Ru1-N1 76.2(2), O2-Ru2-N2 76.6(2).

C 45.23; H 5.26; N 2.09. ^{1}H NMR (Acetone d_6, δ in ppm): 2.09 (s, 18H, C_6Me_6), 7.18 (s, 1H, α-CH), 7.59 (t, 2H, H12, H14-pppdH), 7.75 (t,1H, H13-pppdH), 8.02 (t,1H, H5-pppdH), 8.26 (d, 2H, J_{H-H} = 7.6, H11, H15-pppdH), 8.35 (t, 1H, H4-pppdH), 8.83 (d, 2H, J_{H-H} = 8, H3-pppdH), 9.77 (d, 2H, J_{H-H} = 5.2, H6-pppdH).

2.4 *Synthesis of complexes* ***4–6***

The corresponding starting dimeric complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)_2Cl_2]$ (arene = C_6H_6, $p-{}^{i}PrC_6H_4Me$, C_6Me_6) taken in 1:1 molar ratio with respect to ligand *dppdH* (~0.035 mmol) in the presence of NH_4PF_6/NH_4BF_4 were stirred in dry methanol at room temperature whereby orange to red compound started precipitated out, the reaction was continued for 6 h. The work out method after completion of the reaction was proceeded following the same method described (section 2.3) for complexes **1**–**3**.

2.4a *Complex* $[(\eta^6\text{-}C_6H_6)_2Ru_2(\kappa^4\text{-N-O-dppd})Cl_2]PF_6$ ***4***: Colour: dark orange; Yield = 65 mg (85%). IR (KBr, cm^{-1}): 1639 $\nu_{(C=O)}$, 1540 $\nu_{(C-O)}$, 1460

$\nu_{(C-N\ aromatic)}$, 844 $\nu_{(P-F)}$. Elemental anal. (%) Calc. for $C_{25}H_{21}N_2O_2Cl_2PF_6Ru_2$: C 37.56; H 2.65; N 3.50; found: C 37.78; H 2.73; N 3.17. ^{1}H NMR (Acetone d_6, δ in ppm): 5.6 (s, 12H, C_6H_6), 7.11 (s, 1H, α-CH), 7.85 (t, 2H, H5-dppd), 8.16 (t, 2H, H4-dppd), 8.45 (d, 2H, J_{H-H} = 8, H3-dppd), 9.02 (d, 2H, J_{H-H} = 5.2, H6-dppd).

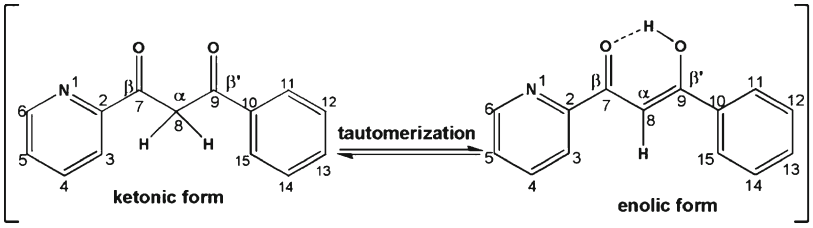
2.4b *Complex[(η^6-p-^{i}PrC$_6$H$_4$Me)$_2$Ru$_2$(κ^4-N-O-dppd)Cl$_2$]BF$_4$* ***5***: Colour: orange; Yield = 65 mg (82%). IR (KBr, cm^{-1}): 1639 $\nu_{(C=O)}$, 1546 $\nu_{(C-O)}$, 1460 $\nu_{(C-N\ aromatic)}$, 1082 $\nu_{(B-F)}$. Elemental Anal. (%) Calc. for $C_{33}H_{41}N_2O_2Cl_2PF_6Ru_2$: C 43.28; H 4.51; N 3.05; found: C 43.34; H 4.68; N 2.88. ^{1}H NMR (Acetone d_6, δ in ppm): 1.26 (d, 6H, J_{H-H} = 6.8, CH(*Me*)$_2$), 1.33 (d, 6H, J_{H-H} = 6.8, CH(*Me*)$_2$), 2.41 (s, 6H, CH_3), 3.02 (m, 1H, C*H*(Me)$_2$), 5.81 (d, 2H, J_{H-H} = 5.6, C_6H_4), 5.87(d, 2H, J_{H-H} = 6, C_6H_4), 6.08 (d, 2H, J_{H-H} = 6, C_6H_4), 6.14 (d, 2H, J_{H-H} = 6, C_6H_4), 7.05 (s, 1H, α-CH), 7.80 (t, 2H, H5-dppd), 8.20 (t, 2H, H4-dppd), 8.55 (d, 2H, J_{H-H} = 8, H3-dppd), 9.50 (d, 2H, J_{H-H} = 5.6, H6-dppd).

2.4c *Complex [(η^6-C$_6$Me$_6$)$_2$Ru$_2$(κ^4-N-O-dppd)Cl$_2$]PF$_6$* ***6***: Colour: red; Yield = 69 mg (86%). IR (KBr, cm^{-1}): 1639 $\nu_{(C=O)}$, 1540 $\nu_{(C-O)}$, 1454 $\nu_{(C-Naromatic)}$, 850 $\nu_{(P-F)}$. Elemental Anal. (%) Calc. for $C_{37}H_{45}N_2O_2Cl_2PF_6Ru_2$: C 43.21; H 3.59; N 2.86; found: C 43.45; H 3.49; N 2.73. ^{1}H NMR (Acetoned$_6$, δ in ppm): 2.21 (s, 36H, C_6Me_6), 7.19 (s, 1H, α-CH), 7.87 (t, 2H, H5-dppd), 8.19 (t, 2H, H4-dppd), 8.50 (d, 2H, J_{H-H} = 8, H3-dppd), 9.02 (d, 2H, J_{H-H} = 5.2, H6-dppd).

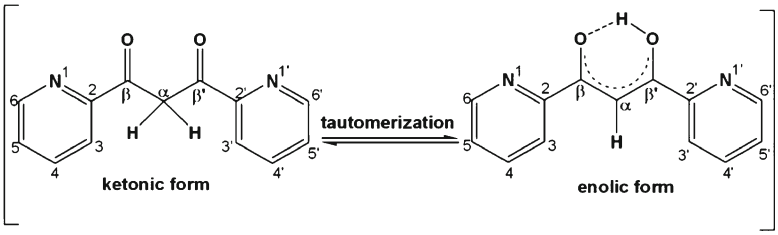
3. Results and discussion

It was reported earlier that ^{1}H NMR spectra of the ligands *pppdH* and *dppdH* exhibit enol tautomer as well as small traces of the diketone tautomer.[31,32] Similarly, in the present work, ^{1}H NMR correlates to the previously reported data.[31,32] On the basis of our present studies, the singlets of α-proton for both keto and enol isomers are observed in the spectra with comparatively higher intensity of the enolic form. On account of the keto-enol tautomerization, α-proton in the enolic isomer resonates downfield and as a result is more acidic compared to α-proton in the ketonic isomer. Along with the existence of the acidic α-proton peak in the enolic form there is concomitant display of a broad signal at 16.49 ppm and 15.94 ppm attributable to the OH proton of *pppdH* and *dppdH*, respectively. Chart 1 represents keto-enol tautomerization of the ligands employed in the study.

The generally reported procedure of complexation with ligand containing acidic hydroxyl group such as diketones (O, O'),[37,38] pyridyl functionalized diketone,[31] pyrazine dicarboxylate[12,13] or hydroxyl quinoline[13] requires the deprotonation of hydroxyl proton by a base. In addition, presence of a broad ^{1}H NMR signal at *ca*. 15–16 ppm corresponding to OH proton gave

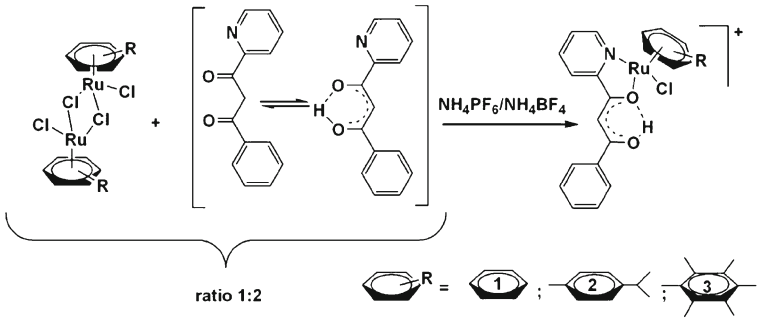


1-phenyl-3-(2-pyridyl) propane-1,3-dione (*pppdH*)



1,3-di(2-pyridyl)propane-1,3-dione (*dppdH*)

Chart 1. Ligands used in this study.



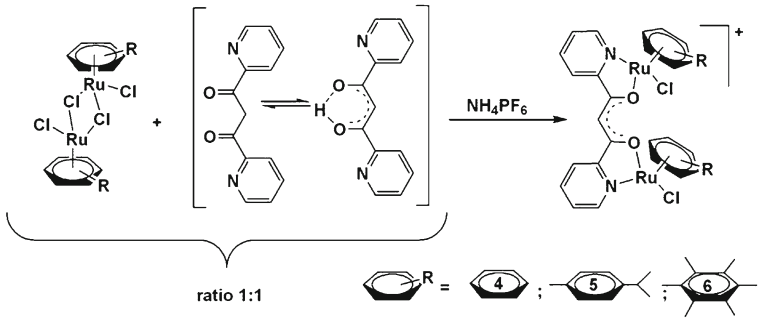
Scheme 1. Preparation of η^6- arene-ruthenium *pppdH* complexes.

an inference of the reaction mechanism which involved deprotonation of hydroxyl proton by a base, prior to complexation to yield neutral species. Therefore, in the reaction of the corresponding pyridyl diketone (*pppdH*/*dppdH*) ligand with dichloro precursor complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ in the presence of NaOMe, we expect the formation of $[(\eta^6\text{-arene})Ru(\kappa^2\text{-N-O-}pppd)Cl]$ and $[(\eta^6\text{-arene})Ru(\kappa^4\text{-N-O-}dppd)Cl]$ (arene = C_6H_6, $p-{}^iPrC_6H_4Me$, C_6Me_6) complexes. However, at room temperature, we observed immediate decomposition of the reaction mixture within few minutes and hence no product was isolated.

Crucial for successful synthesis is the use of a solution of the ligand in methanol as solvent, containing NH_4PF_6/NH_4BF_4. The possible mechanism is the replacement of chloride and simultaneous coordination of solvent molecule followed by subsequent substitution of the labile solvent species by the ligand. Chloride abstraction with NH_4PF_6/NH_4BF_4 [39,40] probably favours substitution, generating complexes [**1**–**6**$^+$] of corresponding PF_6/BF_4 salts in good yield.

Chelating pyridyl functionalized β-diketone, 1-phenyl-3-(2-pyridyl) propane-1,3-dione (*pppdH*) ligand reacts with precursor complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6, $p-{}^iPrC_6H_4Me$, C_6Me_6) in 1:2 molar ratio in the presence of NH_4PF_6 to yield new cationic monomeric $[(\eta^6\text{-arene})Ru(\kappa^2\text{-N-O-}pppdH)Cl]PF_6$ (arene = C_6H_6 **1**, $p-{}^iPrC_6H_4Me$ **2**, C_6Me_6 **3**) (scheme 1) complexes. Similarly, cationic dimeric complexes $[(\eta^6\text{-arene})Ru(\kappa^4\text{-N-O-}dppd)Cl]^+$ (arene = C_6H_6 **4**, $p-{}^iPrC_6H_4Me$ **5**, C_6Me_6 **6**) of PF_6 (complexes **4** and **6**)/BF_4 (complex **5**) salts are obtained by the reaction of 1,3-di(2-pyridyl)propane-1,3-dione (*dppdH*) ligand with respective precursors, $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = C_6H_6, $p-{}^iPrC_6H_4Me$, C_6Me_6) in 1:1 molar ratio in the presence of NH_4PF_6 or NH_4BF_4 salt (scheme 2). The reactions are preceded with substitution of the bridging chloride ligand in the dichloro dimeric precursor complexes with simultaneous formation of new complexes.

These complexes are isolated in good yield of 77% to 86% as orange solid of **1**, **2**, **4** and **5** and intense red solid of **3** and **6**. They are insoluble in non-polar solvents but soluble in chlorinated solvents and polar solvents including water. The monomers (**1**–**3**) are less soluble in polar solvents compared to the dimers (**4**–**6**); however, addition of a base to polar solvent containing the monomers increases the solubility rapidly. The formation of these complexes is supported by elemental and spectroscopic data (IR, ^1H NMR and UV-vis spectroscopy) and by single crystal



Scheme 2. Preparation of η^6- arene-ruthenium *dppd* complexes.

X-ray structure determination of representative complexes [($\eta^6 - p-{}^i$PrC$_6$H$_4$Me)Ru(κ^2-N-O-*pppdH*)Cl] **2**, [($\eta^6 - p-{}^i$PrC$_6$H$_4$Me)$_2$Ru$_2$(κ^4-N-O-*dppd*)Cl$_2$] **5**, [(η^6-C$_6$Me$_6$)$_2$Ru$_2$(κ^4-N-O-*dppd*)Cl$_2$] **6**.

3.1 *Monomeric complexes **1–3***

The important criterion for identification of carbonyl coordinated complexes through IR is that the un-ionized and uncoordinated stretching band occurs at higher frequencies, whereas the ionized and coordinated stretching band is at lower frequency ranges.[41] The IR of these complexes show typical band of C=O absorption to lower frequencies displayed by two distinctive bands in the ranges of 1640–1613 cm^{-1} and 1573–1540 cm^{-1}, respectively, in comparison to strong band at 1645 cm^{-1} of C=O for the free ligands.[31] This indicates binding of metal fragment to carbonyl donor site of the ligand; however, through IR it is not possible to differentiate occurrence of metal-ligand bond either through O, O' or N, O of ligand *pppdH*. The ionic nature of the complexes **1**, **2** and **3** are identified by a strong band at around 850 cm^{-1} due to the $\nu_{(P-F)}$ stretching mode of the PF_6^- counter ion. Furthermore, the IR spectra of monomeric complexes **1–3** exhibit broad absorption frequency in the region *ca.* 3423–3462 cm^{-1} corresponding to hydrogen bonding of the uncoordinated OH group.

In order to confirm the coordination of the N∩O to arene ruthenium(II) fragment, the complexes are further analysed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of **1** shows a singlet at 6.24 ppm assignable to the six benzene protons of the monomer. The ^{1}H NMR spectrum of complex **2** displays one triplet at 1.31 ppm, one singlet at 2.37 ppm and septet at 3.01 ppm corresponding to six isopropyl methyl, three methyl and one isopropyl protons of the *p*-cymene ligand. Two distinct quartets at 5.99 ppm and 6.27 ppm existed due to diastereotopic aromatic hydrogen atoms of the *p*-cymene ligand. The ^{1}H NMR spectrum of complex **3** exhibits singlet at 2.09 ppm assignable to eighteen protons of hexamethylbenzene ligand. The coordinated pyridyl diketone (*pppdH*) ligand in complexes **1–3** exhibits multiplets in the aromatic region with peak multiplicity of four triplets at 7.57–8.35 ppm; one doublet at 8.14–8.26 ppm and two doublets at 8.71–9.77 ppm. The α-proton is acidic in nature and display singlet at 7.22 ppm, 7.53 ppm and 7.18 ppm for complexes **1**, **2** and **3**, respectively. These observations confirmed the formation and existence of these complexes in enolic isomer form. However at room temperature, ^{1}H NMR spectra of **1–3** do not show any signal attributable to the OH proton. Classically inter or intra-molecular hydrogen bond O–H⋯O like N–H⋯N can result in more downfield shift of the *pppd*-OH in comparison with the free ligand.[42] Previous publications suggested occurrence of a broad signal for OH in the downfield region when recorded at very low temperatures.[43]

In the monomeric complexes, the *pppdH* ligand would have coordinated to the metal in O, O' bonding mode to form neutral complexes;[37,38] however, as expected from synthetic and spectral point of view, and taking into account the softer nature of the N-donor compared to O-donor, it may be assumed that pyridyl-N moiety is preferably bonded by the softer ruthenium metal centre[44–46] in N, O bonding mode to form cationic complexes. As a result from IR studies, the occurrence of the counter ion absorption band, as well as the presence of OH absorption band in the spectra suggested κ^2-N∩O bonding in these complexes. Also, the ^{1}H NMR spectra display peaks with multiplicities of the diastereotopic protons in the arene ligand when coordinated to hetero donor sites in these complexes suggesting the formation of monomeric κ^2-N∩O bonded arene ruthenium(II) complexes. To further confirm the bonding modes and structures of the complexes without any ambiguity the molecular structure of representative complex [($\eta^6 - p-{}^i$PrC$_6$H$_4$Me)Ru(κ^2-N-O-*pppdH*)Cl] **2** has been carried out.

3.2 *Dimeric complexes **4–6***

Similar to the monomeric complexes, in the IR spectra of complexes **4–6**, the C=O stretching frequencies are observed as two bands in the regions around 1639 cm^{-1} and at 1540–1546 cm^{-1} compared to that of the free ligand at 1650 cm^{-1} [32]. However, in addition to the existence of hetero donor groups in the coordinated ligand, resonance probably exist in these complexes which makes it difficult to assigned the absorption frequency of C=O between the β and β' (numbering scheme in ligand: chart 1) precisely. In contrast to monomeric complexes, no *OH* absorption band is observed in the IR spectra of dimeric complexes **4–6**. The ionic nature of these complexes is confirmed by a strong band at around 850 cm^{-1} due to $\nu_{(P-F)}$ stretching mode of the PF_6^- counter ion. However, in the case of the complex **5** a strong absorption band at 1085 cm^{-1} is observed due to the BF_4^- ion.

In the ^{1}H NMR of complex **4**, a singlet is observed at 5.60 ppm, which is assignable to twelve arene protons of the dimer. Similarly, in the ^{1}H NMR spectrum of

complex **5**, the aromatic ring protons are diastereotopic exhibiting four distinct doublets centred at 5.81 ppm, 5.87 ppm, 6.08 ppm and 6.14 ppm which is frequently observed in cases where there are hetero donor atoms of the N∩O ligands.[12,13] The methyl groups of ^{i}Pr moiety are also diastereotopic exhibiting two distinct doublets centred at 1.24 ppm and 1.33 ppm with coupling constant of 6.8 Hz, typically observed when the ligand is coordinated through two different donor sites. Besides these, a singlet at 2.41 ppm and septet at 3.04 ppm for methyl and isopropyl protons respectively are also observed. Complex **6** exhibits singlet at δ 2.21 for methyl protons of corresponding to the hexamethylbenzene ligand. Apart from the peaks observed for the corresponding cyclic-hydrocarbon ligand of respective complexes **4**–**6**, the ^{1}H NMR spectra of these complexes support the presence of *dppd* ligand by the display of resonances in the ranges of 7.80–7.90 ppm, 8.15–8.25 ppm, 8.40–8.57 ppm and 8.90–9.50 ppm as two triplets and two doublets associatively. The signal due to the α-proton is observed in the downfield region of 7.1 ppm, 7.05 ppm and 7.19 ppm for complexes **4**–**6**, respectively, which probably indicates fast resonance occurring within the β-diketone moiety of the coordinated ligands, resulting in acidic α-proton which resonates downfield, similar to the enolic tautomer of the free ligand.

The formation of ionic dimeric complexes is supported by spectral studies of these complexes. If the *dppdH* ligand would have coordinated through O, O' donor sites only neutral monomeric analogues of complexes of **4**–**6** would be formed. The formation of dimeric complexes is possible as the ligand is bonded in κ^4-N∩O fashion. The number of the arene protons revealed by the ^{1}H NMR spectra of each complex confirmed formation of dimeric complexes. The serendipitous nature of bonding of the ligand is further confirmed through molecular structures of the representative complexes $[(\eta^6-p-{}^{i}PrC_6H_4Me)_2Ru_2(\kappa^4\text{-N-O-}dppd)Cl_2]$ **5** and $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\kappa^4\text{-N-O-}dppd)Cl_2]$ **6**.

In the ^{1}H NMR of both monomeric and dimeric complexes, the α-proton resonates downfield indicating the existence of the coordinated ligands (*pppdH/dppd*) in these complexes **1**–**6** in the enolic form as well as chelating through (N, O) of the pyridyl functionalized β-diketone.

4. Molecular structure

The molecular structure of the complexes **2**, **5** and **6** has been established by single-crystal X-ray structure analysis. All the three representative complexes crystallize in monoclinic space groups and in all the complexes the metal centres are stereogenic. Crystal X-ray data are presented in table 1.

The ORTEP drawings of mononuclear complex **2** and dinuclear complexes **5** and **6** are shown in figures 1, 2 and 3, respectively along with selected bond lengths and bond angles. The molecular structures of **2** and **6** consist of hexafluorophosphate anion and **5** of tetrafluoroborate anion. The cation is formed by a ruthenium atom η^6-coordinated to an arene ligand, one anionic chlorine atom and to the two donor atoms of the chelating ligand forming a three legged 'piano stool' structure around each ruthenium atom. In complex **5** the two chlorine atoms of the dimer are *cis* to one another {bond distances, Ru1-Cl1 is 2.407(12) and Ru2-Cl2 is 2.388(12)}, while in complex **6** they are in *trans* position of comparable Ru-Cl distances around 2.405(2) Å and 2.393(2) Å for Ru1–Cl1 and Ru2–Cl2, respectively. The geometry of the complexes is distorted octahedral and marked by O–Ru–N bite angle around 76^0. The distance between the ruthenium atom and the centroid of the *p*-cymene ligand of the mononuclear complex **2** is 1.665 Å, the dinuclear complex **5** are 1.673 Å and 1.663 Å and between the ruthenium centre and the hexamethylbenzene molecule of the dinuclear complex **6** are 1.661 Å and 1.681 Å. These values are consistent with distances reported for other *p*-cymene or hexamethylbenzene ruthenium(II) complexes.[13,37,47]

In complex **2**, the +2 oxidation state of the ruthenium is balanced by one anionic chlorine atom and one PF_6 counter ion, indicating that the *pppd* ligand is coordinated as neutral (N, O) donor and in the enolic form. The Ru–O and Ru–N bond lengths are 2.113(11) Å and 2.093(2) Å, respectively. The C–O distance of the coordinated carbonyl is 1.275(3) Å and that of the uncoordinated carbonyl is 1.322(3) Å, which is comparatively longer. Intra-molecular H-bonding O–H…O exists between the free OH group and the coordinated C=O in the molecule with intramolecular distance of 2.580 Å, whereas the O-H bond length is 0.820 Å. Hence, C8-C7 has double bond character with bond length of 1.369(3) Å though probably fast resonance occurs in the complex.

In complexes **5** and **6** the anomalous behaviour of the N∩O ligand is observed. In these complexes the +2 oxidation state of one of the ruthenium metal is balanced by one anionic chlorine atom and one anionic oxygen atom of the bridging N∩O ligand (*dppd*) with the simultaneous coordination of the ligand as neutral N∩O to the other ruthenium centre in which the oxidation state is balanced by one anionic chlorine atom and one counter ion (PF_6/BF_4). This suggests that part of the ligand acts as a $(N, O)^-$ and other part of the

ligand acts as a neutral (N, O) donor. This means one of the chelating ring $(N, O)^-$ double bond is localized whereas the other double bond is not localized. The bond lengths around O1-C6, C6-C7, C7-C8, C8-O2 (numbering scheme in figures 2 and 3) of the diketone fragment is 1.267(5) Å, 1.396(5) Å, 1.397(5) Å, 1.272(4) Å for complex **5** and 1.263(8) Å, 1.396(10) Å, 1.403(9) Å, 1.268(8) Å for complex **6**. The bond distances for C6-C7 and C7-C8 are similar, which clearly indicates delocalization of π electrons occurring in the solid state of the complexes. Due to delocalization, a serendipitous nature observed in these structures is that C6-O1 and C8-O2 bond lengths are almost the same in both complexes **5** and **6**. Therefore, bond lengths in molecular structure analyses are not able to distinguish the carbonyl groups, but formations of mono cationic complexes instead of di-cationic complexes indicate dual nature of the *dppd* ligand. X-ray structure of representative complexes **5** and **6** clearly justify that one of the carbonyl group is coordinated as anionic C–O^-; whereas the other exists as neutral C=O which is compromised by the presence of one counter anion. The PF_6 displays a distorted octahedral geometry in complexes **2** and **6** and the BF_4^- counter ion in **5** has a tetrahedral geometry with F-B-F angles of around 109°.

Therefore, from molecular structure studies we can summarize that in the mononuclear complex **2** the coordinated *pppdH* ligand is not bonded to the ruthenium centre in $(O, O')^-$ anionic fashion or as $(N, O)^-$ uninegative ligand but as neutral (N, O) donor. Coordination of the *dppd* ligand to the ruthenium centre in $(O, O')^-$ anionic mode could have accounted for only monomeric analog of **5** and **6**. However, in dimeric complexes **5** and **6** the *dppd* ligand exhibits a dual coordinate ion mode to ruthenium metal, as neutral (N, O) as well as uninegative $(N, O)^-$ donor sites. The negatively charged *dppd* ligand shows delocalized bonding across the *'O–C–C–C–O'* moiety. The O–C and C–C distances (captions of figures 2 and 3) fall midway between single and double bond lengths, as is appropriate for the delocalized nature of the bonding in this coordinated *dppd* ligand. Therefore, both coordinating oxygen atoms carry significant and approximately equal, partial negative charge. Hence, it is difficult to distinguish which of the two ruthenium centres acquires neutral (N, O) or ionic $(N, O)^-$ bonding mode.

5. UV-visible spectra

UV-vis spectra of complexes were acquired in acetonitrile and spectral data are summarized in table 2. Electronic spectra of these complexes are depicted in figure 4. The low spin d^6 configuration of the mono and dinuclear complexes provides filled orbitals of proper symmetry at the Ru(II) centre, which interact with the low lying π^* orbital of the ligand. Therefore, the electronic spectra are expected to exhibit a band attributable to metal-to-ligand charge transfer (MLCT) ($t_2g \rightarrow \pi^*$) transition.[48,49] Furthermore, the energy of these transitions should vary with the nature of the ligand acting as π acceptors.[50,51] The band on the higher energy side ~300–400 nm have been assigned to ligand centred $\pi \rightarrow \pi^*/n \rightarrow \pi^*$ transition.[52,53] The electronic spectra of these complexes display single band at ~340 nm, the bands in this wavelength are attributed to the intra ligand π–π^* transition. Monomeric complexes **1** and **2** display high intense band while **3** shows very low intensity band. However, the dimeric complexes **4–6** absorb with similar intensity in this wavelength range of the visible region. The electronic spectra of these complexes **1–6** display a medium intensity band in the visible region at ~450–500 nm assignable to metal-to-ligand charge transfer transition (MLCT) (t_2g-π^*). Ruthenium complexes **1–6** experience a bathochromic shift, more prominent in dimeric complexes **4–6** with higher intensity bands compared to monomeric complexes **1–3**. In general, these complexes display $\pi \rightarrow$

Table 2. UV-vis absorption data in acetonitrile at 298K.

Complex	λ_{max}/nm $(\varepsilon/10^{-4}\ M^{-1}cm^{-1})$		
1	356(0.322)	–	449(0.132)
2	341(0.522)	–	453(0.059)
3	338(0.053)	–	450(0.029)
4	354(0.183)	–	487(0.206)
5	358(0.195)	–	495(0.210)
6	352(0.187)	367(0.208)	514(0.153)

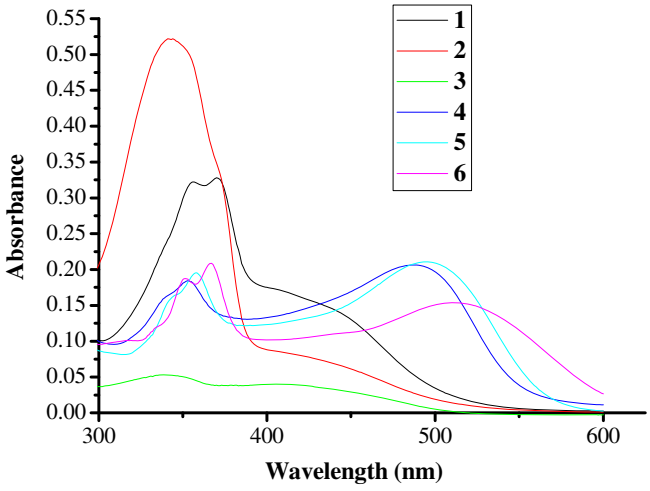


Figure 4. UV-vis spectra of complexes **1**, **2**, **3**, **4**, **5** and **6**.

$\pi^*/n \rightarrow \pi^*$ transition for the pyridyl diketone ligand in the UV region and metal to ligand charge transfer transition in the visible region as observed in previous reports.[12,39,40]

6. Conclusion

The introduction of the title ligands in the arene ruthenium(II) systems revealed an interesting chemistry through their synthesis, spectral and X-ray structures. There can be numerous possible modes of binding of these ligands to the metal through the N, O and/or O, O'-chelating donor sites. The anomalous behaviour of the pyridyl diketone ligands can be conceived from the synthetic point of view, by which their η^6-arene Ru(II) complexes are ionic in nature rather than the expected neutral species. In spectral analyses the presence of acidic α-proton reveals that the ligand coordinated through enolic form. The molecular structure determination of representative complexes reveals that in the mononuclear complexes the ligand is coordinated as neutral (N, O) donor whereas in binuclear complexes the ligand is bonded as a neutral as well as uninegative donor. Also, in both cases the ligands exist in the enolic form.

Supplementary material

CCDC- 838265 for **2**, 838266 for **5** and 838264 for **6** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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