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Stable mononuclear and binuclear ruthenium(II) arene complexes with multiple N-donor poly-pyridyl ligands: synthesis, spectroscopic and structural characterization. Single crystal X-ray structure of $[(\eta^6\text{-}C_{10}H_{14})RuCl(bppz)]BF_4$

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Abstract

The reaction of 2,3-bis(2-pyridyl)-pyrazine (bppz) with dimeric chloro-bridged arene ruthenium complexes $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ (arene = *p*-cymene or hexamethyl benzene) gives highly stable cationic mono and binuclear complexes with the formulation $[(\eta^6\text{-}C_{10}H_{14})RuCl(bppz)]^+$ and $[\{(\eta^6\text{-}C_{10}H_{14})RuCl\}_2(\mu\text{-bppz})]^{2+}$. On the contrary, reactions of the potential bridging ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) or 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) with the chloro-bridged dimeric arene ruthenium complexes $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ under similar reaction conditions led to the formation of binuclear complexes with the formulation $[\{(\eta^6\text{-arene})RuCl\}_2(\mu\text{-L})]^{2+}$ (where η^6-arene = *p*-cymene or hexamethyl benzene and L = tptz or bptz). The reaction products were characterized by various physico-chemical techniques, viz. elemental analyses, IR, $^1H-^1H$ COSY, ^1H-, ^{13}C-NMR, FAB mass spectroscopy and electronic spectral studies. Molecular structure of the representative mononuclear complex $[(\eta^6\text{-}C_{10}H_{14})RuCl(bppz)]BF_4$ was determined by single crystal X-ray diffraction analysis. Crystal data: monoclinic, C_2/c, $a = 16.103(5)$ Å, $b = 16.207(2)$ Å, $c = 19.124(2)$ Å, $\beta = 91.61(2)°$, $Z = 8$, $R = 0.0714$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bridging ligands; Supramolecules; Polyazine ligands; Ruthenium arene complexes; Metallo-ligands

1. Introduction

In recent times, considerable attention has been paid towards designing supramolecular Ru(II) poly-pyridyl complexes owing to their interesting photophysical and photochemical properties [1a–s], as catalysts [2a,b], as multi-electron storage systems [3a–c], in the designing of new materials [4a–f] and molecular devices [5a–f]. In such systems, coupling between the metal centers is propagated via bridging ligands possessing two or more bidentate set of coordination sites. The photophysical and photochemical properties of the oligonuclear complexes are determined by the nature of the bridging ligand. The interaction between bridged metal fragments depends largely on the size, shape and electronic properties of the bridge. To be effective, molecular orbitals of the bridging ligand must have matching symmetry and comparable energy to interact with the acceptor and donor orbital of the metal centers. In this regard, multiple nitrogen donor bridging ligands, viz. 2,3-bis(2-pyridyl)-pyrazine, 2,5-bis(2-pyridyl)-pyrazine, 2,3-bis(2-pyridyl)-quinoxaline, 2,4,6-tris(2-pyridyl)-1,3,5-triazine, and 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine have received special attention [6a–l]. These ligands mediate intermetallic interactions through low lying π^* orbital (LUMOs) by invoking the electron transfer super-exchange mechanism. The η^6-arene ruthenium complexes play a vital role in organometallic chemistry [7a–d]. Reactions of the chloro-bridged dimeric arene ruthenium complexes $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ with the Lewis bases and a variety of ligands have been studied extensively. However, there are only a few reports dealing with the reaction of η^6-arene ruthenium com-

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plexes with the above-mentioned novel bridging ligands and other related systems [8a–e]. Because of our continuing interest in the arene ruthenium chemistry and in designing of *metallo-ligand or synthon* based on organometallic systems [9a–f], we have made a detailed study on the reactivity of the chloro-bridged arene ruthenium complexes $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ (arene = *p*-cymene or hexamethyl benzene) with 2,3-bis(2-pyridyl)-pyrazine (bppz), 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) and 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz). We found that the reaction of bppz with arene ruthenium complexes led to the formation of mono and binuclear complexes $[(\eta^6\text{-}C_{10}H_{14})RuCl(bppz)]BF_4$ and $[\{(\eta^6\text{-}C_{10}H_{14})RuCl\}_2(\mu\text{-bppz})](BF_4)_2$, while, reactions of bptz or tptz gave binuclear complexes $[\{(\eta^6\text{-}C_{10}H_{14})\text{-}RuCl\}_2(\mu\text{-L})](BF_4)_2$. In this paper we report a reproducible synthesis and spectral characterization of mono and binuclear complexes with the formulation $[\{(\eta^6\text{-}C_{10}H_{14})RuCl(L)]BF_4$ and $[\{(\eta^6\text{-}C_{10}H_{14})RuCl\}_2(\mu\text{-L})]\text{-}(BF_4)_2$. We also present herein single crystal X-ray structure of the representative mononuclear complex $[(\eta^6\text{-}C_{10}H_{14})RuCl(bppz)]BF_4$.

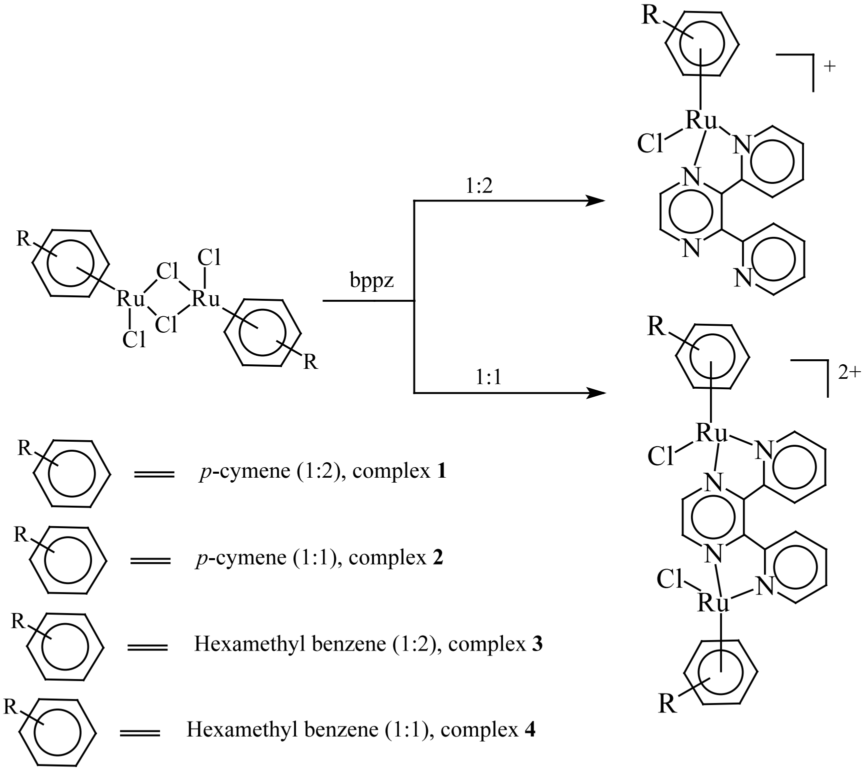
2. Results and discussion

The reaction of bppz with the chloro-bridged arene ruthenium complexes, $[\{(\eta^6\text{-arene})RuCl_2\}_2]$, in methanol in 1:2 and 1:1 molar ratio gave mono and binuclear complexes $[(\eta^6\text{-arene})RuCl(bppz)]BF_4$ and $[\{(\eta^6\text{-arene})RuCl\}_2(\mu\text{-bppz})](BF_4)_2$, respectively, in quantitative yield (Scheme 1).

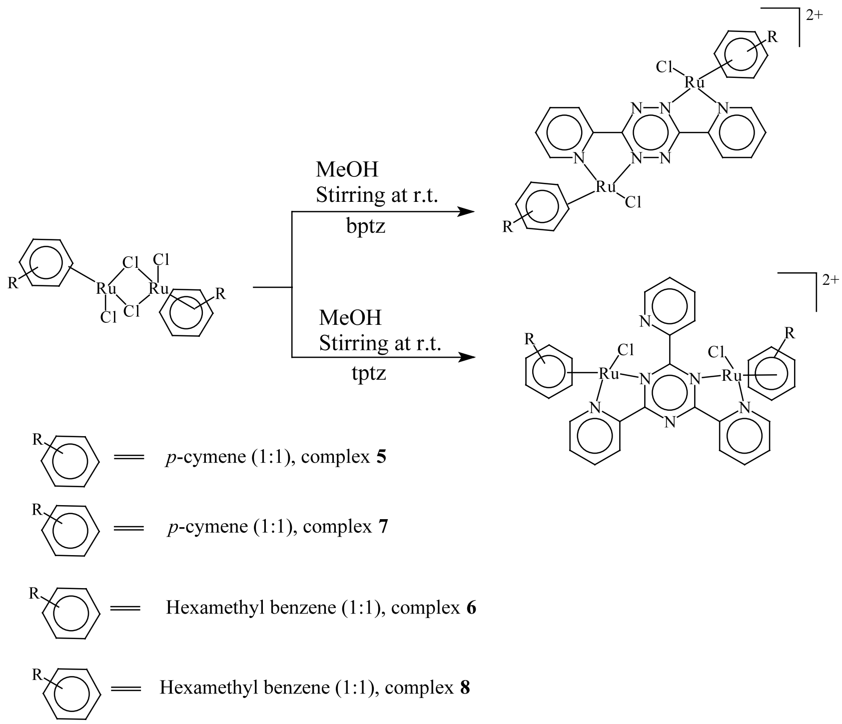
On the contrary, reactions of the symmetrical bridging ligands tptz or bptz with the chloro-bridged dimeric arene ruthenium complexes $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ in boiling methanol lead to binuclear complexes with the formulation $[\{(\eta^6\text{-arene})RuCl\}_2(\mu\text{-L})](BF_4)_2$ (Scheme 2).

It was further observed that the reactions of even a large excess of the ligand bptz or tptz with arene ruthenium complexes lead to binuclear complexes. The greenish-red to bluish cationic complexes resulting from these reactions are non-hygroscopic, air stable, shiny crystalline solids having high melting points. These are sparingly soluble in methanol and benzene, soluble in acetone, dichloromethane, chloroform, acetonitrile and dimethyl formamide, and insoluble in petroleum ether and diethyl ether.

Analytical data of the complexes (recorded in Section 5) conformed well with their formulations. Further information about the composition of the complexes was obtained from FAB mass spectroscopy (FABMS). The FABMS spectra of all these complexes showed a peak corresponding to the molecular ion. The position of different peaks and the overall fragmentation patterns are consistent with the formulation of the complexes and strongly support the mono and binuclear nature of the complexes.



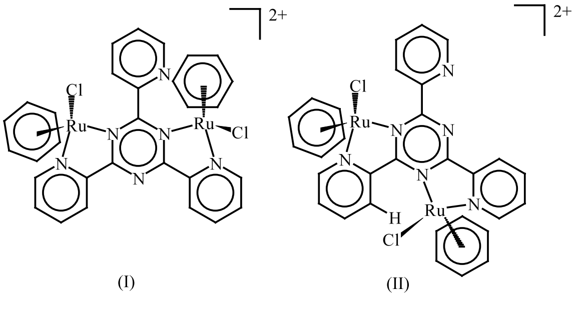
Scheme 1.



Scheme 2.

Infrared (IR) spectra of the complexes in Nujol displayed bands in the region of 1670–1500 cm^{-1}, which are assigned to ν(C–N) and ν(C = C) stretching vibrations of the ligand. Precise assignment of different vibrations for all the complexes is not possible as vibrations are often coupled. All the complexes displayed broad bands due to the presence of counter anion BF_4^- at ~1054 cm^{-1}.

Binuclear complexes resulting from the reaction of tptz with arene ruthenium complexes may have any of the following two configurations.



Among these configurations, **I** is preferred over configuration **II**, since in the latter there may be a steric interaction between H_3 and the metal centre Ru. However, such a steric hindrance is not possible in configuration **I**, since the uncoordinated pyridyl ring is twisted out of the triazine plane. It is well supported by ^{1}H-NMR spectral data (vide infra).

^{1}H- and ^{13}C-NMR spectral data of the complexes (recorded in Section 5) are in good agreement with the proposed molecular formula. Scheme showing the numbering of protons used for assignment in ^{1}H-NMR spectra is shown in Fig. 1. To facilitate the assigned resonances, ^{1}H–^{1}H COSY experiment was carried out and the resulting spectrum for complex **1** is shown in Fig. 2. Doublets are assigned for the protons at 1/2, 6/6′, 3/3′ positions and triplets are assigned to the protons at 5/5′ and 4/4′ positions. The ^{1}H-NMR spectra of the mononuclear complex **1** $[Ru(\eta^6\text{-}C_{10}H_{14})Cl(bppz)]^+$ exhibited 09 distinct resonances at δ 9.67 (d, 1H, 3.0, H_1), 9.50 (d, 1H, 5.4, H_6), 9.00 (d, 1H, 2.7, H_2), 8.59 (d, 1H, 6.6, H_6), 8.14 (t, 1H, 7.8, H_4), 8.00 (d, 2H, 7.5, H_3), 7.90 (t, 1H, 7.8, H_4), 7.69 (m, 2H, $H_{5+5'}$) and 6.93 (d, 1H, 8.1, H_3) assignable to pyrazyl and pyridyl protons of ligand bppz [6k]. This region of the spectrum integrated for ten protons as expected for the coordinated pyrazine, coordinated pyridyl and uncoordinated pyridyl rings. These protons exhibited a downfield shift compared with that in the free ligand on coordination with the metal center. The protons due to *p*-cymene are displayed at δ 6.03 (AB pattern, 4H, 6.3, C_6H_4), 2.658 (sep, 1H, 6.9, $CH(CH_3)_2$), 2.21 (s, 3H, C–CH_3) and 0.98 (d, 6H, 6.9, $CH(CH_3)_2$). The position and integrated intensity of different signals corroborated well with the formulation of the complex. $^{13}C\{^1H\}$-NMR spectra of complex **1** followed the trends observed in ^{1}H-NMR spectra. The bppz carbons resonated at 156.5, 153.43, 149.42, 138.2, 128.1 and 124.7 ppm, whereas the *p*-cymene carbons resonated at δ 107.5 (*C*–$CH(CH_3)_2$), 101.9 (*C*–CH_3), 85.8 (C_6H_4),

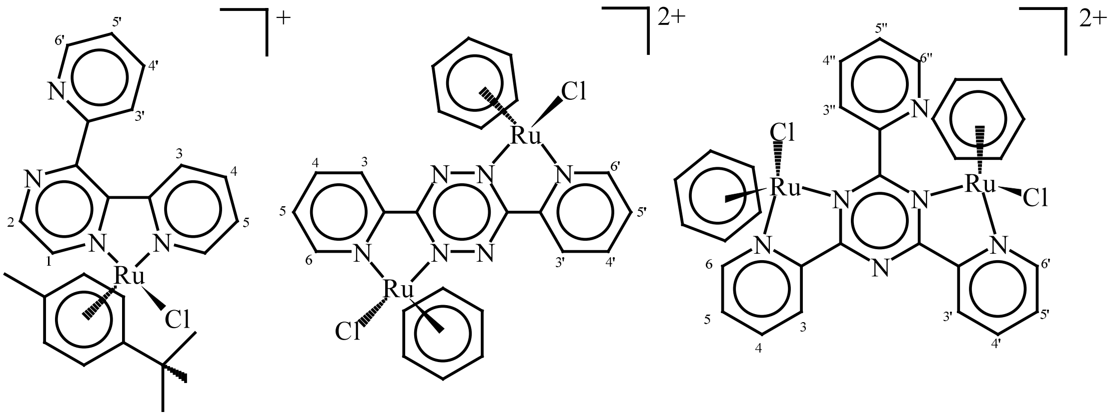


Fig. 1. Numbering scheme of the protons in the complexes.

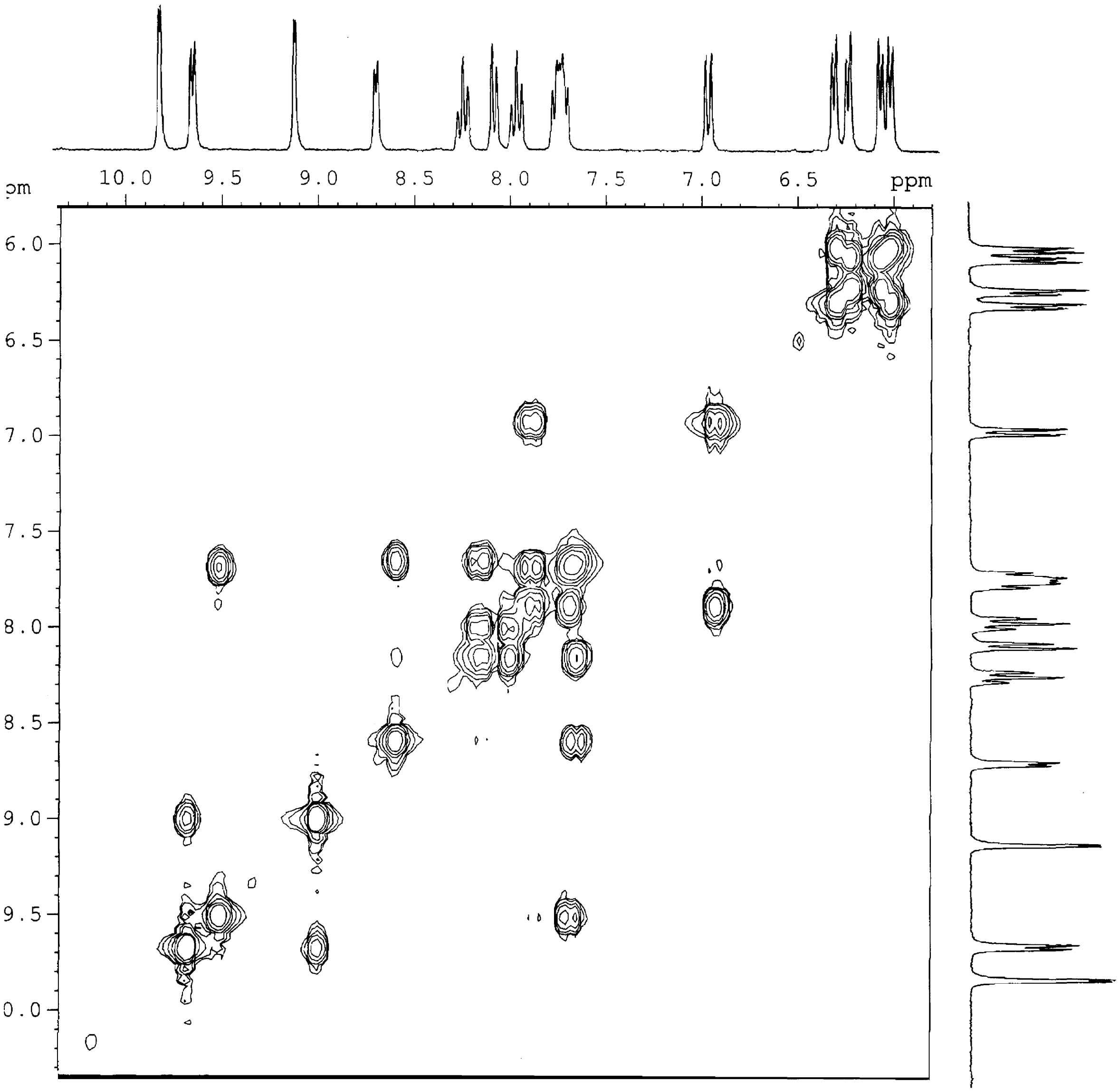


Fig. 2. ^1H–^1H COSY spectra of the complex [Ru(η^6-$C_{10}H_{14}$)Cl(bppz)](BF_4).

30.5 ($CH(CH_3)_2$), 22.1 (C–CH_3), 18.9 ppm (C–CH_3). In the ^{1}H-NMR spectra of binuclear complex **2**, only 05 distinct resonances were observed in the δ 9.35–7.12 ppm range. It exhibited a singlet at δ 9.69 ppm, two doublets at δ 9.53 and δ 8.56, and two multiplets at δ 8.16 and δ 7.92 ppm, respectively. The *p*-cymene protons in this complex also resonated at almost the same position as observed in complex **1**. It accounts well for a single, highly symmetrical complex in which two *p*-cymene rings are either *cis* or *trans* disposed with respect to the pyrazine plane. The ^{1}H-NMR spectra of complexes **3** or **4** followed the general trends observed in the ^{1}H-NMR spectra of complexes **1** or **2**. The hexamethyl benzene protons in these complexes resonated as singlets at δ 2.12 and 2.14 ppm, respectively. The ^{1}H-NMR spectra of complexes **5** and **6** showed resonances at δ 9.40 (d, $H_{6+6'}$), 8.51 (d, $H_{4+4'}$), 8.19 (m, $H_{5+5'}$) and 7.75 ppm (m, $H_{3+3'}$) along with the resonances caused by the respective η^6-arene protons [6a]. The presence of different signals suggested that in these complexes the ligand bptz forms a symmetrical bridge between the two ruthenium centers in which the two η^6-arene rings are *trans* disposed with respect to the tetrazine ring. Downfield shift of the pyridyl protons indicates the coordination of the bptz ligand with the metal centers. The ^{1}H-NMR spectra of complexes **7** or **8** displayed signals at about 9.26 (d, 4.2, $H_{6+6'}$), 8.94 (d, 7.8, $H_{3+3'}$), 8.56 (d, 6.6, $H_{5''}$), 8.34 (m, 7.8, $H_{3''+4'+4''}$), 7.86 (dd. 7.8, $H_{5+5'}$), 7.60 (m, 7.8, $H_{6''}$) corresponding to the pyridyl protons of the tptz ligand along with the resonances caused by the respective coordinated η^6-arene. The resonances assignable to pyridyl protons integrated for 12 protons in the region, which is expected for the two magnetically equivalent pyridyl groups and one uncoordinated pyridyl group. It strongly suggested that the ligand tptz symmetrically bridge the two ruthenium(II) centers. This observation is consistent with the earlier reports [10].

The low spin d^6 configuration of the mono and binuclear series of complexes provides filled orbital of proper symmetry on Ru(II), which can interact with the low lying π^* orbital of the poly-pyridyl ligands such as bppz, bptz or tptz. One should therefore expect a band attributable to the metal-to-ligand charge transfer MLCT ($t_{2g} \rightarrow \pi^*$) transition in the electronic spectra of these complexes. Further, the energy of these transitions should vary with the nature of the bridging ligand acting as an π acceptor. Electronic spectra of the mononuclear complexes **1** and **3** displayed medium intensity bands in the visible region at ~420 nm, and an intense band at ~350 and at ~265 nm. The low intensity band centered at ~420 nm has been assigned to the metal-to-ligand charge transfer transition $Ru(t_{2g}) \rightarrow \pi^*$(bppz) bands. It was observed that the position of this band remained practically unaltered by changing the solvent, indicating no change in the dipole moments of the molecule between the ground and excited states. This observation is consistent with the charge transfer assignment [11]. The intense band at ~350 nm has been assigned to the metal-perturbed LC transition by its analogy with the band in the free ligand. The high-energy band at ~265 nm has been assigned to intra-ligand $\pi \rightarrow \pi^*$ transitions.

The position of the MLCT transitions in the spectra of binuclear complexes **2** or **4** exhibited significant red shifts as compared to their mononuclear counterparts (**2**: 455 nm; **4**: 485 nm). In general, coordination of another metal ion at a remote coordination site of the bridging ligand stabilizes the π^* orbital of the bridging ligand. Since the energy of the MLCT transition is related to that of the LUMO of the ligand it results in an increase in $d\pi \rightarrow \pi^*$overlap [12]. This effect lowers the HOMO–LUMO gap leading to a red shift of the MLCT band in binuclear complexes. This observation is consistent with the other reports and strongly suggests the binuclear nature of complexes **2** and **4** [10,13].

Electronic spectra of the bptz- or tptz-bridged binuclear complexes displayed bands in the visible region at ~650 nm with shoulders at ~715 nm. In general, these complexes followed the typical trends observed in the electronic spectra of the poly-pyridyl complexes, which display a ligand based $\pi \rightarrow \pi^*$ transitions for each polyazine ligand in the UV region and metal-to-ligand charge transfer transitions in the visible region.

3. Single crystal X-ray structure of [(η^6-$C_{10}H_{14}$)RuCl(bppz)]BF_4 (1)

Molecular geometry of the complex cation with the atom numbering scheme is shown in Fig. 3 and selected bond lengths, bond angles and torsion angles are given in Table 1. The metal atom Ru(1) is coordinated through the pyridyl ring nitrogen N(1), pyrazyl nitro-

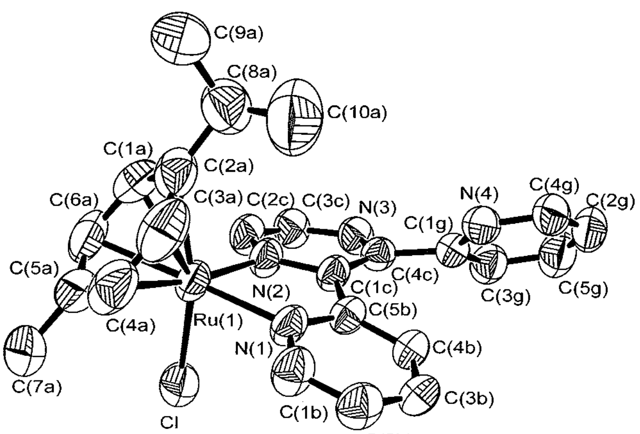


Fig. 3. ORTEP view of the complex cation of [Ru(η^6-$C_{10}H_{14}$)Cl(bppz)](BF_4).

Table 1
Selected bond lengths (Å) bond angles (°) and torsion angles for $[Ru(\eta^6\text{-}C_{10}H_{14})Cl(bppz)](BF_4)$

Bond lengths	
Ru(1)–N(2)	2.060(5)
Ru(1)–N(1)	2.079(4)
Ru(1)–C(1A)	2.164(7)
Ru(1)–C(3A)	2.165(9)
Ru(1)–C(4A)	2.180(8)
Ru(1)–C(6A)	2.195(7)
Ru(1)–C(5A)	2.200(8)
Ru(1)–C(2A)	2.226(7)
Ru(1)–C	1.689(8)
Ru(1)–Cl	2.3868(19)
N(1)–C(1B)	1.338(8)
N(1)–C(5B)	1.362(7)
C(1C)–N(2)	1.365(6)
N(2)–C(2C)	1.343(7)
Bond angles	
N(2)–Ru(1)–N(1)	76.52(19)
N(2)–Ru(1)–Cl	84.30(15)
N(1)–Ru(1)–Cl	86.91(15)
Torsion angles	
N(1)–pyridyl pyrazine	17.6
N(2)–pyridyl pyrazine	40.6
N(4)–C(1g)–C(4c)–N(3)	138.77
N(1)–C(5b)–C(1c)–N(2)	−6.12

gen atom N(2), the chloride ligand and *p*-cymene ring in η^6-manner. Considering the *p*-cymene ring as the single coordination site represented by its centroid, the overall coordination geometry about the metal center might be described as pseudo-tetrahedral or typical 'piano-stool' geometry. The *p*-cymene ring is planar and the Ru–C distances are almost equal with an average bond length of 2.185(8) Å [range 2.164(7)–2.226(7) Å]. Ru(1) to *p*-cymene ring centroid distance is 1.689(8) Å and is consistent with those reported for the other Ru(II) η^6-arene complexes [14a–c]. The C–C bond lengths within the *p*-cymene ring are equal and there are no alternate short and long bond lengths suggesting that there is no localization and shows no trends associated with the non-planarity of the arene ring. The Ru–Cl distance is normal and slightly shorter than the average bond length of 2.429 Å in the other Ru(II) complexes [15a–c].

The molecular structure of complex **1** shows that the coordinated pyridyl [N(1)–C(1b)–C(2b)–C(3b)–C(4b)–C(5b)] and pyrazine rings [N(2)–C(1c)–C(4c)–N(3)–C(3c)–C(2c)] are non-planar and the pyridyl ring forms an angle of 17.53° with respect to the pyrazine ring. The uncoordinated pyridyl ring [N(4)–C(4g)–C(2g)–C(5g)–C(3g)–C(1g)] makes a larger dihedral angle (40.59°) with respect to the pyrazine ring plane [N(2)–C(1c)–C(4c)–N(3)–C(3c)–C(2c)]. In the uncoordinated bppz 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(1) and N(2) atoms the dihedral angle between the coordinated pyridyl and pyrazine rings is reduced to 17.53°, while the uncoordinated pyridyl ring maintains the dihedral angle of 40.59° with respect to the pyrazine ring plane. At the same time, corresponding torsion angle in complex **1** is found to be −6.12° as compared with the torsion angle of 136.1° in the free ligand [16a,b]. It may result from the bidentate coordination of the ligand with the $[(\eta^6\text{-}C_{10}H_{14})RuCl]^+$ moiety, which brings the coordinated part of the ligand towards planarity. The pyridyl and pyrazine Ru–N distances Ru(1)–N(1) and Ru(1)–N(2) are essentially identical and are in the range of Ru–N distances. These are smaller than Ru–(N-amine) and Ru–(N-pyridine) [17a–e].

4. Conclusions

In the present study we have shown that the reaction of an excess of bridging ligand bppz with the chloro-bridged dimeric arene ruthenium complexes $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ in methanol lead to the formation of cationic mononuclear complexes $[(\eta^6\text{-arene})RuCl(bppz)]^+$, while such a reaction in 1:1 molar ratio gave the binuclear complex $[\{(\eta^6\text{-arene})RuCl\}_2(\mu\text{-bppz})]^{2+}$ in quantitative yield. The structure of the representative mononuclear complex $[(\eta^6\text{-}C_{10}H_{14})RuCl(bppz)]BF_4$ has been confirmed by single crystal X-ray diffraction studies. It is the representative structure within the family of piano stool $[(\eta^6\text{-arene})RuCl]^+$ with poly-pyridyl ligands. Owing to the presence of uncoordinated donor sites the mononuclear complexes offer an unique opportunity of behaving either as a *synthon* or a *metallo-ligand* which can find wide applications in the synthesis of $[(\eta^6\text{-arene})RuCl]^{+2}$-containing homo/heterometallic binuclear complexes in which the two different moieties are bound by poly-pyridyl like ligands and are expected to show interesting properties. More detailed work in this direction is in progress in our laboratory.

5. Experimental

Analar grade chemicals were used throughout the study. All the synthetic manipulations were performed under oxygen free dry nitrogen atmosphere. Solvents were dried and distilled before use following the standard literature procedures. Hydrated ruthenium(III) chloride, 2,3-bis(2-pyridyl)-pyrazine, 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine, 2,4,6-tris(2-pyridyl)-1,3,5-triazine, α-terpinene, hexamethylbenzene and tetrabutylammonium perchlorate were obtained from Aldrich Chemical Company Inc., USA and were used without further purification. The precursor complexes $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ (arene = *p*-cymene or hexamethyl benzene) were prepared and purified as outlined in Ref. [18].

5.1. Physical measurements

Micro analytical data of the complexes were obtained from Micro analytical Laboratory of the R.S.I.C., Central Drug Research Institute Lucknow. IR spectra in Nujol mull in the 4000–400 cm^{-1} region and electronic spectra were recorded in a Shimadzu-8201 PC and Shimadzu UV-160 spectrophotometers, respectively. ^{1}H–^{1}H COSY and ^{1}H-, ^{13}C-NMR spectra with Me_4Si as the internal reference at room temperature (r.t.) were obtained in a Bruker DRX-300-NMR machine. FABMS spectra were recorded in 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 r.t. using *m*-nitrobenzyl alcohol as the matrix.

5.2. Synthesis

5.2.1. $[(\eta^6\text{-}C_{10}H_{14})RuCl(bppz)]BF_4$ (**1**)

A suspension of the complex $[\{(\eta^6\text{-}C_{10}H_{14})RuCl_2\}_2]$ (612 mg, 1 mmol.) in MeOH (30 ml) was treated with bppz (468 mg, 2 mmol) and stirred continuously at r.t. After half an hour the precursor complexes were dissolved and the color of the solution turned orange–yellow. The resulting solution was further stirred for ~4.0 h and filtered through celite to remove solid impurities if any. To the filtrate, a saturated solution of NH_4BF_4 dissolved in MeOH (10 ml) was added and left in a refrigerator for slow crystallization. After a couple of days, greenish-red microcrystalline compound separated out. It was filtered, washed with MeOH, Et_2O and dried in vacuo. The product was further recrystallized from CH_2Cl_2–petroleum ether (40:60). Yield: 90% (532 mg). Anal. Calc. for $BC_{24}ClF_4H_{24}N_4Ru$: C, 48.64; H, 4.05; N, 9.45. Found: C, 48.88; H, 4.31; N, 9.41%. FABMS; *m*/*z* obs. (calc.): 505 (505); 470 (469); 235 (235). ^{1}H-NMR ($CDCl_3$, Me_4Si, δ ppm, *J* Hz): 9.67 (d, 1H, 3.0, H_1); 9.50 (d, 1H, 5.4, $H_{6'}$); 9.00 (d, 1H, 2.7, H_2); 8.59 (d, 1H, 6.6, H_6); 8.14 (t, 1H, 7.8, H_4); 8.00 (d, 2H, 7.5, H_3); 7.90 (t, 1H, 7.8, $H_{4'}$); 7.69 (m, 2H, 7.5, $H_{5+5'}$); 6.93 (d, 1H, 8.1, H_3); 6.03 (AB, 4H, 6.6), 2.56 (sep, 1H, 6.9); 2.21 (s, 3H); 0.98 (d, 6H, 6.9). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, Me_4Si, δ ppm): 156.5; 153.4; 149.4; 138.2; 128.1; 124.7 (pyrazyl and pyridyl carbons); 107.5 (*C*–$CHMe_2$); 101.9 (*C*–CH_3); 85.8 (C_6H_4); 30.5 ($CH(CH_3)_2$); 22.1 ($CH(CH_3)_2$); 18.9 (*C*–CH_3). UV–vis: λ_{max} (nm) (ε, 10^{-4} $dm^{-3}\,mol^{-1}\,cm^{-1}$): 420 (16 700), 335 (15 050), 264 (14 470).

5.2.2. $[\{(\eta^6\text{-}C_{10}H_{14})RuCl\}_2(\mu\text{-}bppz)](BF_4)_2$ (**2**)

This complex was prepared by following the above-mentioned procedure (Section 5.2.1) except that the complex $[\{(\eta^6\text{-}C_{10}H_{14})RuCl_2\}_2]$ and the ligand bppz were taken in 1:1 molar ratio. It separated as brown microcrystalline solid and was further recrystallized from CH_2Cl_2–petroleum ether. Yield: 70% (721 mg). Anal. Calc. for $B_2C_{34}Cl_2F_8H_{38}N_4Ru_2$: C, 42.99; H, 4.00; N, 5.90. Found: C, 42.81; H, 4.05; N, 5.88%. FABMS; *m*/*z* obs. (calc.): 778 (775); 505 (505); 470 (468); 335 (334). ^{1}H-NMR ($CDCl_3$, Me_4Si, δ ppm, *J* Hz): 9.69 (s, 2H, 7.3); 9.53 (d, 4H, 7.5); 7.92 (m, 2H, 6.3); 8.16 (m, 2H, 8.1); 8.53 (d, 1H, 7.8); 6.10 (AB, 4H, 6.4); 2.74 (sep, 1H, 6.6); 2.16 (s, 3H); 1.13 (d, 6H, 6.9). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, Me_4Si, δ ppm): 156.8; 152.6; 149.4; 139.5; 127.4; 123.2 (pyrazyl and pyridyl carbons); 106.1 (*C*–$CHMe_2$); 100.6 (*C*–CH_3); 86.9–85.8 (C_6H_4); 31.5 ($CH(CH_3)_2$); 22.0 ($CH(CH_3)_2$); 17.6 (C–CH_3). UV–vis: λ_{max} (nm) (ε, 10^{-4} $dm^{-3}\,mol^{-1}\,cm^{-1}$): 455 (17 420), 365 (19 110), 272 (14 980).

5.2.3. $[(\eta^6\text{-}C_6Me_6)RuCl(bppz)]BF_4$ (**3**)

This complex was prepared following the above-mentioned procedure (Section 5.2.1) except that the complex $[\{(\eta^6\text{-}C_6Me_6)RuCl_2\}_2]$ was used in place of $[\{(\eta^6\text{-}C_{10}H_{14})RuCl_2\}_2]$. It isolated in the form of dark-red microcrystalline solid. Yield: 72% (446 mg). Anal. Calc. for $BC_{26}ClF_4H_{28}N_4Ru$: C, 50.32; H, 4.51; N, 9.03. Found: C, 50.12; H, 4.53; N, 9.28%. FABMS; *m*/*z* obs. (calc.): 533 (533); 498 (497); 263 (263). ^{1}H-NMR ($CDCl_3$, Me_4Si, δ ppm, *J* Hz): 9.73 (d, 1H, 3.6); 9.25 (d, 1H, 7.5); 9.10 (d, 1H, 4.8); 8.45 (d, 1H, 6.6); 8.21 (m, 2H, 7.5); 8.06 (d, 1H, 7.5); 7.84 (t, 1H, 7.8); 7.63 (t, 1H, 6.0); 6.87 (d, 1H, 6.0); 2.12 (s, 18H). UV–vis: λ_{max} (nm): 426, 335, 267.

5.2.4. $[\{(\eta^6\text{-}C_6Me_6)RuCl\}_2(\mu\text{-}bppz)](BF_4)_2$ (**4**)

This complex was prepared following the procedure outlined in Section 5.2.2 starting from $[\{(\eta^6\text{-}C_6Me_6)RuCl_2\}_2]$ (668 mg, 1 mmol) and bppz (234 mg, 1 mmol). It was separated as brown microcrystalline solid. Yield: 74% (743 mg). Anal. Calc. for $B_2C_{38}Cl_2F_8H_{46}N_4Ru_2$: C, 45.37; H, 4.57; N, 5.57. Found: C, 45.40; H, 4.51; N, 5.67%. FABMS; *m*/*z* obs. (calc.): 832 (833); 533 (533); 498 (497). ^{1}H-NMR ($CDCl_3$, Me_4Si, δ ppm, *J* Hz): 9.73 (d, 1H, 3.6); 9.68 (d, 2H, 8.4); 8.25 (m); 8.48 (m); 7.84 (m); 2.14 (s). UV–vis: λ_{max} (nm) (ε, 10^{-4} $dm^{-3}\,mol^{-1}\,cm^{-1}$): 489 (23 380), 385 (25 530), 256 (14 300).

5.2.5. $[\{(\eta^6\text{-}C_{10}H_{14})RuCl\}_2(\mu\text{-}bptz)](BF_4)_2$ (**5**)

In a typical reaction a suspension of the complex $[\{(\eta^6\text{-}C_{10}H_{14})RuCl_2\}_2]$ (612 mg, 1 mmol.) in MeOH (30 ml) was treated with bptz (236 mg, 1 mmol) and the resulting solution was heated under reflux for about 4 h. The color of the solution changed to bluish-green. After cooling to r.t., it was filtered through celite to remove any solid residue. To the filtrate, a saturated solution of NH_4BF_4 in MeOH (10 ml) was added and

Table 2
Crystal data and structure refinement parameters for $[Ru(\eta^6\text{-}C_{10}H_{14})Cl(bppz)](BF_4)$

Empirical formula	$C_{24}H_{24}BClF_4N_4Ru$
Formula weight	591.80
Color, shape	Greenish–brown, plate
Crystal system	Monoclinic
Space group	C_2/c
Unit cell dimensions	
a (Å)	16.103(5)
b (Å)	16.207(2)
c (Å)	19.124(2)
β	91.61(2)
V (Å^3)	4989.0(5)
Z	8
$D_{(calc)}$ (g cm^{-3})	1.576
Absorption coefficient (mm^{-1})	6.516
F(000)	2384
Crystal size (mm)	0.3125 × 1.0 × 1.563
Reflections collected	5089
Independent reflections	4854 [$R_{int} = 0.0391$]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0669$, $wR_2 = 0.215$
Number of parameters	317
R indices (all data)	$R_1 = 0.0729$, $wR_2 = 0.2207$
Goodness-of-fit on F_2	1.790
Largest difference peak and hole (e A^{-3})	1.072 and −1.813

left in a refrigerator for slow crystallization. The dark-blue powder thus obtained was filtered, washed with a little of MeOH, Et_2O and dried under vacuo. It was then recrystallized from acetone–Et_2O. Yield: 55% (523 mg). Anal. Calc. for $B_2C_{32}Cl_2F_8H_{36}N_6Ru_2$: C, 40.37; H, 3.78; N, 8.83. Found: C, 40.18; H, 3.75; N, 8.79%. ^{1}H-NMR ($CDCl_3$, Me_4Si, δ ppm, J Hz): 9.40 (d, $H_{6+6'}$); 8.51 (t, $H_{4+4'}$); 8.19 (t,.$H_{5+5'}$); 7.75 (d, 1H, 3.0, $H_{3+3'}$); 5.86 (AB, 4H, 5.4); 2.70 (sep, 1H, 6.6); 1.96 (s, 3H); 1.22 (d, 6H, 6.9). UV–vis λ_{max} (nm) (ε, 10^{-4} dm^{-3} mol^{-1} cm^{-1}): 622 (14 570), 446 (10 230), 329 (16 120).

5.2.6. $[\{(\eta^6\text{-}C_6Me_6)RuCl\}_2(\mu\text{-}bptz)](BF_4)_2$ (**6**)

This complex was prepared by following the procedure outline in Section 5.2.5 except that complex $[\{(\eta^6\text{-}C_6Me_6)RuCl_2\}_2]$ was used in place of $[\{(\eta^6\text{-}C_{10}H_{14})\text{-}RuCl_2\}_2]$. It separated as dark-brown microcrystalline solid. Yield: 62% (625 mg). Anal. Calc. for $B_2C_{36}Cl_2F_8H_{44}N_6Ru_2$: C, 42.89; H, 4.36; N, 8.34. Found; C, 42.31; H, 4.21; N, 8.09%. FABMS; m/z obs. (calc.): 831 (833); 797 (797); 535 (534); 500 (498); 336 (336). ^{1}H-NMR ($CDCl_3$, Me_4Si, δ ppm, J Hz): 9.58 (d, 1H, 6.9); 9.12 (d, 1H, 12.0); 8.22 (t, 2H, 10.72); 7.86 (t, 1H, 9.6); 2.14 (s, 18H). UV–vis: λ_{max} (nm): 635, 440, 335, 280.

5.2.7. $[\{(\eta^6\text{-}C_{10}H_{14})RuCl\}_2(\mu\text{-}tptz)](BF_4)_2$ (**7**)

This complex was prepared following the procedure outlined in Section 5.2.5 except that tptz was used in place of bptz. It gave a dark-blue complex. Yield: 85% (873 mg). Anal. Calc. for $B_2C_{38}Cl_2F_8H_{40}N_6Ru_2$: C, 44.40; H, 3.89; N, 8.17. Found: C, 44.26; H, 3.75; N, 8.12%. FABMS; m/z obs. (calc.): 890 (890); 752 (747); 578 (576); 263 (263). ^{1}H-NMR ($CDCl_3$, Me_4Si, δ ppm): 9.26 (d, 4.2, $H_{6+6'}$); 8.94 (d, 7.8, $H_{3+3'}$); 8.56 (d, 6.6, $H_{5''}$); 8.34 (m, 7.8, $H_{3''+4'+4''}$); 7.86 (dd. 7.8, $H_{5+5'}$); 7.60 (m, 7.8, $H_{6''}$); 6.08 (AB, 4H,); 2.86 (sep, 1H, 6.6); 2.06 (s, 3H); 1.26 (d, 6H, 6.9). UV–vis: λ_{max} (nm) (ε, 10^{-4} dm^{-3} mol^{-1} cm^{-1}): 603 (24 413), 350 (23 210), 265 (21 780).

5.2.8. $[\{(\eta^6\text{-}C_6Me_6)RuCl\}_2(\mu\text{-}tptz)](BF_4)_2$ (**8**)

This complex was prepared following the above-mentioned procedure (Section 5.2.7) starting from $[\{(\eta^6\text{-}C_6Me_6)\ RuCl_2\}_2]$ (668 mg, 1 mmol) and tptz (312 mg, 1 mmol). Yield: 74% (830 mg). Anal. Calc. for $B_2C_{42}Cl_2F_8H_{48}N_6Ru_2$: C, 46.53; H, 4.43; N, 7.75. Found: C, 46.47; H, 4.46; N, 7.41%. ^{1}H-NMR ($CDCl_3$, Me_4Si, δ ppm): 9.12 (d); 8.88 (d); 8.49 (d); 8.38 (m); 7.92 (AB); 7.66 (m); 1.12 (s). UV–vis: λ_{max} (nm): 603, 450, 332.

5.3. X-ray structure determination of $[(\eta^6\text{-}C_{10}H_{14})RuCl(BPPZ)](BF_4)$ (**1**)

Crystals of the complex **1** suitable for X-ray crystallographic studies were obtained from CH_2Cl_2–petroleum ether at r.t. over a period of 3 days. All the pertinent crystallographic data are given in Table 2. Intensity data were collected at 293(2) K on an Enraf–Nonius CAD-4 automatic diffractometer using Cu–K_α radiation ($\lambda = 1.5418$ Å) from plate-like red crystal with the dimensions 0.312 × 1.000 × 1.563 mm in the ω–2θ scan mode in the range from 3.87 to 75.14°. Intensities of the three reflections were measured periodically to monitor the crystal decay.

The structure was solved by direct methods and refined by full matrix least-squares on F^2 (SHELX-97) [19]. In the final cycles of refinement all the non-H atoms were treated anisotropically. The H-atoms attached to carbon atoms were included as fixed contribution. The function minimized was $\Sigma w(F_o - F_c)^2$ where $w^{-1} = \sigma^{-2}(F) + 0.0012F^2$, resulting in $R = 0.0729$; $wR_2 = 0.2207$; goodness-of-fit = 1.790.

6. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 161927 for the compound $[(\eta^6\text{-}C_{10}H_{14})RuCl(bppz)]BF_4$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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