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# Cationic half-sandwich complexes (Rh, Ir, Ru) containing 2-substituted-1,8-naphthyridine chelating ligands: Syntheses, X-ray structure analyses and spectroscopic studies

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A B S T R A C T

Reactions of the dinuclear complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = $C_6H_6$, *p*-$^i$PrC$_6$H$_4$Me) and $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) with 2-substituted-1,8-naphthyridine ligands, 2-(2-pyridyl)-1,8-naphthyridine (pyNp), 2-(2-thiazolyl)-1,8-naphthyridine (tzNp) and 2-(2-furyl)-1,8-naphthyridine (fuNp), lead to the formation of the mononuclear cationic complexes $[(\eta^6\text{-}C_6H_6)Ru(L)Cl]^+$ {L = pyNp (**1**); tzNp (**2**); fuNp (**3**)}, $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(L)Cl]^+$ {L = pyNp (**4**); tzNp (**5**); fuNp (**6**)}, $[(\eta^5\text{-}C_5Me_5)Rh(L)Cl]^+$ {L = pyNp (**7**); tzNp (**8**); fuNp (**9**)} and $[(\eta^5\text{-}C_5Me_5)Ir(L)Cl]^+$ {L = pyNp (**10**); tzNp (**11**); fuNp (**12**)}. All these complexes are isolated as chloro or hexafluorophosphate salts and characterized by IR, NMR, mass spectrometry and UV/Vis spectroscopy. The molecular structures of [**1**]Cl, [**2**]$PF_6$, [**4**]$PF_6$, [**5**]$PF_6$ and [**10**]$PF_6$ have been established by single crystal X-ray structure analysis.

*Keywords:* Arene ligands N-ligands Pentamethylcyclopentadienyl Ruthenium Rhodium Iridium

## 1. Introduction

Mononuclear complexes of platinum group metals containing heterocyclic nitrogen based ligands have received considerable attention owing to their photochemical properties [1], catalytic activities [2], electrochemical behaviour [3], as well as in the development of new biologically active agents [4]. Ruthenium, rhodium and iridium unsubstituted 1,8-naphthyridine based complexes are interesting in their own right of uses as dye – sensitized solar cells and photophysical effects [5]. The reactivity of these metals with substituted 1,8-naphthyridine based ligands have also been reported: Examples with dinuclear metal–metal bonded compounds [6], and mononuclear compounds [6c,7] being known. However no reports dealing with $\eta^5$-pentamethylcyclopentadienyl or $\eta^6$-arene platinum group metal (Rh, Ir, or Ru) in connectivity with substituted 1,8-naphthyridine ligands have been reported so far.

Herein, we describe the synthesis of twelve $\eta^5$-$C_5Me_5$ rhodium, iridium and $\eta^6$-$C_6H_6$, $\eta^6$-*p*-$^i$PrC$_6$H$_4$Me ruthenium complexes incorporating 2-substituted-1,8-naphthyridine ligands; 2-(2-pyridyl)-1,8-naphthyridine (pyNp), 2-(2-thiazolyl)-1,8-naphthyridine (tzNp) and 2-(2-furyl)-1,8-naphthyridine (fuNp). All complexes are characterized by IR, NMR, mass spectrometry and UV/Vis spectroscopy. The molecular structures of five representative complexes are presented as well.

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## 2. Experimental

### 2.1. General remarks

All solvents were dried and distilled prior to use. Ruthenium trichloride hydrate (Arora Matthey Ltd.), 2-aminonicotinaldehyde (Acros Organics), 2-acetylpyridine, 2-acetylthiazole and 2-acetylfuran (Aldrich) were purchased and used as received. $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$, $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mu\text{-}Cl)Cl]_2$ [8], and $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl]_2$ (M = Rh, Ir) [9] were prepared according to literature methods. The ligands pyNp, tzNp and fuNp were prepared by the Friedlander condensation of 2-aminonicotinaldehyde with the corresponding acyl derivatives [10]. NMR spectra were recorded on AMX-400 MHz spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer 983 spectrophotometer; elemental analyses of the complexes were performed on a Perkin–Elmer-2400 CHN/S analyzer. Mass spectra were obtained from ZQ mass spectrometer by ESI method. Absorption spectra were obtained at room temperature using a Perkin–Elmer Lambda 25 UV/Vis spectrophotometer. All the new complexes gave satisfactory CHN values.

*2.2. Preparation of the cationic complexes **1–6***

*Synthesis of [($\eta^6$-$C_6H_6$)Ru(pyNp)Cl]Cl ([**1**]Cl)*: A mixture of [($\eta^6$-$C_6H_6$)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.09 mmol) and pyNp (42 mg, 0.18 mmol) in 10 ml of acetonitrile was refluxed for 90 min. A colour change from light brown to dark brown was observed. The resulting solution was concentrated under vacuum (2 ml). Then 15 ml of hexane was added to induce precipitation. The yellowish brown solid was filtered off, washed with diethyl ether and dried under vacuum.

Yield: 80 mg, (87%). Anal. Calc. for $C_{19}H_{15}Cl_2N_3Ru$ (457.31): C, 49.90; H, 3.31; N, 9.19. Found: C, 50.08; H, 3.69; N, 9.15%.

$^1$H NMR ($CDCl_3$, $\delta$): 9.56 (d, 1H, $J_{H-H}$ = 8 Hz), 9.38 (q, 1H), 8.76 (d, 1H), 8.58 (m, 2H), 8.48 (d, 1H), 7.91 (td, 1H), 7.90 (q, 1H), 7.78 (td, 1H), 6.15 (s, 6H, $C_6H_6$). ESI-MS (*m*/*z*): 419.8 (100%) [M−Cl]$^+$.

*Synthesis of [($\eta^6$-$C_6H_6$)Ru(tzNp)Cl]$PF_6$ ([**2**]$PF_6$)*: A mixture of [($\eta^6$-$C_6H_6$)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.09 mmol), tzNp (43 mg, 0.20 mmol) and 2.5 equiv. of $NH_4PF_6$ in 10 ml of acetonitrile was stirred at room temperature for 12 h. A color change was observed from light brown to yellowish brown during the process. The reaction mixture was filtered off and washed with acetonitrile. The filtrate was reduced under vacuum (2 ml) and 15 ml of diethyl ether was then added to induce precipitation. After standing for 15 min, a yellow precipitate was settled down. The resulting precipitate was filtered, washed with diethyl ether and dried under vacuum.

Yield: 85 mg (76%). Anal. Calc. for $C_{17}H_{13}ClN_3F_6SPRu$ (572.85): C, 35.64; H, 2.29; N, 7.34. Found: C, 35.75; H, 2.35; N, 7.46%.

$^1$H NMR ($CD_3CN$, $\delta$): 9.40 (q, 1H), 8.74 (d, 1H, $J_{H-H}$ = 8.12 Hz, tz-$H_1$), 8.69 (d, 1H), 8.56 (dd, 1H), 8.24 (d, 1H, $J_{H-H}$ = 4 Hz, tz-$H_2$), 8.19 (d, 1H), 7.9 (q, 1H), 6.20 (s, 6H, $C_6H_6$). ESI-MS (*m*/*z*): 425.2 (100%) [M−$PF_6$]$^+$, 389.4 (20%) [M−$PF_6$−Cl]$^+$.

*Synthesis of [($\eta^6$-$C_6H_6$)Ru(fuNp)Cl]$PF_6$ ([**3**]$PF_6$)*: A mixture of [($\eta^6$-$C_6H_6$)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.09 mmol), fuNp (36 mg, 0.18 mmol) and 2.5 equivalents of $NH_4PF_6$ was used and treated following a procedure similar to that described in the synthesis of complex [**2**]$PF_6$. The resulting precipitate was filtered, washed with benzene and dried under vacuum.

Yield 70 mg, (63%). Anal. Calc. for $C_{18}H_{14}ClF_6N_2OPRu$ (555.80): C, 38.90; H, 2.54; N, 6.38. Found: C, 38.70; H, 2.45; N, 6.56%.

$^1$H NMR ($CDCl_3$, $\delta$): 9.52 (dd, 1H), 8.49 (dd, $J_{H-H}$ = 7.12 Hz, 1H), 8.09 (dd, 1H, $J_{H-H}$ = 8.08 Hz), 7.84 (d, 1H), 7.71 (d, 1H), 7.67 (q, 1H), 7.57 (q, 1H), 6.81 (q, 1H), 5.93 (S, 6H, $C_6H_6$). ESI-MS (*m*/*z*): 408.9 (100%) [M−$PF_6$]$^+$, 374.1 (20%) [M−$PF_6$−Cl]$^+$.

*Synthesis of [($\eta^6$-*p*-$^i$Pr$C_6H_4$Me)Ru(pyNp)Cl]$PF_6$ ([**4**]$PF_6$)*: A mixture of [($\eta^6$-*p*-$^i$Pr$C_6H_4$Me)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.081 mmol), pyNp (34 mg, 0.163 mmol) and 2.5 equiv. of $NH_4PF_6$ in 10 ml of acetonitrile were stirred at room temperature for 5 h. A white precipitate ($NH_4Cl$) was removed by filtration. The filtrate was concentrated to 2 ml and diethyl ether was added to induce precipitation. After standing for 15 min, an orange-yellowish precipitate was observed. After filtration, the solid was washed with diethyl ether and dried under vacuum.

Yield: 82 mg, (81%). Anal. Calc. for $C_{23}H_{23}ClF_6N_3PRu$ (622.93): C, 44.35; H, 3.72; N, 6.75. Found: C, 44.70; H, 4.05; N, 6.76%.

$^1$H NMR ($CD_3CN$, $\delta$): 9.46 (d, 1H, $J_{H-H}$ = 12 Hz,), 9.37 (q, 1H, $J_{H-H}$ = 4 Hz), 8.73 (d, 1H), 8.57 (m, 2H), 8.48 (d, 1H), 8.26 (td, 1H), 7.91 (q, 1H), 7.78 (td, 1H), 6.21 (d, 1H, $J_{H-H}$ = 5.4 Hz, $Ar_{p\text{-}cy}$), 6.13 (d, 2H, $J_{H-H}$ = 6.2 Hz, $Ar_{p\text{-}cy}$), 5.79 (d, 1H, $J_{H-H}$ = 5.2 Hz, $Ar_{p\text{-}cy}$), 2.47 (sept, 1H, $J_{H-H}$ = 4.4 Hz, $CH(CH_3)_2$), 2.27 (s, 3H, $CH_3$), 0.91 (d, 3H, $CH(CH_3)_2$), 0.83 (d, 3H, $CH(CH_3)_2$). ESI-MS (*m*/*z*): 475.9 (100%) [M−$PF_6$]$^+$, 440 (8%) [M−$PF_6$−Cl]$^+$, 306.4 (4%) [M−$PF_6$−Cl−*p*-cy]$^+$.

*Synthesis of [($\eta^6$-*p*-$^i$Pr$C_6H_4$Me)Ru(tzNp)Cl]$PF_6$ ([**5**]$PF_6$)*: A mixture of [($\eta^6$-*p*-$^i$Pr$C_6H_4$Me)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), tzNp (35 mg, 0.17 mmol) and 2.5 equiv. of $NH_4PF_6$ in 10 ml of methanol was refluxed for 3 h. A color change from brown to yellowish brown was observed. The solution was evaporated and the residue extracted with dichloromethane. The white insoluble material was filtered off. The filtrate was concentrated to 2 ml and diethyl ether was added to induce precipitation. The yellowish orange precipitate was washed with diethyl ether and dried under vacuum.

Yield: 80 mg, (78%). Anal. Calc. for $C_{21}H_{21}ClF_6N_3SPRu$ (628.96): C, 40.10; H, 3.37; N, 6.68. Found: C, 40.43; H, 3.35; N, 6.76%.

$^1$H NMR ($CDCl_3$, $\delta$): 9.35 (q, 1H), 8.74 (d, 1H, $J_{H-H}$ = 3.36 Hz), 8.62 (d, 1H), 8.45 (dd, 1H), 8.15 (d, 1H, $J_{H-H}$ = 8.32 Hz), 8.06 (d, 1H), 7.86 (q, 1H), 6.31 (d, 1H, $J_{H-H}$ = 6.2 Hz, $Ar_{p\text{-}cy}$), 6.26 (d, 1H, $J_{H-H}$ = 6 Hz, $Ar_{p\text{-}cy}$), 6.11 (d.1H, $J_{H-H}$ = 5.68 Hz, $Ar_{p\text{-}cy}$), 5.99 (d, 1H, $J_{H-H}$ = 6 Hz, $Ar_{p\text{-}cy}$), 2.79 (sept, 1H, $J_{H-H}$ = 4.14 Hz, $CH(CH_3)_2$), 2.28 (s, 3H, $CH_3$), 1.08 (d, 3H, $CH(CH_3)_2$), 1.02 (d, 3H, $CH(CH_3)_2$). ESI-MS (*m*/*z*): 481.9 (100%) [M−$PF_6$]$^+$, 445.6 (45%) [M−$PF_6$−Cl]$^+$.

*Synthesis of [($\eta^6$-*p*-$^i$Pr$C_6H_4$Me)Ru(fuNp)Cl]$PF_6$ ([**6**]$PF_6$)*: The reaction of [($\eta^6$-*p*-$^i$Pr$C_6H_4$Me)Ru(μ-Cl)Cl]$_2$ (50 mg, 0.08 mmol), fuNp (32 mg, 0.16 mmol) and 2.5 equiv. of $NH_4PF_6$ was carried out following a procedure similar to that described in the synthesis of [**2**]$PF_6$.

Yield: 70 mg, (70%). Anal. Calc. for $C_{22}H_{22}ClF_6N_2OPRu$ (611.91): C, 43.18; H, 3.62; N, 5.79. Found: C, 43.23; H, 3.73; N, 5.46%.

$^1$H NMR ($CD_3CN$, $\delta$): 9.58 (dd, 1H), 9.05 (dd, 1H), 8.32 (dd, 1H, $J_{H-H}$ = 8.12 Hz), 8.10 (d, 1H), 7.99 (d, 1H), 7.76 (d, 1H), 7.57 (q, H), 6.81 (q, 1H), 5.81 (d, 2H, $J_{H-H}$ = 6.24 Hz, $Ar_{p\text{-}cy}$), 5.56 (d, 2 H, $J_{H-H}$ = 6.14 Hz, $Ar_{p\text{-}cy}$), 2.86 (sept, 1H, $J_{H-H}$ = 4.04 Hz, $CH(CH_3)_2$), 2.16 (s, 3H, $CH_3$), 1.18 (d, 3H, $CH(CH_3)_2$), 1.07 (d, 3H, $CH(CH_3)_2$). ESI-MS (*m*/*z*): 464.9 (100%) [M−$PF_6$]$^+$, 429.2 (15%) [M−$PF_6$−Cl]$^+$.

*2.3. Preparation of the cationic complexes **7–12***

*General procedure*: A mixture of [($\eta^5$-$C_5Me_5$)M(μ-Cl)Cl]$_2$ (0.07 mmol), 2-substituted-1,8-naphthyridine ligand (0.14 mmol) and 2.5 equiv. of $NH_4PF_6$ in dry methanol (10 ml) was stirred at room temperature for 8 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane. After filtration, the volume was reduced to 2 ml and excess diethyl ether was added to induce precipitation. The precipitate was washed with diethyl ether and dried under vacuum.

*[($\eta^5$-$C_5Me_5$)Rh(pyNp)Cl]$PF_6$ ([**7**]$PF_6$)*: Orange-yellow solid, yield: 70 mg (79%). Anal. Calc. for $C_{23}H_{24}ClF_6N_3PRh$ (625.77): C, 44.14; H, 3.87; N, 6.71. Found: C, 44.70; H, 4.06; N, 6.76%.

$^1$H NMR ($CD_3CN$, $\delta$): 9.32 (q, 1H, $J_{H-H}$ = 4.08 Hz), 9.03 (d, 1H, $J_{H-H}$ = 4 Hz), 8.78 (d, 1H), 8.55 (m, 2H), 8.5 (d, 1H), 8.29 (td, 1H), 7.87 (td, 2H), 1.60 (s, 15H, $C_5Me_5$). ESI-MS (*m*/*z*): 480.81 (100%) [M-$PF_6$]$^+$, 444.1 (70%) [M−$PF_6$−Cl]$^+$.

*[($\eta^5$-$C_5Me_5$)Rh(tzNp)Cl]$PF_6$ ([**8**]$PF_6$)*: Orange solid, yield: 80 mg (89%). Anal. Calc. for $C_{21}H_{22}ClF_6N_3SPRh$ (628.96): C, 39.72; H, 3.51; N, 6.65. Found: C, 40.03; H, 3.45; N, 6.86%.

$^1$H NMR ($CD_3CN$, $\delta$): 9.34 (q, 1H, $J_{H-H}$ = 1.92 Hz), 8.76 (d, 1H, $J_{H-H}$ = 8.4 Hz), 8.57 (dd, 1H), 8.38 (d, 3H), 8.29 (d, 1H, $J_{H-H}$ = 8.4 Hz), 8.23 (d, 1H), 7.87 (q, 1H), 1.71 (s, 15H, $C_5Me_5$). ESI-MS (*m*/*z*): 485.28 (100%) [M−$PF_6$]$^+$, 450.1 (9%) [M−$PF_6$−Cl]$^+$.

*[($\eta^5$-$C_5Me_5$)Rh(fuNp)Cl]$PF_6$ ([**9**]$PF_6$)*: Orange-yellow solid, yield: 68 mg (78%). Anal. Calc. for $C_{22}H_{23}ClF_6N_2OPRh$ (614.75): C, 42.98; H, 3.77; N, 4.56. Found: C, 42.23; H, 3.73; N, 4.34%.

$^1$H NMR ($CD_3CN$, $\delta$): 9.42 (dd, 1H), 9.09 (dd, 1H), 8.52 (d, 1H), 8.12 (dd, 1H), 7.79 (d, 1H), 7.76 (d, 1H), 7.67 (q, 1H), 7.52 (q, 1H), 1.55 (s, 15H, $C_5Me_5$). ESI-MS (*m*/*z*): 468.6 [M−$PF_6$]$^+$, 433.1 (7%) [M−$PF_6$−Cl]$^+$.

*[($\eta^5$-$C_5Me_5$)Ir(pyNp)Cl]$PF_6$ ([**10**]$PF_6$)*: Orange-yellow solid, yield: 80 mg (89%). Anal. Calc. for $C_{23}H_{24}ClF_6N_3PIr$ (715.09): C, 38.63; H, 3.38; N, 5.58. Found: C, 38.80; H, 3.65; N, 5.66%.

$^1$H NMR ($CDCl_3$, $\delta$): 9.38 (d, 1H), 9.3 (q, 1H), 8.73 (d, 1H), 8.55 (m, 2H), 8.49 (d, 1H), 8.28 (td, 1H), 7.96 (q,1H), 7.87 (td, 1H), 1.71 (s, 15H, $C_5Me_5$). ESI-MS (*m*/*z*): 569.1 (100%) [M−$PF_6$]$^+$, 533.2 (23%) [M−$PF_6$−Cl]$^+$.

*[($\eta^5$-$C_5Me_5$)Ir(tzNp)Cl]$PF_6$ ([**11**]$PF_6$)*: Orange-yellow solid, yield: 82 mg (91%). Anal. Calc. for $C_{21}H_{22}ClF_6N_3SPIr$ (721.11): C, 34.98; H, 3.08; N, 5.83; S, 4.45. Found: C, 34.63; H, 3.15; N, 5.76; S, 4.42%.

$^1$H NMR ($CD_3CN$, $\delta$): 9.32 (q, 1H), 8.73 (d, 1H), 8.58 (dd, 1H), 8.37 (d, 3 H), 8.31 (d, 1H), 8.21 (d, 1H), 7.89 (q, 1H), 1.71 (s, 15H, $C_5Me_5$). ESI-MS (*m*/*z*): 575.1 (100%) $[M-PF_6]^+$, 539.4 (35%) $[M-PF_6-Cl]^+$.

*[($\eta^5$-$C_5Me_5$)Ir(fuNp)Cl]$PF_6$ ([**12**]$PF_6$)*: Orange-yellow solid, yield: 61 mg (69%). Anal. Calc. for $C_{22}H_{23}ClF_6N_2OPIr$ (704.06): C, 37.53; H, 3.29; N, 3.98. Found: C, 37.23, H, 3.23; N, 4.14%.

$^1$H NMR ($CDCl_3$, $\delta$): 9.40 (dd, 1H), 9.06 (m, 1H), 8.51 (dd, 1H), 8.13 (d, 1H), 7.84 (d, 1H), 7.72 (d, 1H),7.65 (q, 1H), 7.55 (q, 1H), 1.56 (s, 15H, $C_5Me_5$). ESI-MS (*m*/*z*): 558.9 (100%) $[M-PF_6]^+$, 522.4 (10%) $[M-PF_6-Cl]^+$.

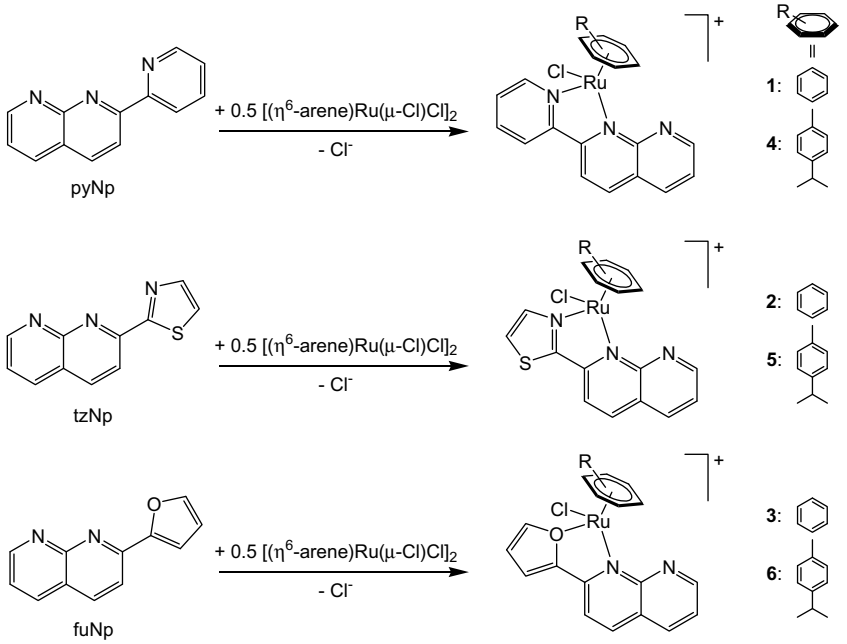
### 2.4. Single crystal X-ray structure analyses

X-ray quality crystals of the complexes [**1**]$Cl \cdot 3H_2O$, [**2**]$PF_6$, [**4**]$PF_6$, [**5**]$PF_6$ and [**10**]$PF_6$ were grown by slow diffusion of diethyl ether into an acetonitrile/dichloromethane solution mixture of [**1**]Cl, [**2**]$PF_6$, [**4**]$PF_6$, [**5**]$PF_6$ and [**10**]$PF_6$, respectively. Crystals of [**1**]$Cl \cdot 3H_2O$, [**2**]$PF_6$, [**4**]$PF_6$, [**5**]$PF_6$ and [**10**]$PF_6$ were mounted on a Stoe Image Plate Diffraction system equipped with a $\phi$ circle goniometer, using Mo K$\alpha$ graphite monochromated radiation ($\alpha$ = 0.71073 Å) with $\phi$ range 0–200°. The structures were solved by direct methods using the program SHELXS-97 [11]. Refinement and all further calculations were carried out using SHELXL-97 [12]. The H-atoms were included in calculated positions and treated as

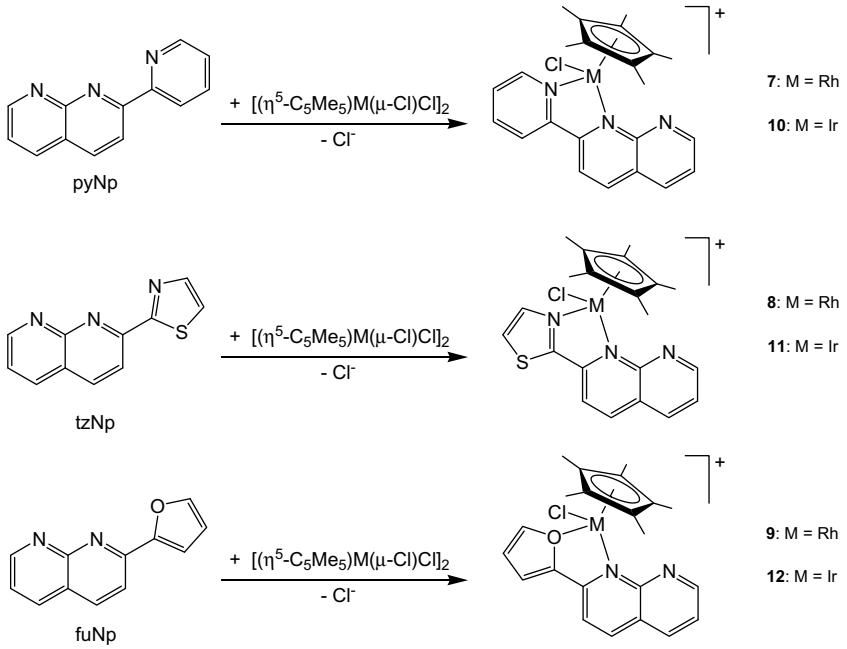
**Table 1**
Crystallographic and structure refinement parameters for complexes [**1**]$Cl \cdot 3H_2O$, [**2**]$PF_6$, [**4**]$PF_6$, [**5**]$PF_6$ and [**10**]$PF_6$

| | [**1**]$Cl \cdot 3H_2O$ | [**2**]$PF_6$ | [**4**]$PF_6$ | [**5**]$PF_6$ | [**10**]$PF_6$ |
|---|---|---|---|---|---|
| Chemical formula | $C_{19}H_{21}Cl_2N_3O_3Ru$ | $C_{17}H_{13}ClF_6N_3PRuS$ | $C_{23}H_{23}ClF_6N_3PRu$ | $C_{21}H_{21}ClF_6N_3PRuS$ | $C_{23}H_{24}ClF_6N_3PIr$ |
| Formula weight | 511.36 | 572.85 | 622.93 | 628.96 | 715.07 |
| Crystal system | Triclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ (No. 2) | $P\,2_1/a$ (No. 14) | $P\,2_1/c$ (No. 14) | $P\,2_1/n$ (No. 14) | $P\,2_1/n$ (No. 14) |
| Crystal color and shape | Orange block | Orange rod | Orange block | Orange rod | Yellow block |
| Crystal size | 0.23 × 0.17 × 0.16 | 0.28 × 0.23 × 0.18 | 0.35 × 0.26 × 0.21 | 0.27 × 0.19 × 0.16 | 0.36 × 0.19 × 0.18 |
| *a* (Å) | 6.8771(9) | 8.1508(7) | 13.5963(11) | 12.2831(11) | 9.1766(4) |
| *b* (Å) | 11.8984(15) | 24.707(3) | 12.6953(17) | 15.1758(18) | 27.5266(16) |
| *c* (Å) | 12.6683(15) | 9.3945(8) | 14.1956(13) | 13.2454(12) | 9.5593(5) |
| $\alpha$ (°) | 77.873(14) | | | | |
| $\beta$ (°) | 85.670(15) | 94.007(10) | 107.432(10) | 91.372(10) | 94.747(4) |
| $\gamma$ (°) | 75.733(14) | | | | |
| *V* (Å$^3$) | 981.9(2) | 1887.3(3) | 2337.8(4) | 2468.3(4) | 2406.4(2) |
| *Z* | 2 | 4 | 4 | 4 | 4 |
| *T* (K) | 173(2) | 173(2) | 173(2) | 173(2) | 173(2) |
| $D_c$ (g cm$^{-3}$) | 1.730 | 2.016 | 1.770 | 1.693 | 1.974 |
| $\mu$ (mm$^{-1}$) | 1.097 | 1.236 | 0.920 | 0.953 | 5.790 |
| Scan range (°) | 2.19 < $\theta$ < 26.01 | 2.17 < $\theta$ < 26.00 | 2.20 < $\theta$ < 26.12 | 2.04 < $\theta$ < 26.09 | 1.48 < $\theta$ < 29.22 |
| Unique reflections | 3112 | 3497 | 4401 | 4809 | 6505 |
| Reflections used [$I > 2\sigma(I)$] | 3579 | 2990 | 2082 | 126 | 4695 |
| $R_{int}$ | 0.0582 | 0.0351 | 0.1881 | 0.0532 | 0.0678 |
| Final *R* indices [$I > 2\sigma(I)$][a] | 0.0329, $wR_2$ 0.0795 | 0.0242, $wR_2$ 0.0612 | 0.0551, $wR_2$ 0.1013 | 0.0320, $wR_2$ 0.0821 | 0.0737, $wR_2$ 0.1907 |
| *R* indices (all data) | 0.0382, $wR_2$ 0.0826 | 0.0304, $wR_2$ 0.0648 | 0.1252, $wR_2$ 0.1176 | 0.0377, $wR_2$ 0.0838 | 0.0958, $wR_2$ 0.2012 |
| Goodness-of-fit | 1.005 | 1.052 | 0.775 | 1.043 | 1.077 |
| Maximum, minimum $\Delta\rho$ (e Å$^{-3}$) | 0.617, −0.853 | 0.529, −0.929 | 0.639, −0.897 | 1.443, −0.634 | 11.432, −4.606 |

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




**Scheme 1.**




**Scheme 2.**

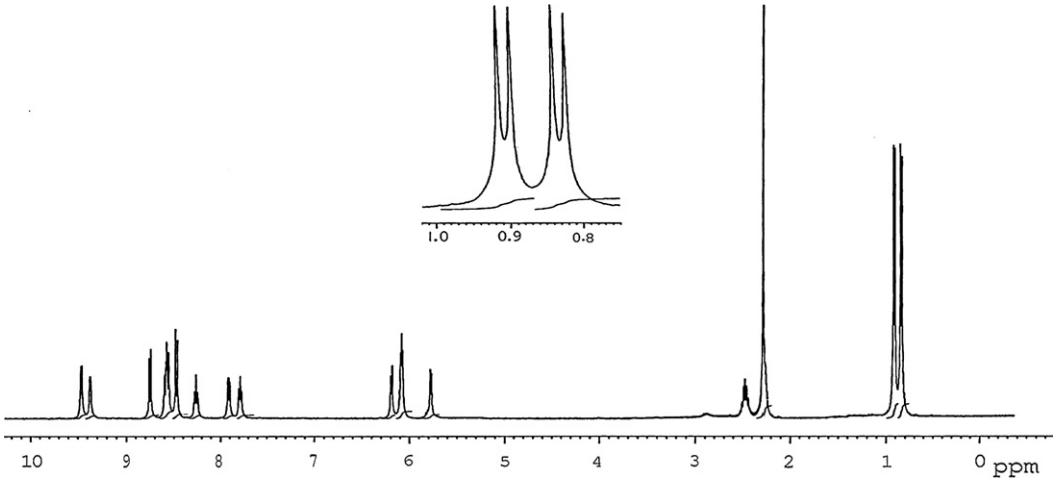



**Fig. 1.** $^1$H NMR spectrum of complex **4** in acetonitrile-$d_3$.

riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on $F^2$. In [**10**]$PF_6$, a positive residual electron density of 11.43 e Å$^{-3}$ (0.80 Å from Ir) and an electron density hole of −4.61 e Å$^{-3}$ (0.66 Å from Ir) surround the heavy iridium atom. Crystallographic details are summarised in Table 1. Figs. 3 and 4 were drawn with ORTEP-32 [13] and Figs. 4 and 5 with the software MERCURY [14].

## 3. Results and discussion

### 3.1. Syntheses

The dinuclear arene ruthenium complexes [($\eta^6$-arene)Ru(μ-Cl)Cl]$_2$ (arene = $C_6H_6$, *p*-$^i$Pr$C_6H_4$Me) react in acetonitrile with the 2-substituted-1,8-naphthyridine ligands – 2-(2-pyridyl)-1,8-naphthyridine (pyNp), 2-(2-thiazolyl)-1,8-naphthyridine (tzNp) and 2-(2-furyl)-1,8-naphthyridine (fuNp) to give the mononuclear cationic complexes [($\eta^6$-$C_6H_6$)Ru(L)Cl]$^+$ {L = pyNp (**1**); tzNp (**2**); fuNp (**3**)}, [($\eta^6$-*p*-$^i$Pr$C_6H_4$Me)Ru(L)Cl]$^+$ {L = pyNp (**4**); tzNp (**5**); fuNp (**6**)} (Scheme 1). Cation **1** is isolated as its chloro salt, while the other cationic ruthenium complexes are obtained as their hexafluorophosphate salts.

Similarly, the reaction in methanol of the dimeric chloro-bridged complexes [($\eta^5$-$C_5Me_5$)M(μ-Cl)Cl]$_2$ (M = Rh, Ir) with the same 2-substituted-1,8-naphthyridine ligands leads to the formation of the mononuclear cationic complexes [($\eta^5$-$C_5Me_5$)Rh(L)Cl]$^+$ {L = pyNp (**7**); tzNp (**8**); fuNp (**9**)} and [($\eta^5$-$C_5Me_5$)Ir(L)Cl]$^+$ {L = pyNp (**10**); tzNp (**11**); fuNp (**12**)} (Scheme 2). All rhodium and iridium complexes are isolated as their hexafluorophosphate salts.

All complexes are orange yellow in color, non-hygroscopic, air stable solids. However, the complexes with the fuNp ligand (**3, 6, 9** and **12**) are unstable in solution. They are soluble in acetonitrile

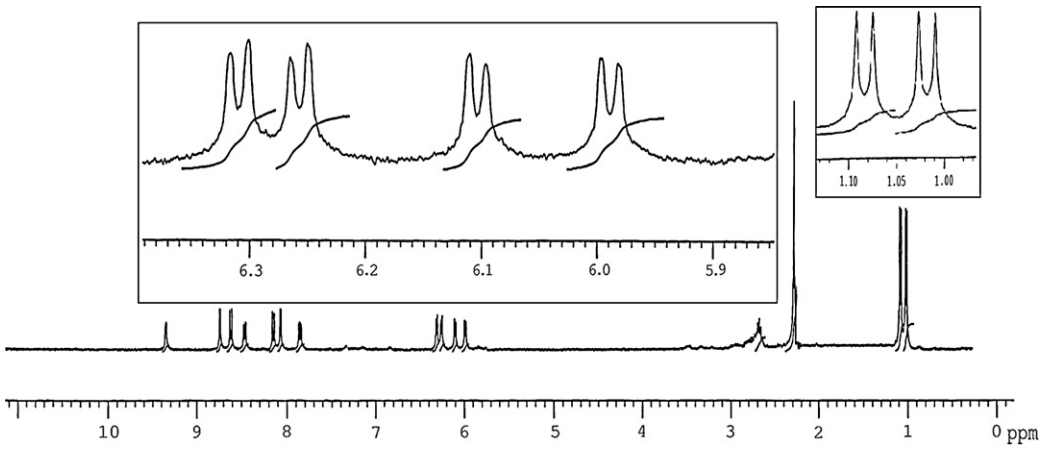



**Fig. 2.** $^1$H NMR spectrum of complex **5** in acetonitrile-$d_3$.

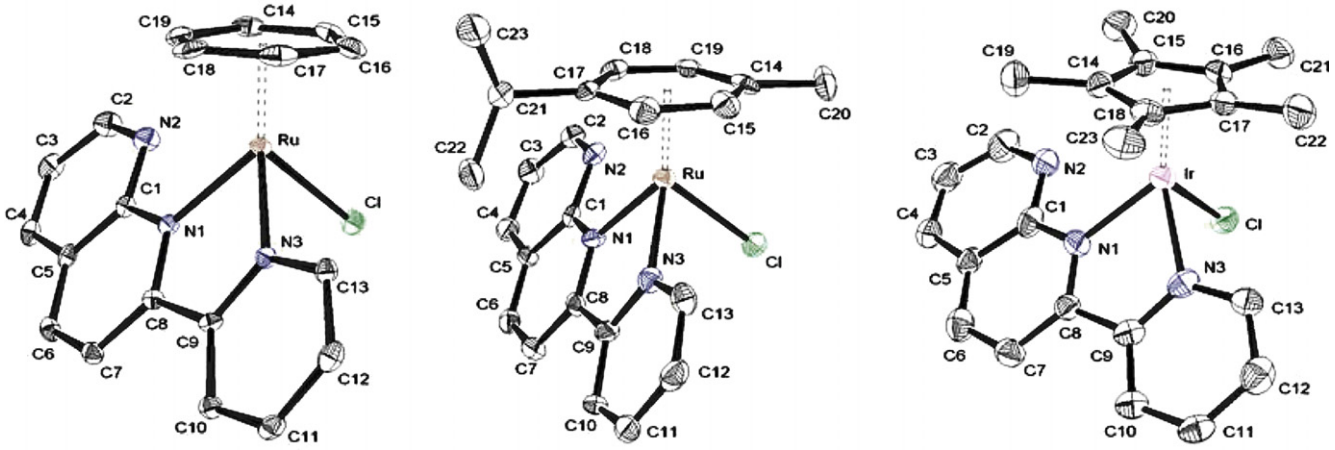



**Fig. 3.** ORTEP diagram of cations **1** (left), **4** (middle) and **10** (right) at 35% probability level with anion and H atoms being omitted for clarity.

but partially soluble in dichloromethane, chloroform and acetone. The reactions of pyNp and tzNp with the dinuclear rhodium and iridium precursors are instantaneous as compared to those with the ruthenium precursors. However, the reaction is comparatively slow for fuNp with these dinuclear precursors.

The infrared spectra of the complexes **2**–**12** exhibit a strong band in the region 844–850 $cm^{-1}$, a typical $\nu_{P-F}$ stretching band for the $PF_6$ anions. Moreover, all complexes show absorption bands at 1600–1610 $cm^{-1}$ and 1470–1474 $cm^{-1}$ for the $\nu_{C=C}$ and $\nu_{C=N}$ vibrations of the 1,8-naphthyridine moiety [14b]. The complexes **2**, **5**, **8** and **11** show two additional absorption bands at 1450–1452 $cm^{-1}$ and 1480–1484 $cm^{-1}$ corresponding to the $\nu_{C=N}$ and $\nu_{C=S}$ stretching frequency of the thiazolyl group. The complexes **3**, **6**, **9** and **12** show a characteristic absorption band at 1626–1630 $cm^{-1}$ which correspond to $\nu_{C=C}$ of the furyl group.

### 3.2. NMR spectrometry

The $^1$H NMR spectra of the benzene, *p*-cymene and pentamethylcyclopentadienyl derivatives which have pyNp, tzNp and fuNp as ligands exhibit nine resonances in the region $\delta$ = 9.56–7.78, seven resonances around $\delta$ = 9.41–7.90, and eight resonances around $\delta$ = 9.58–6.68 in the aromatic region, respectively. In addition to these signals, complexes **1**, **2** and **3** exhibit a singlet resonance for the benzene ring protons at $\delta$ = 6.20–5.93. Complexes **4**, **5** and **6** exhibit an unusual pattern of resonances for the *p*-cymene ligand. For instance, the methyl protons of the isopropyl group displays two doublets at ca. $\delta$ = 1.18–1.07, instead of one doublet (see Figs. 1 and 2) as in the starting complex. The aromatic protons of the *p*-cymene ligand displays three doublets for complex **4** (see Fig. 1) and four doublets for complex **5** (see Fig. 2) at ca. $\delta$ = 6.31–5.79, instead of two doublets as in the starting precursor. This unusual pattern is due to the diastereotopic methyl protons of the isopropyl group and aromatic protons of the *p*-cymene ligand, since the ruthenium atom is stereogenic due to the coordination of four different ligand atoms [15]. The other reason could be due to the loss of planarity of the *p*-cymene ligand, because of the steric nature of the ligand [16].

All these complexes show down field shift for all protons compared to the starting precursors, which might result from the charge transfer from metal centre to naphthyridine-based ligands such as pyNp and tzNp. Complexes **7** to **12** exhibit a singlet resonance at $\delta$ = 1.71–1.55 for the five methyl groups of the pentamethylcyclopentadienyl ligand.

### 3.3. X-ray structural study

The molecular structure of the benzene derivatives [($\eta^6$-$C_6H_6$)Ru(pyNp)Cl]Cl or [**1**]Cl and [($\eta^6$-$C_6H_6$)Ru(tzNp)Cl]$PF_6$ or [**2**]$PF_6$, the *p*-cymene derivatives [($\eta^6$-*p*-$^i$Pr$C_6H_4$Me)Ru-(pyNp)Cl]$PF_6$ or [**4**]$PF_6$ and [($\eta^6$-*p*-$^i$Pr$C_6H_4$Me)Ru(tzNp)Cl]$PF_6$ or [**5**]$PF_6$ as well as the pentamethylcyclopentadienyl iridium com-

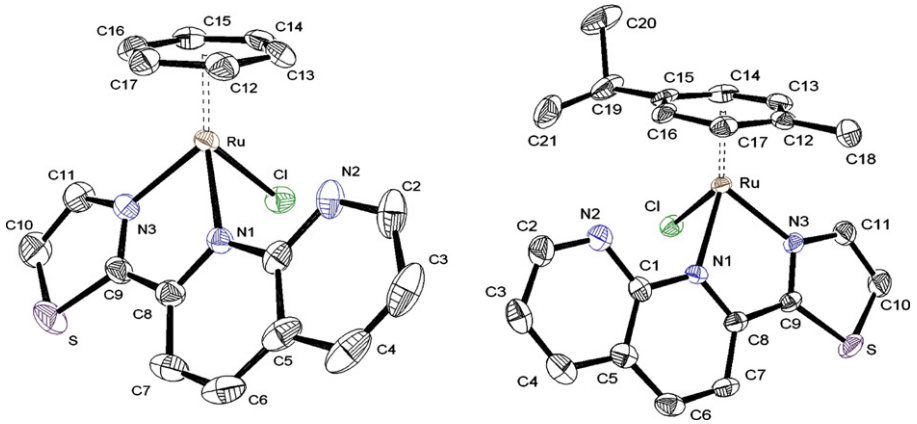



**Fig. 4.** Hydrogen-bonded network observed in [**1**]Cl · $3H_2O$ with H–Cl distances.

plex [($\eta^5$-$C_5Me_5$)Ir(pyNp)Cl]$PF_6$ or [**10**]$PF_6$ have been established by single crystal X-ray structure analysis. All cationic complexes show a typical piano-stool geometry with the metal centre being coordinated by an aromatic ligand, a terminal chloro ligand and a chelating 2-substituted-1,8-naphthyridine ligand. Formally, the 2-substituted-1,8-naphthyridine ligand can coordinate to the metal centre either through one or two nitrogen atoms of the naphthyridine moiety or through the N, O or S atoms of the 2-substituted ring. Interestingly, in this study, all metal centres were found to be coordinated to the 2-substituted-1,8-naphthyridine ligand in a five-membered ring chelating fashion involving one nitrogen atom of the naphthyridine moiety and the nitrogen atom of the 2-pyridyl or 2-thiazolyl group and the oxygen atom of the 2-furyl group. Indeed, in [**1**]Cl, [**4**]$PF_6$ and [**10**]$PF_6$ the pyNp ligand is found as a five-membered ring *N,N*-chelating ligand (see Fig. 3).

Similarly, in [**2**]$PF_6$ and [**5**]$PF_6$, the tzNp ligand is found to coordinate through the N1 atom of the naphthyridine moiety and the N3 atom of the 2-substituted thiazolyl ring to generate a five-membered ring metallocycle (see Fig. 4). In these tzNp complexes, the S atom points away from the metal centre and show no interaction with neighbouring cations. Selected bond lengths and angles for [**1**]Cl · $3H_2O$, [**2**]$PF_6$, [**4**]$PF_6$, [**5**]$PF_6$ and [**10**]$PF_6$ are presented in Table 2.

As amplified in Figs. 3 and 4, all cations possess metal-centred chirality as the metal atom is coordinated to four different ligand atoms. However, since none of the ligands contains chiral centres, they are all obtained as a racemic mixture and they all crystallise in centrosymmetric space groups.

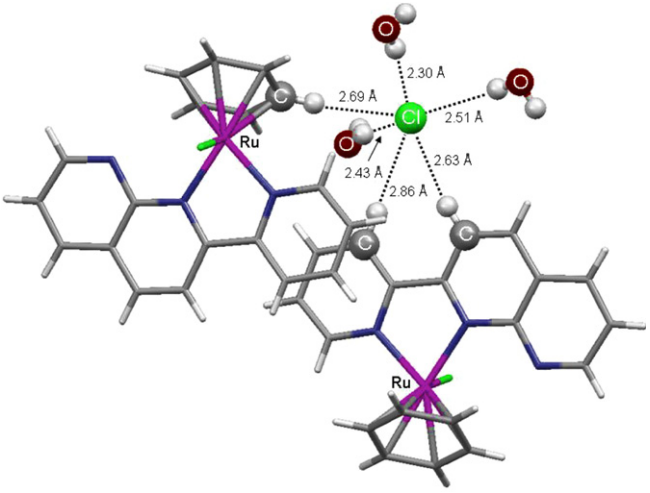
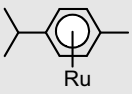
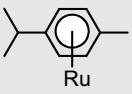
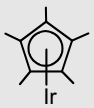



**Fig. 5.** ORTEP diagram of cations **2** (left) and **5** (right) at 50% probability level with anion and H atoms being omitted for clarity.

The distances between the ruthenium atom and the centroid of the $C_6$ aromatic ring in **1**, **2**, **4** and **5** are comparable (1.67–1.69 Å)

**Table 2**
Selected bond lengths and angles for complexes [**1**]Cl · $3H_2O$, [**2**]$PF_6$, [**4**]$PF_6$, [**5**]$PF_6$ and [**10**]$PF_6$

| | **1** (pyNp) | **2** (tzNp) | **4** (pyNp) | **5** (tzNp) | **10** (pyNp) |
|---|---|---|---|---|---|
| |  |  |  |  |  |
| *Distances (Å)* | | | | | |
| M–Cl | 2.4147(8) | 2.4045(7) | 2.396(2) | 2.4080(7) | 2.412(3) |
| M–N1 | 2.109(3) | 2.123(2) | 2.112(6) | 2.152(2) | 2.107(9) |
| M–N3 | 2.088(2) | 2.091(2) | 2.078(6) | 2.073(2) | 2.136(9) |
| M–centroid[a] | 1.68 | 1.67 | 1.69 | 1.68 | 1.79 |
| C8–C9 | 1.478(4) | 1.448(4) | 1.485(9) | 1.444(4) | 1.51(2) |
| *Angles (°)* | | | | | |
| N1–M–N3 | 76.60(9) | 76.82(8) | 76.9(2) | 76.07(9) | 74.9(4) |
| N1–M–Cl | 85.75(7) | 83.99(6) | 83.3(2) | 84.76(6) | 87.7(3) |
| N3–M–Cl | 85.13(6) | 86.12(6) | 84.9(2) | 86.24(7) | 87.4(3) |

[a] Calculated centroid of the $C_5$ or $C_6$ coordinated aromatic ring.

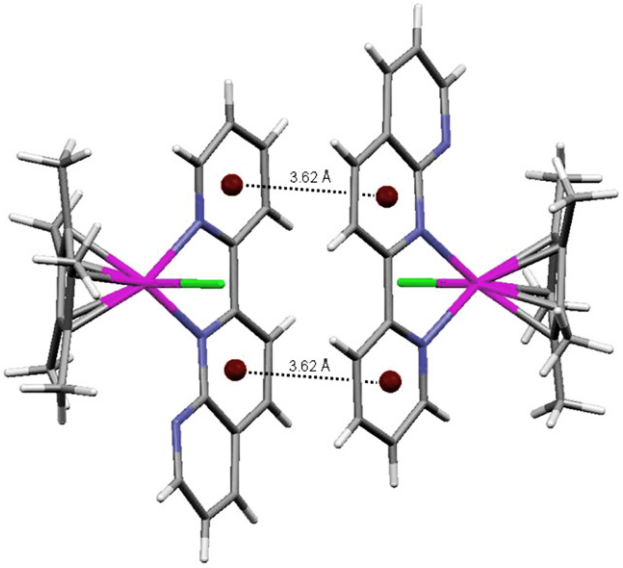



**Fig. 6.** Dimeric structure of [**10**]$PF_6$ showing the separation of the π-stacking system.

**Table 3**
UV/Vis data for selected complexes in acetonitrile at 298 K

| No. | Complex | $\lambda_{max}$ (nm)/$\varepsilon$ $10^{-5}$ $M^{-1}$ $cm^{-1}$ |
|---|---|---|
| 2 | [($\eta^6$-$C_6H_6$)Ru(tzNp)Cl]$^+$ | 342 (0.30) 357 (0.37) 422 (0.12) |
| 3 | [($\eta^6$-$C_6H_6$)Ru(fuNp)Cl]$^+$ | 338 (0.70) 352 (sh) 385 (sh) ($10^{-3}$ $M^{-1}$ $cm^{-1}$) |
| 5 | [($\eta^6$-*p*-$^i$PrC$_6$H$_4$Me)Ru(tzNp)Cl]$^+$ | 342 (0.34) 357 (0.37) 435 (0.11) |
| 7 | [($\eta^5$-$C_5Me_5$)Rh(pyNp)Cl]$^+$ | 342 (0.24) 385 (0.25) 436 (0.11) |
| 9 | [($\eta^5$-$C_5Me_5$)Rh(fuNp)Cl]$^+$ | 334 (0.41) 348 (sh) 390 (sh) |

but quite shorter than the distance between the iridium atom and the $C_5$ aromatic ring observed in **10** (1.79 Å). The M–N1 bond distances [2.107(9)–2.152(2) Å] are comparable to those in [($\eta^6$-*p*-$^i$PrC$_6$H$_4$Me)RuCl(2,3-bis(2-pyridyl)pyrazine)]$BF_4$ [17] [($\eta^6$-$C_6H_6$)RuCl(2-(1-imidazol-2-yl)pyridine)]$PF_6$ [18a] and [($\eta^5$-$C_5Me_5$)Ir(2-(2'-pyridyl)imidazole)Cl]$PF_6$ [18b]. The Ir–N3 bond distance (2.136(9) Å) in **10** is slightly longer than the corresponding distances in the ruthenium complexes **1**, **2**, **4** and **5** (2.073(2)–2.091(2) Å), while the M–Cl bond lengths show no significant differences among the five cations. However, a noticeable difference is observed in the distances of the C8–C9 connecting bond (naphthyridine 2-substituted ring C–C bond). In the tzNp derivatives, the C8–C9 distances [1.448(4) in **2** and 1.444(4) Å in **5**] are shorter than those found in the pyNp derivatives **1**, **4** and **10** [1.478(4), 1.485(9) and 1.51(2) Å].

Complex [**1**]Cl crystallises with three molecules of water per asymmetric unit, forming an intricate hydrogen-bonded network around the chloride atom. It involves the three water molecules and some hydrogen atoms of the pyNp and $C_6H_6$ ligands (see Fig. 5). The O–O and O–C distances of the hydrogen bonds range from 3.12 to 3.77 Å, with O–H...O or C–H...O angles ranging from 137.6° to 177.0°.

In the crystal packing of [**10**]$PF_6$, two cationic molecules of **10** form a dimer through π-stacking interactions (see Fig. 6). The distance observed between the two π-stacking interacting systems (centroid···centroid 3.62 Å) is in good agreement with the theoretical value calculated for a slipped parallel stacking mode [19].

### 3.4. UV/Vis spectroscopy

Electronic absorption spectral data of selected complexes at $10^{-5}$ M concentration in the range 320–520 nm are summarised in Table 3. The spectra of these complexes are characterized by two main features, *viz*., an intense ligand-localized or intra-ligand $\pi \rightarrow \pi^*$ transition in the ultraviolet region and metal-to-ligand charge transfer (MLCT) $d\pi(M) \rightarrow \pi^*$ (Np-based ligands) bands in the visible region [20]. Since the low spin $d^6$ configuration of the mononuclear complexes provides filled orbitals of proper symmetry at the Ru(II), Rh(III) and Ir(III) centres, these can interact with low lying $\pi^*$ orbitals of the ligands. All these complexes show two absorption bands in the region 340–390 nm, while the complexes bearing fuNp ligand (N,O donor) exhibit two absorption bands in blue shift at 330–355 nm, the second being a shoulder of the first band. It shows a series of ligand-centred $\pi$–$\pi^*$ transitions with high intensity absorption bands in the UV region. One should therefore expect a band attributable to the metal-to-ligand charge transfer (MLCT) ($t_{2g}$–$\pi^*$) transitions in their electronic spectra [21]. All these complexes exhibit a broad absorption band with low intensity and low energy at 420–440 nm, while the complexes bearing fuNp ligand exhibit a very low intensity shoulder in the near visible region 385–390 nm, which originate from dπ (Ru, Rh and Ir) → $\pi^*$ (naphthyridine based ligands) metal-to-ligand charge transfer transitions. Representative spectra of these complexes are presented in Fig. 7.

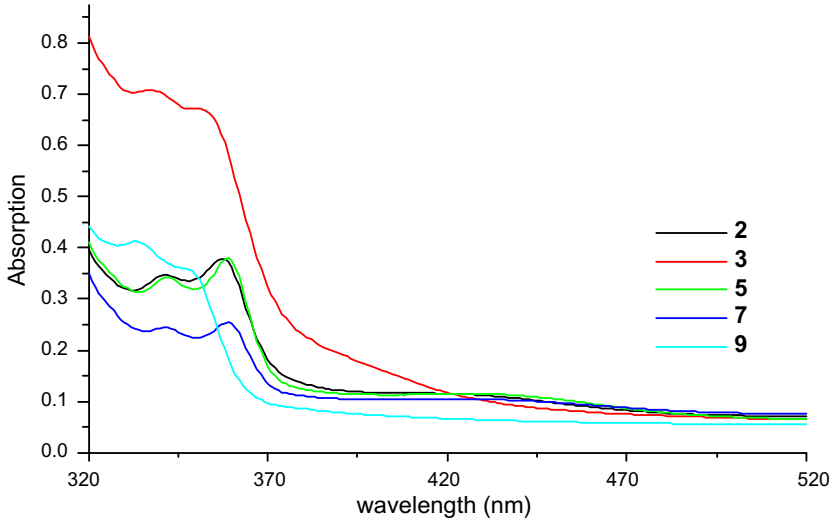



**Fig. 7.** Selected UV/Vis electronic spectrum in acetonitrile at 298 K.

## 4. Conclusion

In this work we demonstrated that all metal centres are coordinated to the 2-substituted-1,8-naphthyridine ligand in a five-membered ring chelating fashion involving one nitrogen atom of the naphthyridine moiety and the nitrogen atom of the 2-pyridyl or 2-thiazolyl group and the oxygen atom of the 2-furyl group. The formation of bridging complexes with the remaining nitrogen atom of the naphthyridine moiety was unsuccessful in our hand.

## 5. Supplementary material

CCDC 680855, 680856, 680857, 680858 and 680859 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## Acknowledgements

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