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Synthetic, spectral and structural studies of some homo and hetero binuclear arene ruthenium (II) polypyridyl complexes

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Abstract

Homo-hetero binuclear cationic complexes with the formulation $[(\eta^6\text{-arene})RuCl(\mu\text{-dpp})(L)]^+$ (η^6-arene = benzene; L = $PdCl_2$ (**1a**); $PtCl_2$ (**1b**), and η^6-arene = *p*-cymene; L = $PdCl_2$ (**2a**); $PtCl_2$ (**2b**)), $[(\eta^6\text{-arene})RuCl(\mu\text{-dpp})(L)]^{2+}$ (η^6-arene = *p*-cymene; L = $[(\eta^6\text{-}C_6H_6)RuCl]$ (**2c**), and $[(\eta^6\text{-}C_{10}H_{14})RuCl]$ (**2d**)) were prepared. Molecular structure of the representative homo binuclear complex $[\{(\eta^6\text{-}C_{10}H_{14})RuCl\}(\mu\text{-dpp})\{(\eta^6\text{-}C_{10}H_{14})RuCl\}](PF_6)_2$ (**2d**) was determined crystallographically. Weak interaction studies on the complex **2d** revealed stabilisation of the crystal packing by weak inter and intra molecular C–H···X (X = F, Cl, π) and π–π interactions. The C–H···F interactions lead to parallel helical chains and encapsulation of counter anion in self-assembled cavity arising from C–H···π and π–π weak interactions.
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1. Introduction

Multiple homo-hetero mixed valance compounds have been suggested in the design of electrochromic devices, solar energy conversion, catalysts, photo-induced magnetic memory devices, chemical sensors, nano-scale switches with ultra fast write times and molecular scale rectifiers [1]. Despite the diversity of these potential applications, relatively little is known about how the properties of electron transfer between a single donor and acceptor is influenced by their inclusion into larger supramolecular assemblies. In this regard, ruthenium complexes bridged by multiple nitrogen donor polypyridyl ligands have received considerable recent attention because of their possible applications in homogeneous catalysis [2], as multi electron storage system [3], in the designing of new materials [4] and in photo physical

and photochemical molecular devices [5]. One of the simplest linkers commonly used in assembling metals in such arrays is 2,3-bis(2-pyridyl)pyrazine(dpp). This molecule acts as a bis-chelating ligand to bridge two metal centres and by virtue of its π system, often function as conduits for good π-acceptors. Relatively low-energy LUMO of the pyrazine moiety in this molecule is expected to facilitate electronic delocalisation between the bridged metal centers [6].

Arene ruthenium complexes play an important role in organometallic chemistry. Reactions of the chloro-bridged dimeric arene ruthenium complexes $[\{(\eta^6\text{-arene})RuCl(\mu\text{-Cl})\}_2]$ with Lewis bases and a variety of different ligands have extensively been studied. However, there are only a few reports dealing with the reactivity of η^6-arene ruthenium complexes with polypyridyl ligands leading to homo/hetero binuclear complexes [7]. Recently, we have reported mononuclear arene ruthenium complexes $[(\eta^6\text{-arene})RuCl(dpp)]^+$ (arene = hexamethylbenzene or *p*-cymene) containing 2,3-bis

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(2-pyridyl)-pyrazine(dpp) [8]. It was observed that the complexes [{(η^6-arene)RuCl(dpp)]$^+$ (arene = hexamethylbenzene or p-cymene) have the potential to behave as metallo-ligands in the development of homo/hetero bimetallic systems [9]. Further, mixed metal complexes in which Ru(II) is coupled to Pt(II) through polyazine bridging ligands have been of recent interest [10]. Systems of the type [(bpy)$_2$Ru(dpp)PtCl$_2$]$^{+2}$ has shown that the coordination of Pt(II) centre to the remote nitrogen of the bridging ligand stabilizes $\pi*$ orbitals of the bridging ligand [11]. This results in a red shift of the bridging ligand based MLCT transitions.

During past few years we have been interested in the synthesis of mononuclear organometallic systems and possible use of such systems in the development of homo/hetero binuclear complexes [12]. The present work is an extension in this direction and in this article, we report synthetic, spectral, and structural studies on the homo-hetero binuclear cationic complexes [(η^6-arene)RuCl(μ-dpp)(L)]$^+$ (η^6-arene = benzene; L = PdCl$_2$, **1a**; PtCl$_2$, **1b**, and η^6-arene = p-cymene; L = PdCl$_2$, **2a**; PtCl$_2$, **2b**), [(η^6-arene)RuCl(μ-dpp)(L)]$^{2+}$ (η^6-arene = p-cymene; L = [(η^6-C$_6$H$_6$)RuCl], **2c**, and [(η^6-C$_{10}$H$_{14}$)-RuCl], **2d**). We also describe herein molecular structure of the binuclear complex [{(η^6-C$_{10}$H$_{14}$)RuCl}(μ-dpp)-{(η^6-C$_{10}$H$_{14}$)RuCl}](PF$_6$)$_2$ (**2d**) and weak interaction studies on this complex.

2. Results and discussion

2.1. Synthesis

The mononuclear arene ruthenium complexes were obtained in usual manner from the reactions of the dimeric chloro bridged complexes [{(η^6-arene)RuCl(μ-Cl)}$_2$] (arene = benzene or p-cymene) with dpp in methanol and were isolated in pretty good yield following our earlier method [8] and that of Marco et al. [10a]. The cationic mononuclear complexes upon treatment with [{(η^6-C$_6$H$_6$)RuCl$_2$}$_2$], [{(η^6-C$_{10}$H$_{14}$)RuCl$_2$}$_2$], K$_2$PtCl$_4$ and [PdCl$_2$(C$_6$H$_5$CN)$_2$] in methanol under refluxing conditions gave homo-hetero binuclear arene ruthenium complexes. The Ru centre in these complexes is a stereogenic centre it may lead to several stereoisomers, but we have isolated the major product and our studies mainly deal with the major product. (Scheme 1)

2.2. Characterization

The binuclear complexes are air stable, non-hygroscopic shiny crystalline solids, sparingly soluble in common organic solvents, and insoluble in diethyl ether and petroleum ether. The complexes were fully characterised by IR, NMR (^{1}H and ^{13}C), UV–Vis, FAB-MS spectroscopy. Analytical data of the complexes (recorded in the
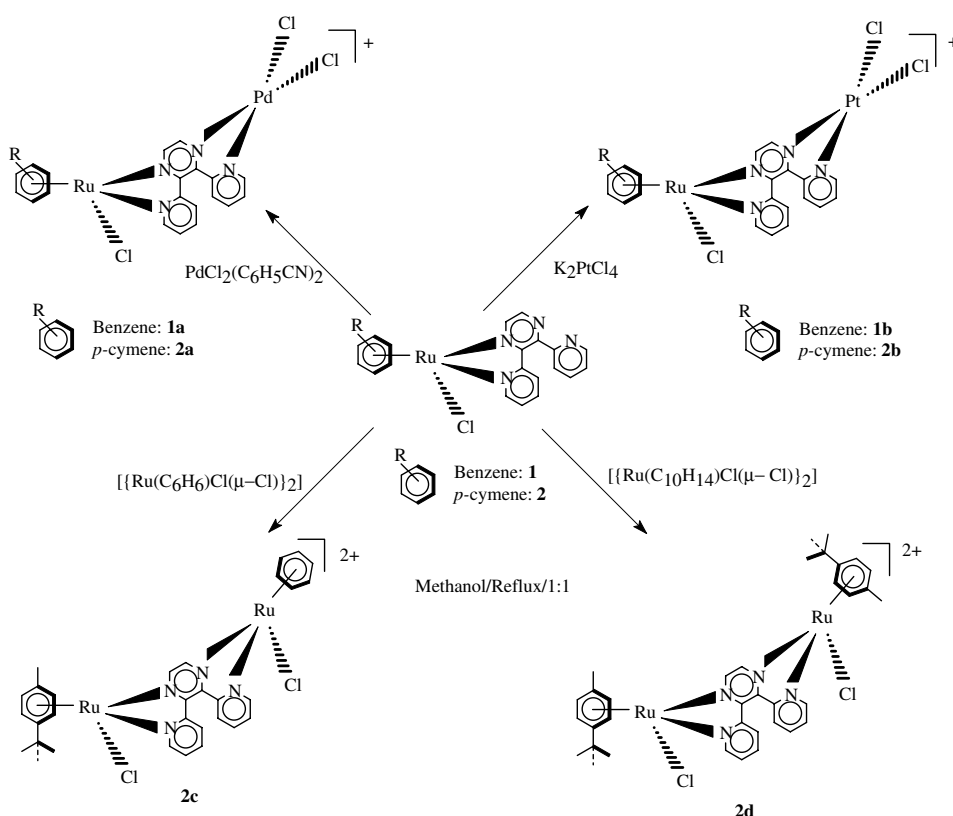
Scheme 1.

Section 3) corroborated well to their respective formulations. The FAB-MS spectra of the complexes correspond to the respective formulations. The position of various peaks and overall fragmentation pattern (recorded in Section 3) are consistent with the formulation of the respective complexes and strongly support the homo-hetero binuclear nature of the complexes.

Infrared spectra of the complexes in nujol displayed bands in the region of 1674–1490 cm^{-1}, assignable to ν(C–N) and ν(C=C) stretching vibrations of the ligand and the bands around 289–355 cm^{-1}, assignable to ν(M–Cl) (M = Ru, Pd, Pt). The complexes displayed bands at 1054 and 845 cm^{-1}, associated with the counter anion BF$_4^-$ and PF$_6^-$, respectively [1d,13].

The ^{1}H and ^{13}C NMR spectral data of the complexes (recorded in Section 3) are in good agreement with the formation of the respective complexes. Protons of the bridged ligand dpp exhibited a downfield shift as compared to that in the mononuclear complexes. Scheme showing numbering of the protons used for assignment of the ^{1}H NMR spectra for **2a** is shown in Fig. 1. Doublets are assigned for the protons a/d, e/h, i/j positions and triplets are assigned to the protons b/c and f/g of the bridged dpp ligand. The ^{1}H NMR spectra of the binuclear complex **2a** exhibited resonance at δ 9.62 (d, 1Ha, 3.0 Hz), 9.49 (d, 1Hh, 5.1 Hz), 8.90 (d, 1Hi, 2.7 Hz), 8.63 (d, 1Hj, 3.9 Hz), 8.09 (t, 1Hb, 7.8 Hz), 7.99 (d, 1Hd, 7.8 Hz), 7.76 (t, 1Hg, 7.5 Hz), 7.63 (m, 2Hcf), 7.05 (d, 1He, 7.8 Hz) assignable to pyrazyl and pyridyl protons of the ligand dpp [7]. This region of the spectrum integrated for ten protons as expected for the coordinated dpp ligand. The protons due to p-cymene resonated at δ6.124 (dd, 2Hk, 6.0 Hz), 5.952 (dd, 2Hl, 6.3 Hz), 2.673 (sep, 1H, 6.9 Hz), 2.332 (s, 3H) and 1.123 (d, 6H, 4.2 Hz) ppm. The position and integrated intensity of different signals conformed well to the formation of hetero binuclear complex **2a**. Similar trends were observed in the ^{1}H NMR spectra of the other complexes. ^{13}C{^{1}H} NMR spectra of the complex **2a** followed the trends observed in the ^{1}H NMR spectra. The dpp car-

bons resonated at 153.2, 151.4, 147.2, 137.8, 127.4 and 124.4, whereas the p-cymene carbons resonated at 106.2 (C–CHMe$_2$), 99.8 (C–CH$_3$), 87.4–85.2 (C_6H$_4$), 30.5 (CH(CH$_3$)$_2$), 21.7 (CH(CH_3)$_2$), 16.9 (C–CH_3) ppm.

Absorption spectra of the binuclear complexes **1a–b** and **2a–2d**, in acetone displayed bands in the range 430–456 nm, and an intense higher energy band at $\sim$341 nm and at $\sim$292 nm. The lowest energy band range 430–456 nm have been assigned to metal to ligand charge transfer transition MLCT (d$\pi \to \pi$*dpp). The intense band at $\sim$341 nm has been assigned to dpp-centered intra-ligand (π–π*) transitions. The high-energy band $\sim$292 nm has been assigned to benzene-centered intra-ligand (π–π*) transitions [8]. The position of the MLCT (d$\pi \to \pi^*_{\text{dpp}}$) transitions in the spectra of binuclear complexes **1a**, **2a**, **1b**, **2b**, **2c**, and **2d** exhibited significant bathochromic shifts as compared to the mononuclear complexes **1**, **2** (**1a**: 435 nm (33 nm); **2a**: 445 nm (25 nm); **1b**: 433 nm (31 nm); **2b**: 432 nm (12 nm); **2c**: 430 nm (10 nm); **2d**: 456 nm (31 nm)) (Fig. 2). In general, coordination of another electropositive
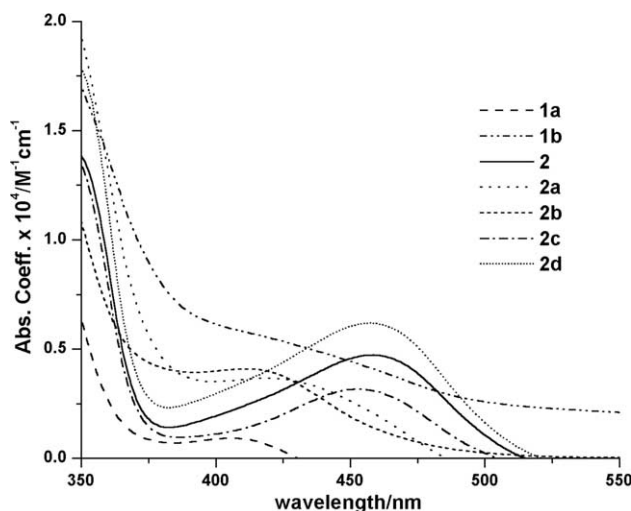

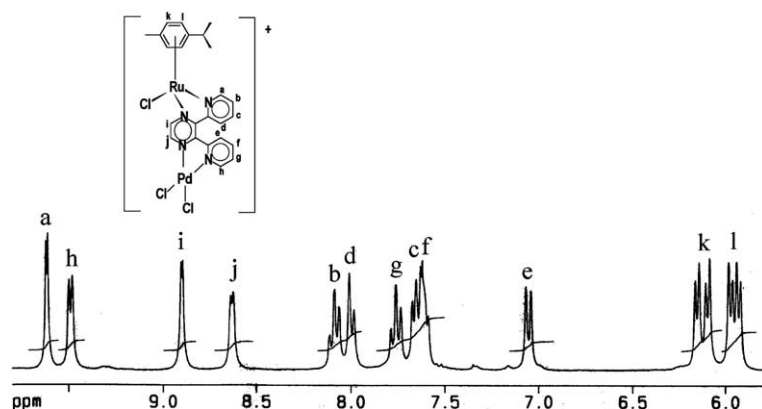Fig. 2. Absorption spectra of the complexes in acetone.

Fig. 1. ^{1}H NMR spectra of [{(η^6-C$_{10}$H$_{14}$)RuCl}$_2$(μ-dpp)(PdCl$_2$)]BF$_4$ (**2a**) in CDCl$_3$.

M(II) metal centre through the vacant donor sites of dpp in the mononuclear complex stabilizes the π* orbital of the ligand by lowering the HOMO–LUMO gap. This may account for the observed bathochromic shifts in the position of MLCT of the binuclear complexes and it is consistent with other reports [7].

2.3. Molecular structure determination

Molecular structure of the representative complex **2d** was determined by single crystal X-ray diffraction analyses. Details about the data collection, solution and refinement are recorded in Table 1. Molecular structure of the complex **2d** with atom numbering scheme is shown in Fig. 3 and important geometrical parameters are tabulated in Table 2. Complex **2d** crystallizes in the monoclinic space group $P2_1/a$ with two-ruthenium

Table 1
Crystal data for the complex **2d**

Empirical formula	$C_{34}H_{38}Cl_2F_{12}N_4P_2Ru_2$
Formula weight	1065.66
Colour and habit	Red, block
Crystal size (mm)	$0.5 \times 0.3 \times 0.2$
Crystal system, space group	Monoclinic, $P2_1/a$
a (Å)	14.521(9)
b (Å)	19.089(7)
c (Å)	15.926(8)
β (°)	109.58(8)
V (Å^3)	4159(4)
Z, D_c (g cm^{-3})	4, 1.702
μ (mm^{-1})	8.558
T (K)	293(2)
λ(Cu Kα) (Å)	1.54180
No. of reflections	7303
No. of refined parameter	517
R factor [$I > 2\sigma(I)$]	0.0649
wR_2 [$I > 2\sigma(I)$]	0.1728
R factor (all data)	0.0827
wR_2 (all data)	0.1960
Goodness-of-fit	0.785

Table 2
Selected bond lengths (Å) bond angles (°) and torsion angles for the complex **2d**

Ru(1)–N(1)	2.058(5)
Ru(1)–N(3)	2.072(5)
Ru(2)–N(2)	2.037(6)
Ru(2)–N(4)	2.069(5)
Ru(1)–Cl(1)	2.381(2)
Ru(2)–Cl(2)	2.395(3)
Ru(1)–C(2)	2.202(5)
Ru(1)–C(3)	2.182(6)
Ru(1)–C(4)	2.217(6)
Ru(1)–C(6)	2.205(6)
Ru(1)–C(5)	2.236(6)
Ru(1)–C(7)	2.200(6)
Ru(1)–Ct(01)	1.698(6)
Ru(2)–C(12)	2.196(8)
Ru(2)–C(13)	2.207(7)
Ru(2)–C(14)	2.197(6)
Ru(2)–C(15)	2.251(6)
Ru(2)–C(16)	2.191(7)
Ru(2)–C(17)	2.204(7)
Ru(2)–Ct(02)	1.703(6)
N(1)–Ru(1)–N(3)	76.44(18)
N(1)–Ru(1)–Cl(1)	84.00(18)
N(3)–Ru(1)–Cl(1)	85.74(13)
N(2)–Ru(2)–N(4)	76.79(18)
N(2)–Ru(2)–Cl(2)	87.56(19)
N(4)–Ru(2)–Cl(2)	84.80(15)
N(1)–C(26)–C(25)–N(3)	−9.8(7)
N(2)–C(29)–C(30)–N(4)	−18.4(7)
N(1)–C(26)–C(29)–N(2)	−17.4(8)
N(1)–C(27)–C(28)–N(2)	−11.3(11)

centres bridged by dpp in the crystallographic asymmetric unit. The molecular structure of the complex **2d** shows a distorted octahedral coordination geometry about both the ruthenium centres and is completed by pyrazyl nitrogen atom N(1), pyridyl nitrogen N(3), the chloride ligand Cl(1) and *p*-cymene ring [C(2)–C(7)] about Ru(1). Similarly Ru(2) is coordinated through pyrazyl nitrogen N(2), pyridyl nitrogen N(4), the chloride ligand Cl(2) and *p*-cymene ring [C(12)–C(17)] in
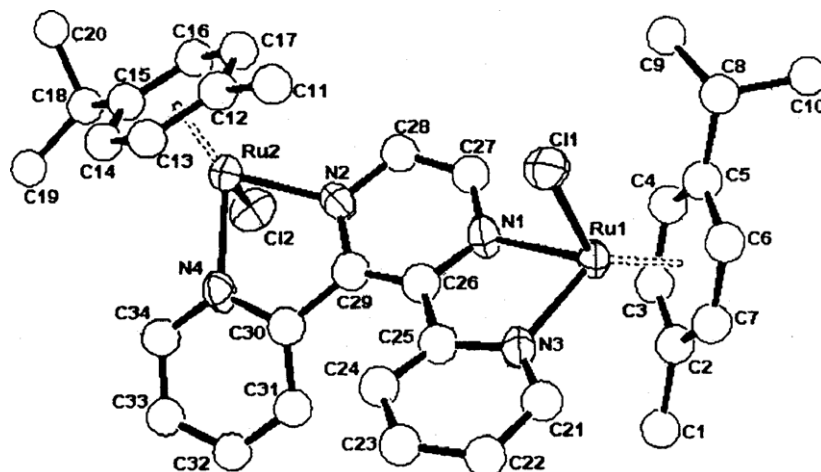

Fig. 3. Molecular representation of the complex **2d**.

η^6-manner. The *p*-cymene ring is planar and the Ru–C distances are almost equal with an average bond length of 2.208(7) Å [range, 2.182(6)–2.236(6) Å]. The Ru(1) to *p*-cymene ring centroid distance is 1.698(6) Å and Ru(2) to centroid distance is 1.703(6) Å, which are consistent with those reported for other Ru(II) η^6-arene complexes [14]. The Ru–Cl bond distances are normal and slightly shorter than the average bond length of 2.429 Å in other Ru(II) complexes [15].

The molecular structure of **2d** shows that the coordinated pyridyl [N(3)–C(21)–C(22)–C(23)–C(24)–C(25)], [N(4)–C(30)–C(31)–C(32)–C(33)–C(34)], and pyrazine ring [N(2)–C(29)–C(26)–N(1)–C(27)–C(28)] are almost planar and the pyridyl ring forms an angle of 10° and 18°, respectively, with respect to the pyrazine ring. In the uncoordinated dpp ligand, the dihedral angles between the pyrazine and pyridyl rings are 42.2°. Upon coordination with the $[(\eta^6\text{-}C_{10}H_{14})RuCl]^+$ moiety through pyridyl N(4) and pyrazine N(2) from one side

and pyridyl N(3) and pyrazine N(1) from the other side the dihedral angle is reduced to 10° and 18°, respectively. At the same time, corresponding torsion angles in the complex **2d** is found to be −9.8°(7) from one side coordinated through N(1)–C(26)–C(25)–N(3) and −18.4°(7) from other side coordinated through N(4)–C(30)–C(29)–N(2) [16]. It may result from the bidentate coordination of the dpp ligand with the $[(\eta^6\text{-}C_{10}H_{14})RuCl]^+$ moiety which leads the ligand close to planarity. The pyridyl and pyrazine Ru–N distances Ru(1)–N(1), Ru(1)–N(3) and Ru(2)–N(2), Ru(2)–N(4) are essentially identical and are in the range of Ru–N distances. These are smaller than Ru–(N-amine) and Ru–(N-pyridine) [17].

Crystal packing in the complex **2d** is stabilised by C–H⋯X (X = Cl, F, π) inter and intra molecular weak interactions. Contact distances between C–H⋯F and C–H⋯Cl are 2.38–2.60 and 2.83–2.91 Å, respectively. The C–H⋯F interactions in complex **2d** lead to a parallel helical chain like network (Fig. 4). It also exhibits C–H⋯π interaction between *p*-cymene rings (C–H⋯π distance = 2.90–2.99Å) (Figs. 4 and 5) and π–π stacking interaction (π–π distances = 3.645(111) Å) which together forms chain of void space and encapsulated two-counter anion per void space (Fig. 6). Systematically arranged distorted flower motif is observable when the complex **2d** is viewed parallel to the crystallographic *c*-axis (Fig. 7). Twisted dpp ligand forms two of the elongated arms of each flower, while other arms are composed of methyl and isopropyl groups of the *p*-cymene. Twisted dpp ligand of complex **2d** are stacked to form a chain of alternately close packed flowers via the intermediacy of π–π stacking interactions [3.645(111) Å].

2.4. Conclusion

In the present study, we have presented synthesis, spectral, and structural properties of homo-hetero mixed binuclear cationic complexes. Detailed study, in order to exploit the reactivity of these complexes is now in progress in our laboratory.
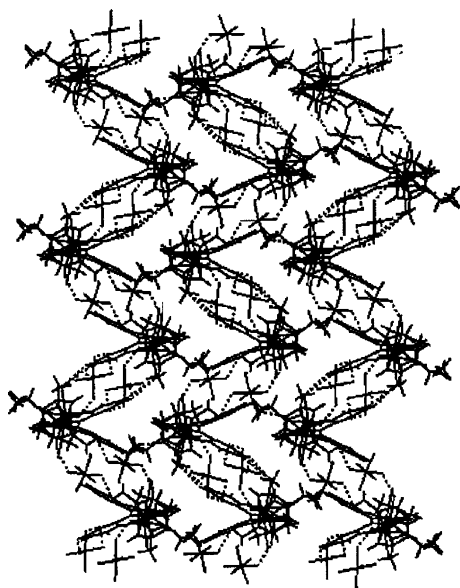

Fig. 4. Parallel helical chains linkage in complex **2d** accompanied by C–H⋯F interactions.
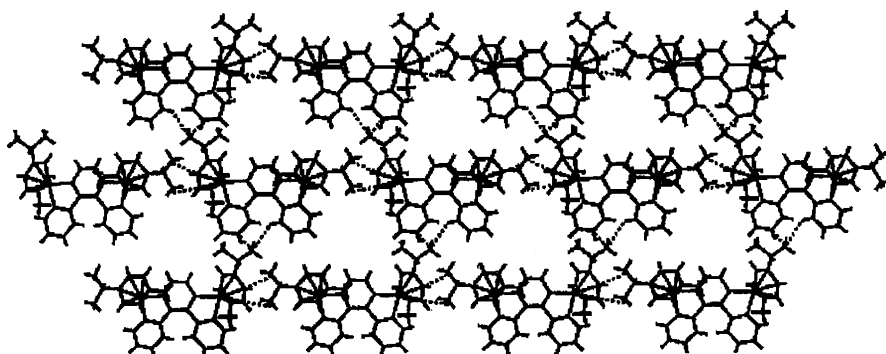
Fig. 5. Crystal packing in the complex **2d** showing C–H⋯π interaction.
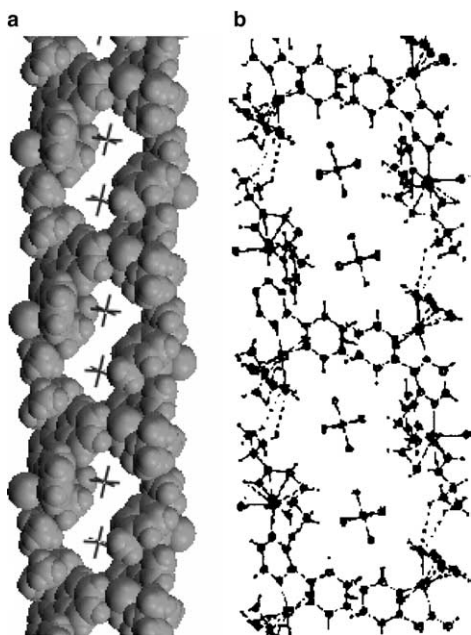
Fig. 6. Counter anion encapsulation {(a) space filled; (b) ball and stick model} in self-assembled cavity of complex **2d**.
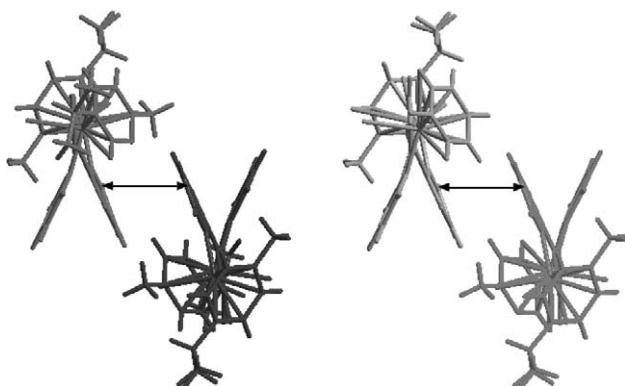

Fig. 7. Alternate arranged self assembled architecture for complex **2d** exhibiting π–π stacking [3.645(111) Å].

3. Experimental

3.1. Materials and physical measurements

All the synthetic manipulations were performed under oxygen free nitrogen atmosphere. Analar grade chemicals were used throughout. Solvents were dried and distilled before use following the standard literature procedures. Hydrated ruthenium (III) chloride, potassium tetrachloroplatinate (II), bis(benzonitrile)palladium (II) chloride, ammonium tetrafluoroborate and ammonium hexafluorophosphate were obtained from Aldrich Chemical Company, Inc., USA and were used without further purification. The precursor complexes [{(η⁶-arene)RuCl(μ-Cl)}₂] (arene = *p*-cymene or benzene) were prepared and purified by the literature procedures [18].

Elemental analyses on the complexes were obtained from Micro analytical Laboratory of the Sophisticated Analytical Instrument Facility, Central Drug Research Institute Lucknow. Infrared spectra in nujol mull in the region 4000–400 cm^{-1} and electronic spectra were recorded on Shimadzu-8201 PC & Shimadzu UV-1601 spectrophotometers, respectively. ^{1}H and ^{13}C NMR spectra with tetramethylsilane as the internal reference at room temperature were obtained on a Bruker DRX-300 NMR machine. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 Mass spectrometer system using Xenon as the FAB gas (6 kV, 10 mA). The accelerating voltage was 10 kV and spectra were recorded at room temperature using *m*-nitrobenzyl alcohol as the matrix.

3.2. Syntheses

The complexes [(η⁶-C₆H₆)RuCl(dpp)]BF₄ (**1**) [7b] and [(η⁶-C₁₀H₁₄)RuCl(dpp)]BF₄ (**2**) [8] were synthesized following the published procedure.

3.2.1. [{(η⁶-C₆H₆)RuCl}(μ-dpp)(PdCl₂)]BF₄ (**1a**)

In a typical reaction a suspension of the complex [(η⁶-C₆H₆)RuCl(dpp)]BF₄ (0.536 g, 1.0 mmol.) in methanol (25 mL) was treated with [Pd(C₆H₅CN)₂Cl₂] (0.383 g, 1.0 mmol) and the resulting solution was stirred at room temperature for ∼4.0 h. The colour of the solution changed to brown-red. The brown-red crystalline product thus obtained was filtered and washed with methanol, diethyl ether and dried under vacuo. The product was further recrystallised from dichloromethane/petroleum ether (40–60°). Yield: 0.499 g (70%). Anal. Calc. for BC₂₀Cl₃F₄H₁₆N₄PdRu: C, 33.66; H, 2.24; N, 7.85. Found: C, 33.78; H, 2.41; N, 7.63%. FAB-MS: *m/z* 724 (10%); 589 (10%); 520 (5%), 414 (10%). ^{1}H NMR (δ ppm, 300 MHz, CDCl₃, 298 K): 9.79 (d, 1H, 3.1 Hz), 9.61 (d, 1H, 5.4 Hz), 9.15 (d, 1H, 6.3 Hz), 8.99 (d, 1H, 4.2 Hz), 8.61 (d, 1H, 6.3 Hz), 8.48 (t, 1H, 7.2 Hz), 8.01 (m, 2H), 7.69 (d, 1H, 7.5 Hz), 6.92 (d, 1H, 6.8 Hz), 6.29 (s, 6H). ^{13}C{^{1}H} NMR (δ ppm, CDCl₃): 156.2, 153.2 148.4, 138.4, 127.0, 125 (pyrazyl and pyridyl carbon), 89.9 (C₆H₆). UV–Vis {acetone, λ$_{max}$ nm (ε/M^{-1} cm^{-1})}: 435 (1.9 × 10³), 289 (1.9 × 10⁴) and 262 (1.9 × 10⁴).

3.2.2. [{(η⁶-C₆H₆)RuCl}(μ-dpp)(PtCl₂)]BF₄ (**1b**)

This complex was prepared following the above procedure except that K₂PtCl₄ (0.415 g, 1.0 mmol) was used in place of [Pd(C₆H₅CN)₂Cl₂]. It isolated in the form of brown green microcrystalline solid. It was filtered and washed with methanol, diethyl ether and dried in vacuo. Yield: 0.545 g (68%). Anal. Calc. for BC₂₀Cl₃F₄H₁₆N₄PtRu: C, 29.92; H, 1.99; N, 6.98. Found: C, 29.17; H, 1.83; N, 6.79%. FAB-MS: *m/z* 715 (5%); 448 (25%); 218 (10%). ^{1}H NMR (δ ppm, 300 MHz, CDCl₃, 298

K): 9.82 (d, 1H, 3.2 Hz), 9.72 (d, 1H, 5.5 Hz), 9.18 (d, 1H, 6.1 Hz), 9.04 (d, 1H, 4.0 Hz), 8.65 (d, 1H, 6.4 Hz), 8.52 (t, 1H, 7.1 Hz), 8.05 (m, 2H), 7.72 (d, 1H, 7.4 Hz), 7.01 (d, 1H, 6.5 Hz), 6.17 (s, 6H). ^{13}C{^{1}H} NMR (δ ppm, CDCl$_3$): 156.5, 151.6, 149.3, 138.8, 127.3, 126 (pyrazyl and pyridyl carbon), 90.94 (C$_6$H$_6$). UV–Vis {acetone, λ_{max} nm (ε/M^{-1} cm^{-1})}: 433 (2.5 × 10^3), 341 (3.9 × 10^3) and 292 (5.7 × 10^3).

3.2.3. [{(η^6-C$_{10}$H$_{14}$)RuCl}(μ-dpp)(PdCl$_2$)]BF$_4$ (2a)

This complex was prepared following the above procedure for **1a** except that the complex [(η^6-C$_{10}$H$_{14}$)RuCl(dpp)]BF$_4$ (0.592 g, 1.0 mmol) was used in place of [(η^6-C$_6$H$_6$)RuCl(dpp)]BF$_4$. It was isolated in the form of brown-red microcrystalline solid and was filtered and washed with methanol, diethyl ether and dried in vacuo. The product was further recrystallised from dichloromethane/petroleum ether (40–60°). Yield: 0.623 g (81%). Anal. Calc. for BC$_{24}$Cl$_3$F$_4$H$_{24}$-N$_4$PdRu: C, 37.45; H, 3.12; N, 7.28. Found: C, 36.59; H, 3.61; N, 7.78%. FAB-MS: m/z 681 (10%); 647 (10%); 575 (20%); 505 (10%); 470 (20%); 330 (20%). ^{1}H NMR (δ ppm, 300 MHz, CDCl$_3$, 298 K): 9.62 (d, 1H, 3.0 Hz), 9.49 (d, 1H, 5.1 Hz), 8.90 (d, 1H, 2.7 Hz), 8.63 (d, 1H, 3.9 Hz), 8.09 (t, 1H, 7.8 Hz), 7.99 (d, 1H, 7.8 Hz), 7.76 (t, 1H, 7.5 Hz), 7.63 (m, 2H), 7.05 (d, 1H, 7.8 Hz), 6.12 (dd, 2H, 6.0 Hz), 5.95 (dd, 2H, 6.3 Hz), 2.67 (sep, 1H, 6.9 Hz), 2.33 (s, 3H), 1.12 (d, 6H, 4.2 Hz). ^{13}C{^{1}H} NMR (δ ppm, CDCl$_3$): 153.2, 151.4, 147.2, 137.8, 127.4, 124.4 (pyrazyl and pyridyl carbon), 106.2 (C–CHMe$_2$), 99.8 (C–CH$_3$), 87.4–85.2 (C$_6$H$_4$), 30.5 (CH(CH$_3$)$_2$), 21.7 (CH(CH$_3$)$_2$), 16.9 (C–CH$_3$). UV–Vis {acetone, λ_{max} nm (ε/M^{-1} cm^{-1})}: 445 (2.3 × 10^3), 317 (1.3 × 10^4) and 233 (1.9 × 10^4).

3.2.4. [{(η^6-C$_{10}$H$_{14}$)RuCl}(μ-dpp)(PtCl$_2$)]BF$_4$ (2b)

This complex was prepared following the above procedure **1b** except that the complex [(η^6-C$_{10}$H$_{14}$)RuCl(dpp)]BF$_4$ (0.592 g, 1.0 mmol) was used in place of [(η^6-C$_6$H$_6$)RuCl(dpp)] BF$_4$. It isolated in the form of brown yellow microcrystalline solid. Yield: 0.652 g (76%) Anal. calc. for BC$_{24}$Cl$_3$F$_4$H$_{24}$N$_4$PtRu: C, 33.56; H, 2.79; N, 6.52. Found: C, 33.21; H, 2.30; N, 6.18%. FAB-MS: m/z 771 (65%); 505 (40%); 460 (15%); 232 (10%). ^{1}H NMR (δ ppm, 300 MHz, CDCl$_3$, 298 K): 9.67 (d, 1H, 3.1 Hz), 9.56 (d, 1H, 5.2 Hz), 8.95 (d, 1H, 3.2 Hz), 8.71 (d, 1H, 4.2 Hz), 8.11 (t, 1H, 7.6 Hz), 8.02 (d, 1H, 7.6 Hz), 7.88 (t, 1H, 7.2 Hz), 7.69 (m, 2H), 7.08 (d, 1H, 7.7 Hz), 6.12 (dd, 4H, 6.9 Hz), 2.45 (sep, 1H, 6.0 Hz), 2.14 (s, 3H), 1.20 (d, 6H, 6.4 Hz). ^{13}C{^{1}H} NMR (δ ppm, CDCl$_3$): 156.3, 154.5, 152.7, 149.7, 138.7, 127.8,126, 125 (pyrazyl and pyridyl carbon), 105.2 (C–CHMe$_2$), 104.7 (C–CH$_3$), 87.4–85.0 (C$_6$H$_4$), 30.5 (CH(CH$_3$)$_2$), 21.7 (CH(CH$_3$)$_2$), 18.4 (C–CH$_3$). UV–Vis {acetone, λ_{max} nm (ε/M^{-1} cm^{-1})}: 432 (7.2 × 10^3), 339 (8.5 × 10^3) and 274 (3. 1 × 10^4).

3.2.5. [{(η^6-C$_{10}$H$_{14}$)RuCl}(μ-dpp){(η^6-C$_6$H$_6$)RuCl}]-(BF$_4$)$_2$ (2c)

A suspension of [(η^6-C$_{10}$H$_{14}$)RuCl(dpp)]BF$_4$ (0.592 g, 1.0 mmol) in methanol (25 mL) was treated with [{(η^6-C$_6$H$_6$)RuCl(μ-Cl)}$_2$] (0.500 g, 1.0 mmol) and allowed to stir at room temperature. The resulting solution was further stirred for ~4.0 h and filtered through celite to remove any solid impurities. To the filtrate a saturated solution of NH$_4$BF$_4$ dissolved in methanol (10 mL) was added and left in refrigerator for slow crystallization. After a couple of days deep orange red microcrystalline compound was obtained. It was filtered and washed with methanol, diethyl ether and dried in vacuo. The product was further recrystallised from dichloromethane/petroleum ether (40–60°). Yield (77%, 0.688 g). Found: C, 40.11; H, 3.31; N, 6.17%. B$_2$C$_{30}$Cl$_2$F$_8$H$_{30}$N$_4$Ru$_2$ requires: C, 40.31; H, 3.35; N, 6.27. FAB-MS: m/z 719 (90%); 505 (50%); 273 (10%). ^{1}H NMR (δ ppm, 300 MHz, CDCl$_3$, 298 K): 0.96 (d, 6H, 6.9 Hz), 2.76 (sep, 1H, 6.4 Hz), 2.06 (s, 3H), 6.08 (dd, 4H, 7.0 Hz), 5.96 (s, 6H), 9.63 (d, 4H, 7.5), 8.16 (t, 2H, 5.4 Hz), 7.80 (t, 2H, 7.8 Hz), 7.63 (d, 1H, 6.6 Hz), 7.54 (d, 1H, 6.0 Hz). ^{13}C{^{1}H} NMR (δ ppm, CDCl$_3$): 158.2, 153.3, 149.4, 138.2, 127.4, 124 (pyrazyl and pyridyl carbon), 105.6 (C–CHMe$_2$), 102.2 (C–CH$_3$), 95.9–92.3 (C$_6$H$_6$ and C$_6$H$_4$), 31.4 (CH(CH$_3$)$_2$), 22.4 (CH(CH$_3$)$_2$), 18.6 (C–CH$_3$). UV–Vis {acetone, λ_{max} nm (ε/M^{-1} cm^{-1})}: 430 (1.0 × 10^3), 334 (4.1 × 10^3) and 262 (7.9 × 10^3).

3.2.6. [{(η^6-C$_{10}$H$_{14}$)RuCl}(μ-dpp){(η^6-C$_{10}$H$_{14}$)RuCl}]-(PF$_6$)$_2$ (2d)

This complex was prepared by a different method using above procedure for complex **2c** starting from [(η^6-C$_{10}$H$_{14}$)RuCl(dpp)]PF$_6$ (0.650 g, 1.0 mmol) and [{(η^6-C$_{10}$H$_{14}$)RuCl(μ-Cl)}$_2$] (0.612 mg, 1.0 mmol). The orange-red microcrystalline product was further recrystallised from dichloromethane/petroleum ether (40–60°). Yield: 0.746 g (70%). Anal. calc. for C$_{34}$Cl$_2$F$_{12}$H$_{38}$N$_4$P$_2$Ru$_2$: C, 38.30; H, 3.56; N, 5.25. Found: C, 38.11; H, 3.13; N, 5.09%. FAB-MS: m/z 775 (50%); 738 (25%); 505 (20%); 469 (15%); 335 (40%). ^{1}H NMR (δ ppm, 300 MHz, CDCl$_3$, 298 K): 9.65 (d, 2H, 6.7 Hz); 9.43 (d, 4H, 7.1 Hz); 7.56 (t, 2H, 6.1 Hz); 8.12 (t, 2H, 8.6 Hz); 8.49 (d, 1H, 7.3 Hz); 6.13 (dd, 4H, 6.3 Hz); 2.71 (sep, 1H, 6.3 Hz); 2.12 (s, 3H); 1.12 (d, 6H, 6.8 Hz). ^{13}C{^{1}H} NMR (δ ppm, CDCl$_3$): 155.7; 152.7; 148.5; 139.7; 126.4; 124.1 (pyrazyl and pyridyl carbons); 106.3 (C–CHMe$_2$); 100.3 (C–CH$_3$); 85.9–84.8 (C$_6$H$_4$); 31.6 (CH(CH$_3$)$_2$); 22.1 (CH(CH$_3$)$_2$); 17.8 (C–CH$_3$). UV–Vis {acetone, λ_{max} nm (ε/M^{-1} cm^{-1})}: 456 (1.7 × 10^4), 366 (1.9 × 10^4) and 273 (1.5 × 10^4).

3.3. X-ray crystallographic study

Crystals suitable for single crystal X-ray analyses for the complex [{(η^6-C$_{10}$H$_{14}$)RuCl}(μ-dpp){(η^6-C$_{10}$H$_{14}$)-RuCl}](PF$_6$)$_2$(**2d**) was grown from CH$_2$Cl$_2$/petroleum

ether (40–60 °C) at room temperature. Crystal data and structure refinement parameters for the complex **2d** was recorded on Enraf–Nonius CAD-4 automatic diffractometer using employing graphite monochromated Cu Kα radiation ($\lambda = 1.54180$ Å) at 293(2) K. The intensity data was obtained in $\omega - 2\theta$ scan mode in the range from 3.0° to 50.0°. All the pertinent data for complex **2d** are given in Table 1. The structure was solved by direct methods and refined by full matrix least squares on F^2 (SHELX-97) [19]. All the non-hydrogen atoms were refined with anisotropically thermal parameters. The hydrogen atoms were refined with isotropic thermal parameters fixed to those of the atoms to which they are bonded. The function minimized for complex **2d** was $\sum w(F_o - F_c)^2$, where $w^{-1} = [\sigma^{-2}(F_o^2) + (0.2000P)^2 + 0.0000P]$, where $P = ([F_o]^2 + 2[F_c]^2)/3$. Final R-value for complex **2d** on $[I > 2\sigma(I)]$ data was 0.0649 and R for all $[I > 2\sigma(I)]$ data was 0.0827 GOF = 0.785.

Acknowledgements

Appendix A. Supplementary data

Crystallographic data for the structural analysis of complex **2d** are available in CIF format. This material is available free of charge via the Internet and CCDC Reference No. is 264640. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.06.023.

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