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Tuned Helical Array of Rh^{III}/Ir^{III} Cp* Complexes with Polypyridyl Ligands

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Reactions of the chloro-bridged dimeric complexes $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ (M = Rh, Ir) with the polypyridyl ligands 2,3-di(2-pyridyl)pyrazine (dpp) and 2,4,6-tri(2-pyridyl)-1,3,5-triazine (tptz) in the presence of ammonium tetrafluoroborate gave the mononuclear complexes $[(\eta^5\text{-}C_5Me_5)MCl(\kappa^2\text{-}dpp)]BF_4$ [M = Rh (**1**), Ir (**2**)] and $[(\eta^5\text{-}C_5Me_5)MCl(\kappa^2\text{-}tptz)]BF_4$ [M = Rh (**3**), Ir (**4**)]. The complexes have been characterised by elemental analysis, FAB-MS, ESMS, IR, NMR, electronic and emission spectroscopic studies and the molecular structures of **1**, **2** and **3** have been crystallographically determined. Structural studies on the complexes revealed the presence of helical superstructures resulting from C–H···X (X = N, F, Cl and π) interactions.

Introduction

The chemistry and photophysical properties of the Rh^{III} and Ir^{III} complexes of polypyridyl ligands and substituted cyclopentadienyl group are well documented.[1] Since their discovery in 1968 the pentamethylcyclopentadienyl complexes $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ (M = Rh, Ir) have attracted the attention of many research groups because of their potential as precursors and uses as hydride transfer catalysts.[2] The complexes undergo a rich variety of chemical transformations via the intermediacy of chloro bridge cleavage reactions leading to the formation of a series of interesting neutral and cationic mononuclear complexes.[3] Despite extensive studies on the complexes $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ (M = Rh, Ir), their reactivity with potential bridging ligands, viz. 2,3-di(2-pyridyl)pyrazine (dpp) and 2,4,6-tri(2-pyridyl)-1,3,5-triazine, has yet to be explored. Furthermore, the construction of self-assembled structures has attracted increasing scientific attention.[4,5] A properly designed building block with a metal ion defines the morphology of coordination networks and huge supramolecular architectures.[4] The use of forces such as hydrogen bonding and weak interactions as a powerful tool for self-assembling is widely accepted. The introduction of helices into artificial systems (as in supramolecular chemistry) has increased the number of intensive investigations by chemists for many years.[4,5]

During past few years we have become interested in this area and, in continuation of our studies in this direction, we have examined the reactivity of the polypyridyl ligands 2,3-di(2-pyridyl)pyrazine and 2,4,6-tri(2-pyridyl)-1,3,5-triazine with the chloro-bridged complexes $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ (M = Rh, Ir) under varying reaction conditions.[6–7] We present herein, reproducible syntheses and spectroscopic properties of the complexes $[(\eta^5\text{-}C_5Me_5)MCl(\kappa^2\text{-}dpp)]BF_4$ [M = Rh (**1**), Ir (**2**)] and $[(\eta^5\text{-}C_5Me_5)MCl(\kappa^2\text{-}tptz)]BF_4$ [M = Rh (**3**), Ir (**4**)]. We also describe the crystal and molecular structures of the representative dpp and tptz complexes $[(\eta^5\text{-}C_5Me_5)Rh(\kappa^2\text{-}dpp)]BF_4$ **1**, $[(\eta^5\text{-}C_5Me_5)Ir(\kappa^2\text{-}dpp)]BF_4$ **2** and $[(\eta^5\text{-}C_5Me_5)RhCl(\kappa^2\text{-}tptz)]BF_4$ **3** as well as our results from studies of weak interaction in these complexes.

Results and Discussion

Synthesis and Characterisation

The reactions of the chloro-bridged dimeric complexes $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ (M = Rh, Ir) with an excess of the polypyridyl ligands 2,3-di(2-pyridyl)pyrazine and 2,4,6-tri(2-pyridyl)-1,3,5-triazine in methanol afforded cationic mononuclear complexes in reasonably good yields (Scheme 1). The complexes were isolated as their tetrafluoroborate salts $[(\eta^5\text{-}C_5Me_5)RhCl(\kappa^2\text{-}dpp)]BF_4$ (**1**), $[(\eta^5\text{-}C_5Me_5)RhCl(\kappa^2\text{-}tptz)]BF_4$ (**2**), $[(\eta^5\text{-}C_5Me_5)IrCl(\kappa^2\text{-}dpp)]BF_4$ (**3**) and $[(\eta^5\text{-}C_5Me_5)IrCl(\kappa^2\text{-}tptz)]BF_4$ (**4**).

The cationic orange-red crystalline compounds with high melting temperatures were isolated as air-stable, nonhygroscopic solids. The complexes are soluble in methanol, acetone, dichloromethane, chloroform, acetonitrile, dimethylformamide and dimethylsuphoxide but insoluble in petroleum ether and diethyl ether. They form air sensitive solutions in acetonitrile, dimethyl sulfoxide and dimethylformamide and turn brownish-black after a couple of hours. The structural identities and homogeneity of **1**–**4** were estab-

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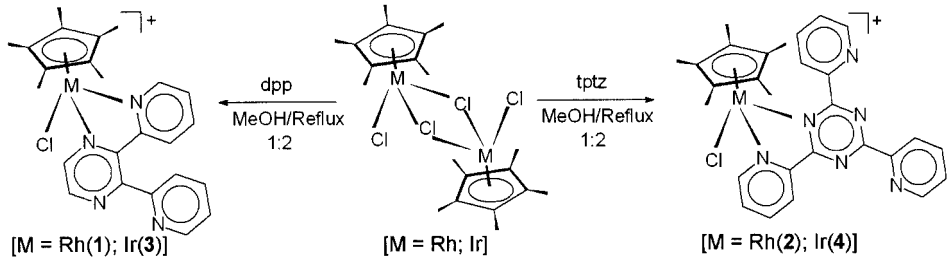

Scheme 1.

lished by analytical techniques, the results of which are consistent with their proposed formulations. Further information regarding compositions was obtained from FAB-mass spectrometry. FAB-mass spectrometric data (reported in the Exp. Sect.) of **1**–**4** are consistent with their respective formulations. ^{1}H NMR spectroscopic data in $CDCl_3$ for **1**–**4** are reported in the experimental section and representative spectra for $[(\eta^5\text{-}C_5Me_5)RhCl(\kappa^2\text{-dpp})]BF_4$ (**1**) in $CDCl_3$ are shown in Figure 1. The ^{1}H NMR spectrum of **1** exhibits distinct resonances at δ = 7.14 (d, J = 6.0 Hz, 1 H), 7.60 (dd, J = 4.5 Hz, 1 H), 7.78 (t, J = 2.9 Hz, 2 H), 8.08 (d, J = 3.9 Hz, 2 H), 8.64 (d, J = 4.5 Hz, 1 H), 8.89 (t, J = 3.3 Hz, 1 H), 9.00 (d, J = 2.7 Hz, 1 H) and 9.07 (d, J = 2.7 Hz, 1 H) ppm corresponding to the pyrazyl and pyridyl protons of 2,3-di(2-pyridyl)pyrazine (dpp). The η^5-Cp* protons resonate as a singlet at δ = 1.80 ppm. The positions and integrated intensities of the various resonances corroborate well with the formulation of **1**. The ^{1}H NMR spectrum of the complex $[(\eta^5\text{-}C_5Me_5)RhCl(\kappa^2\text{-tptz})]BF_4$ **2** exhibits signals at δ = 7.61 (t, J = 7.2 Hz, 2 H), 7.95 (t, J = 5.4 Hz, 2 H), 8.03 (m, 2 H), 8.22 (t, J = 7.8 Hz, 1 H), 8.95 (m, 4 H) and 9.19 (d, J = 7.8 Hz, 1 H) ppm assignable to the pyridyl protons of the coordinated tptz ligand and a singlet at δ = 1.79 ppm corresponding to η^5-Cp* protons. A similar trend was observed in the resonances of the analogous iridium complexes **3** and **4**.

Comparative absorption spectra of **1**–**4** recorded in dichloromethane are shown in Figure 2a. Transitions in the 327–455 nm region can be assigned to $M_{d\pi}\rightarrow L_{\pi}^*$ metal to ligand charge-transfer bands (MLCT) and higher energy transitions at ca. 280 nm to the intra-ligand π–π* transition. The absorption bands for the rhodium complexes **1** and **2** are blue shifted relative to those of the iridium(III) counterpart. The complexes were found to be luminescent at room temperature in dichloromethane. Emission spectra of **1** and **2** are shown in Figure 2b. Upon excitation at their respective excitation bands (in parentheses) the complexes exhibit moderate green-yellow to yellow-orange luminescence [449 nm (396 nm) for **1**; 427 nm (351 nm) for **2**; 475 nm (415 nm) for **3** and 469 nm (347 nm) for **4**]. The resultant emissions correspond to $[M_{d\pi}\rightarrow L_{\pi}^*]$ ^{3}MLCT transitions for the polypyridyl ligand since the MCp*Cl moiety does not emit. The Rh–dpp, **1** and Ir–dpp, **3** complexes exhibit analogous emission spectra suggesting $M_{d\pi}\rightarrow dpp_{\pi}^*$ as a common transition origin. This view is further strengthened by a significantly red shifted emission band for the iridium complexes compared with the analogous rhodium complex. This is in keeping with the fact that the d_{π} orbitals of Rh^{III} are more stable than those of Ir^{III}. Rigidity and the delocalisation factor of the acceptor ligand play an appreciable role in the overall photophysical properties of the complexes because they decrease the extent of structural changes in the excited state which in turn decreases the nonradiative decay and stabilises the ^{3}MLCT based excited state. The analogous Rh–tppz, **2** and Ir–tppz, **4** complexes exhibit equally intense emissions as the respective dpp complexes. These emissions, however, are blue shifted, much broader and less distinct. These results may be better viewed as a consequence of more delocalisation and rigidity of the framework in the coordinated dpp than in tptz.

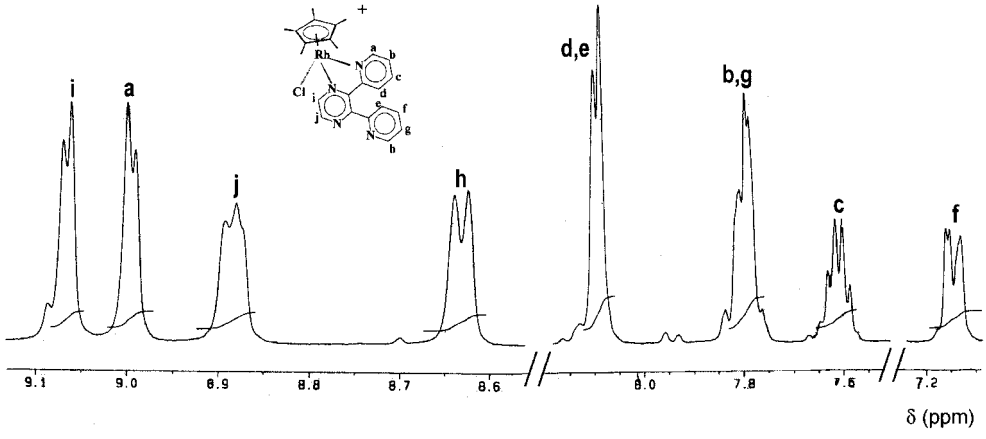

Figure 1. ^{1}H NMR spectra of **1** in $CDCl_3$.

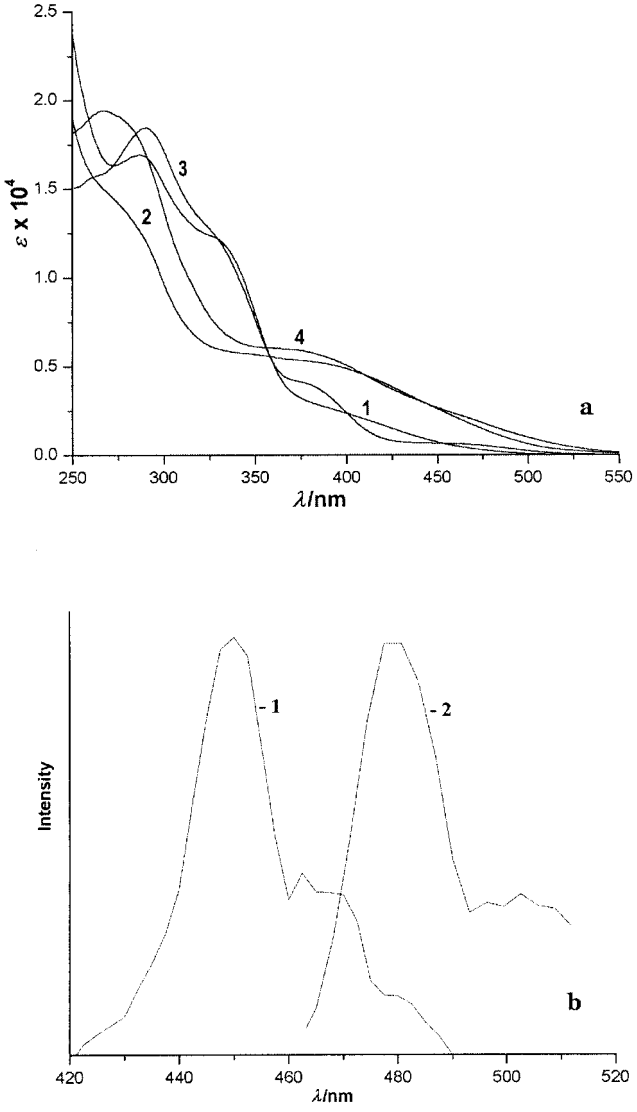

Figure 2. (a) Electronic spectra of **1**, **2**, **3** and **4**; (b) emission spectra of **1** (λ_{ex} = 396 nm) and **2** (λ_{ex} = 351 nm) in dichloromethane.

Solid-State Characterisation of 1, 2 and 3

Suitable crystals with distinct morphologies of **1**, **2**·CH_2Cl_2, and **3**·0.5H_2O were grown from dichloromethane and petroleum ether (40–60°) by diffusion. ORTEP[8] depictions, including atom-numbering schemes of the cations of **1**, **2** and **3** are shown in Figure 3 with selected bond lengths and bond angles listed in Table 1. Complexes **1** and **3** crystallise in the monoclinic space groups $P2_1$ and $P2_1/n$, respectively, while **2** crystallises in the orthorhombic $P2_12_12_1$ space group. Two crystallographically independent molecules can be observed in the unit cell of **1**, the only major difference between them being the orientation and a lengthening of the Rh–Cl and Ru–N bonds in one molecule. The solid-state structures of **1** and **3** are analogous, each metal centre is coordinated to a pyridyl nitrogen, a pyrazyl nitrogen, a chlorine ligand and an η^5-coordinated Cp* group. In **2**, the Rh metal centre is coordinated to N(1) and N(2) from the tptz ligand, the chlorine ligand Cl(1) and the η^5 Cp* group. Considering the Cp* as a single coordination site, the overall coordination geometry about the metal centres in the complexes **1**, **2** and **3** is pseudo-octahedral or typical piano stool geometry. Average $M–C_{Cp^*}$ distances in **1** (two asymmetric units), **2** and **3** are 2.141 Å [range 2.114(18)–2.19(2) Å; Rh–C_{ct} 1.759 Å], 2.179 Å [range 2.135(19)–2.231(19) Å; Rh–C_{ct} 1.817 Å], 2.154 Å [range 2.127(10)–2.184(12) Å; Rh–C_{ct} 1.776 Å] and 2.169 Å [range 2.154(10)–2.190(10) Å; Ir–C_{ct} 1.795 Å], respectively.[9,10a] The C–C bond lengths within the Cp* ring and the C–CH_3 bond lengths are normal. The M–Cl distances in **1**, **2** and **3** are normal [Rh–Cl 2.378(5), 2.403(6) Å **1**; 2.408(3) Å **2** and Ir–Cl 2.395(3) Å **3**].[9a,10] The Rh–N bond lengths in **1** and **2** are all within reported values.[9a,10,13] The Ir–N distances are comparable with those in related Cp*Ir complexes.[3c,3d,9a] The angles N–M–N and N–M–Cl (M = Rh, Ir) are as expected for all the complexes. The molecular structures of **1** and **3** show that the coordinated pyridyl ring and pyrazine ring deviate slightly from planarity [9(2)°, 10(2)° **1** and 9(2)° **3**] while the uncoordinated pyridyl ring is inclined at an angle of ca. 44° with respect to the coordinated pyrazine ring plane [44(2)°, 42(3)° **1** and 44.6(15)° **3**]. However, in the free dpp ligand, the dihedral angles between the pyrazine and pyridyl rings are 42.2°.[11] The pyrazyl rings in both the **1** and **3** are planer with a deviation of ca. 8°. In **2**, upon coordination with the metal centre rhodium in the κ^2-mode, the tptz ligand loses its planarity. The coordinated pyridyl ring subtends an angle of 11.9(13)° with respect to central triazine ring whereas the uncoordinated pyridyl rings are inclined from the central triazine ring by 9.6(14)° for the N(1)–C(5) ring and 34.6(14)° for the N(6)–C(14) ring. The average C–C(C_5Me_5) bond lengths in the Cp* group are 1.415 Å and 1.438 Å in **1**, 1.432 Å in **2** and 1.443 Å in **3** and the exterior C(C_5Me_5)–C(C_5Me_5) average bond lengths are 1.482 Å and 1.500 Å in **1**, 1.479 Å in **2** and 1.493 Å in **3**.[12]

Weak interaction studies on the isostructural complexes **1**, **2** and **3** revealed the presence of supramolecular helical self-assembled architectures with their individual peculiarities (Figure 4). Various intra- and intermolecular C–H···X (X = F, Cl, N, and π) weak interactions are involved in stabilising the helical superstructures of the complexes **1**–**3**.[4,5,13] Determinant intermolecular interactions D–H···A–X (d = H···A, D = D–H···A, θ = D–H···A, φ H···A–X and ω = D–H···A–X) which stabilise the helical superstructures are listed in Table 2. A distorted circular void space can be visualised for the complexes when viewed parallel to the a axis as depicted in Figure 5. A correlation between the pitch length and void size has been established. The helical superstructures for all the complexes involve two molecular residues in each coil though a steady contraction of the void space may be observed upon moving from **1** to **3**. The observed pitches are 7.639, 11.354 and 15.186 Å for **1**, **2** and **3**, respectively. Furthermore, it was observed that as the pitches of the helical superstructures show an increase of almost 50% (ca. 7.5 Å) and the diameter of the void spaces decrease by ca. 8.0 Å (80%) (diameters of the void space are ca. 10.0 Å in **1**, ca. 5.0 Å in **2** and ca. 2.0 Å in **3** as

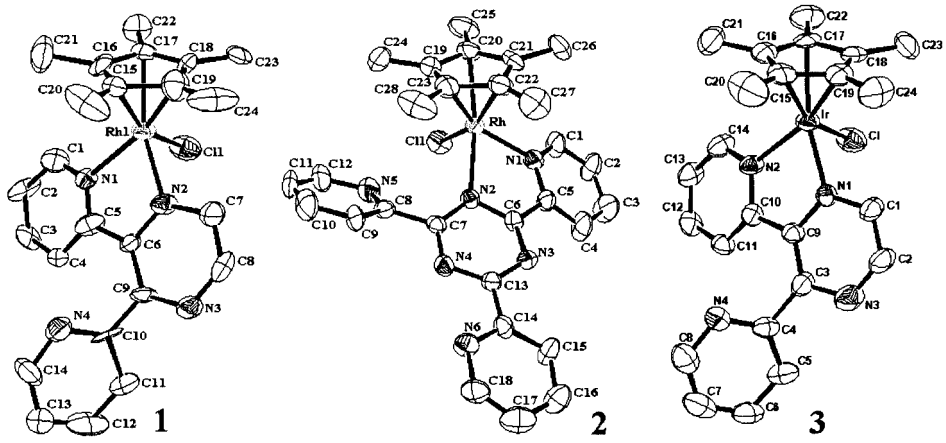

Figure 3. ORTEP view of **1**, **2** and **3**.

Table 1. Selected bond length [Å], bond angles [°] and torsion angles [°] in **1**, **2** and **3**.

1		**2**	**3**
Rh(1)–N(1) 2141(14)	Rh(2)–N(5) 2.049(13)	Rh–N(1) 2.114(8)	Ir–N(1) 2.090(8)
Rh(1)–N(2) 2.084(14)	Rh(2)–N(6) 2.106(16)	Rh–N(2) 2.191(7)	Ir–N(2) 2.074(8)
Rh(1)–Cl(1) 2.403(6)	Rh(2)–Cl(2) 2.378(5)	Rh–Cl(1) 2.378(5)	Ir–Cl 2.395(3)
Rh(1)–Ct 1.759	Rh(2)–Ct 1.817	Rh–Ct 1.776	Ir–Ct 1.795
Rh(1)–Cav 2.141	Rh(2)–Cav 2.179	Rh–Cav 2.154	Ir–Cav 2.1694
N(1)–Rh(1)–N(2) 74.9(5)	N(5)–Rh(2)–N(6) 77.2(6)	N(1)–Rh–N(2) 76.3(3)	N(1)–Ir–N(2) 75.6(3)
N(1)–Rh(1)–Cl(1) 85.7(4)	N(5)–Rh(2)–Cl(2) 86.9(5)	N(1)–Rh–Cl 96.4(2)	N(1)–Ir–Cl 84.9(2)
N(2)–Rh(1)–Cl(1) 86.6(5)	N(6)–Rh(2)–Cl(2) 86.3(5)	N(2)–Rh–Cl 85.8(3)	N(2)–Ir–Cl 84.7(3)
N(1)–C(5)–C(6)–N(2) 10(2)	N(5)–C(29)–C(30)–N(6) 9(2)	N(1)–C(5)–C(6)–N(2) 11.9(13)	N(1)–C(5)–C(6)–N(2) 9(12)
N(2)–C(7)–C(8)–N(3) 0(3)	N(6)–C(31)–C(32)–N(7) 16(4)	N(2)–C(7)–C(8)–N(5) 34.6(14)	N(2)–C(7)–C(8)–N(3) 9(2)
N(3)–C(9)–C(10)–N(4) 44(2)	N(7)–C(33)–C(34)–N(8) 140.5(16)	N(4)–C(13)–C(14)–N(6) 9.6(14)	N(3)–C(9)–C(10)–N(4) 136.3(11)

shown in Figure 5).[14] Thus it is noteworthy to mention here that *the pitch size is inversely proportional to the diameter of the void space in the helical superstructure.* Though no guest molecules are included in the void spaces of the helical frameworks in any of the complexes they are, however, prospective hosts for guest inclusion.

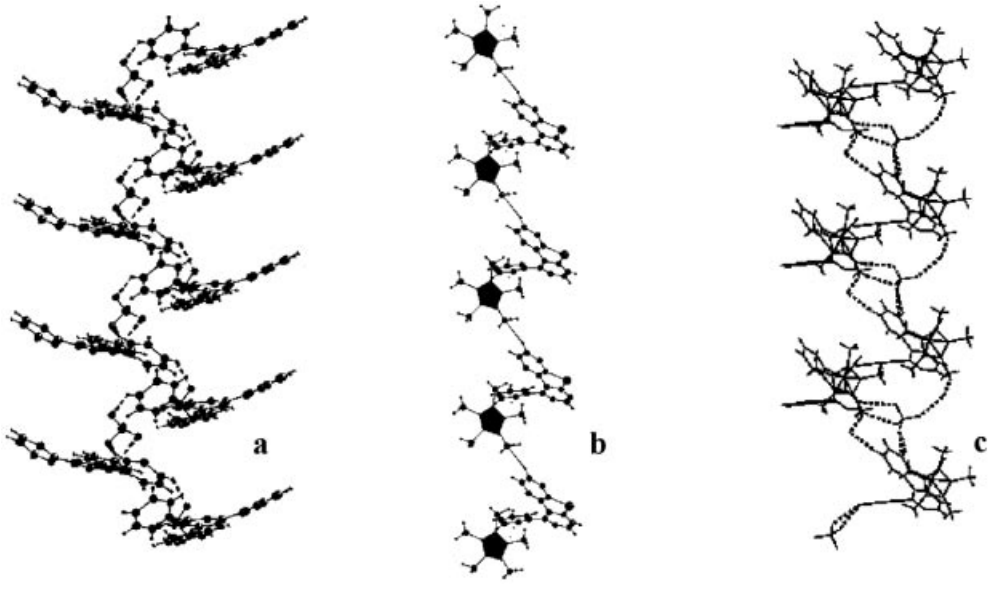

Figure 4. Helical arrangements of **1** (a) (*P*-type), **2** (b) (*M*-type) and **3** (c) (*M*-type).

Table 2. Hydrogen bond parameters for **1**, **2** and **3**.

D–H···A–X	*d* H···A [Å]	*D* D···A [Å]	θ D–H···A [°]	φ H···A–X [°]	ω D–H···A–X [°]
1					
C1–H1···F7–B2[a]	2.53	3.26	135.5	149.0	161.7
C13–H13···F7–B2[b]	2.55	3.25	132.9	129.5	0.2
C8–H8···π	2.85	3.37	116.2	–	–
C46–H46A···π	2.87	3.71	145.9	–	–
2					
C1–H1···Cl3–C29[c]	2.58	3.40	146.8	119.9	37.7
C11–H11···Cl3–C29[d]	2.34	3.04	132.4	125.5	41.5
3					
C7–H7···F2–B[e]	2.43	3.20	140.1	119.4	88.9
C1–H1···F1–B[f]	2.39	3.13	137.1	149.3	164.1
C23–H23A···N4[g]	2.58	3.43	148.3	–	–

[a] $-x + {}^1/_2, y + {}^1/_2, -z + {}^1/_2$. [b] $x + 1, y, z + 1$. [c] $x - {}^1/_2, -y + {}^3/_2, -z$. [d] $-x + 1, y + {}^1/_2, -z + {}^1/_2$. [e] $-x + {}^3/_2, y - {}^1/_2, -z + {}^1/_2$. [f] $-x + 1, -y + 1, -z + 1$. [g] $x - {}^1/_2, -y + {}^1/_2, z - {}^1/_2$.

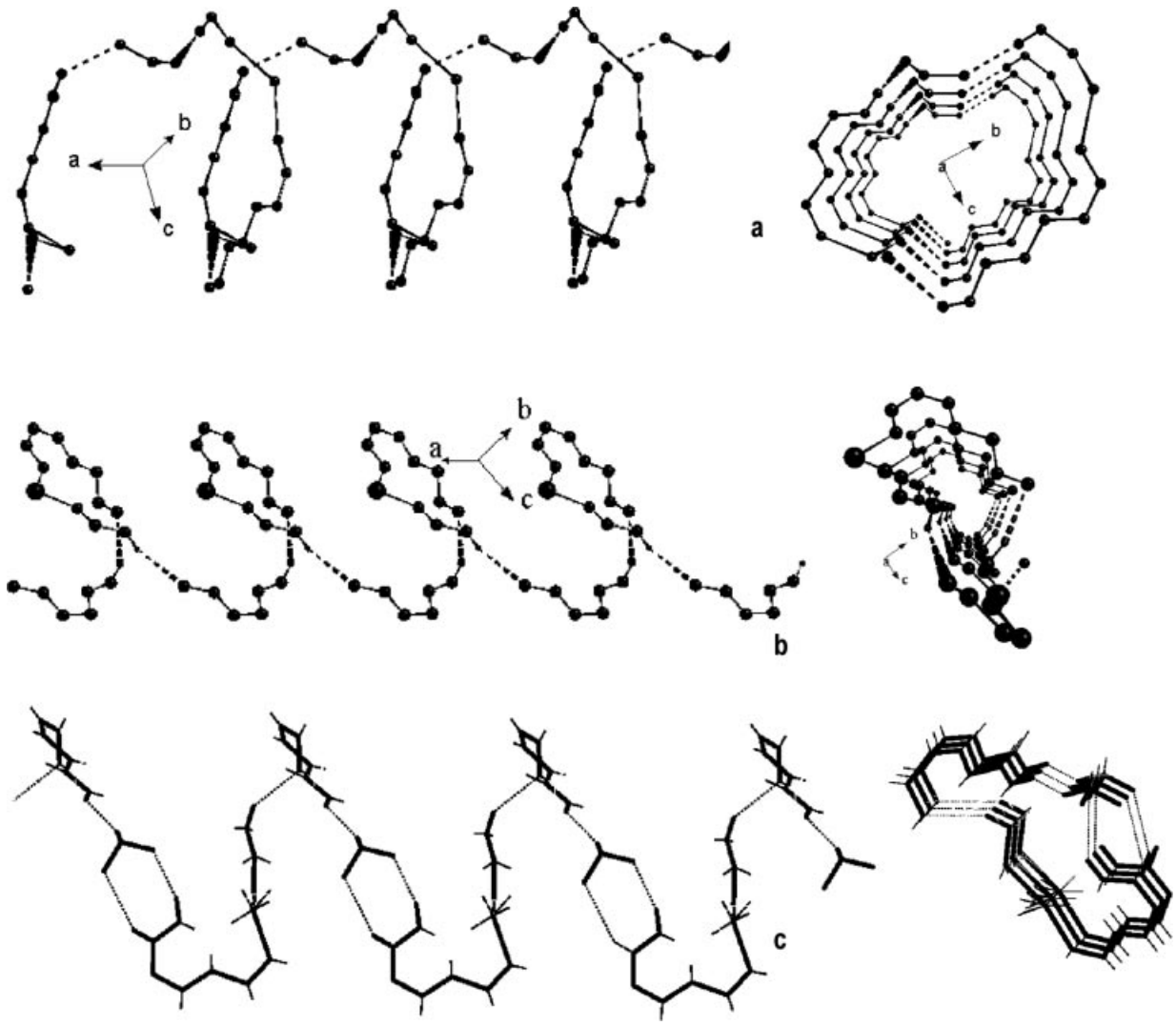

Figure 5. Helical superstructure with circular cavity for **1** (a), **2** (b) and **3** (c).

Conclusions

In this work we have presented four new cationic mononuclear rhodium(III) and iridium(III) complexes $[(\eta^5\text{-}C_5Me_5)MCl(\kappa^2\text{-}L)]BF_4$ (M = Rh, L = dpp **1**, tptz **2** and M = Ir, L = dpp **3**, tptz **4**) and have described spectroscopic properties and molecular structures of three representative complexes. Due to the presence of uncoordinated pendant donor sites, these have the potential to behave as *synthons* or *metallo-ligands* and could find applications in the synthesis of $[(\eta^5\text{-}C_5Me_5)MCl]$ (M = Rh, Ir) containing homo- or heterobimetallic complexes. We have also illustrated here an approach towards the organisation of 3D helices, which are stabilised by weak interactions in the crystalline state. Furthermore, a noteworthy relationship between the pitches and the diameters of the void space in the helical superstructures has been observed.

Experimental Section

General: Analytical grade chemicals were used throughout. Solvents were dried and distilled prior to use following standard literature procedures. 2,3-di(2-pyridyl)pyrazine, 2,4,6-tri(2-pyridyl)-1,3,5-triazine, pentamethylcyclopentadiene, ammonium tetrafluoroborate, hydrated rhodium(III) chloride and iridium(III) chloride (all from Aldrich) were used as received. The precursor complexes $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ (M = Rh, Ir) were prepared by literature procedures.[15] Elemental analyses on the complexes were performed by the Microanalytical Laboratory, Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow. Electronic and emission spectra in dichloromethane were obtained on a Shimadzu UV-1601 and a Perkin–Elmer-LS 55 luminescence spectrometer, respectively. Infrared spectra were recorded on a Perkin–Elmer-577 spectrophotometer. ^1H NMR spectra in $CDCl_3$, using tetramethylsilane as an internal reference, were recorded at room temperature on a Bruker-DRX 300 NMR machine. FAB mass spectra were obtained 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.

Synthesis of $[(\eta^5\text{-}C_5Me_5)RhCl(\kappa^2\text{-}dpp)]BF_4$ (1): A suspension of $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl\}_2]$ (0.618 g, 1.0 mmol) in methanol (30 mL) was treated with 2,3-di(2-pyridyl)pyrazine (0.468 g, 2.0 mmol) and stirred at room temperature. The precursor complex slowly dissolved resulting in an orange-red solution. The resultant solution was further stirred at room temperature for about 4 h and then filtered through celite to remove any solid residue. To the filtrate was added a saturated methanolic solution of NH_4BF_4 (10 mL) and the resultant solution was left for slow crystallization in the refrigerator at ca. 4 °C. After a couple of days, a shiny crystalline product appeared which was separated by filtration, washed with methanol (2×10 mL), diethyl ether (2×10 mL) and dried in vacuo. Red-brown solid, yield 0.363 g (61%). $C_{24}H_{25}BClF_4N_4Rh$ (594.65): calcd. C 48.47, H 4.23, N 9.42; found C 48.21, H 4.35, N 9.24. IR (nujol): $\tilde{\nu}$ = 1079 cm^{-1} (B–F). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.80 (s, 15 H, C_5Me_5), 7.14 (d, J = 6.0 Hz, 1 H), 7.60 (dd, J = 4.5 Hz, 1 H), 7.78 (t, J = 2.9 Hz, 2 H), 8.08 (d, J = 3.9 Hz, 2 H), 8.64 (d, J = 4.5 Hz, 1 H), 8.89 (t, J = 3.3 Hz, 1 H), 9.00 (d, J = 2.7 Hz, 1 H), 9.07 (d, J = 2.7 Hz, 1 H). FAB-MS: m/z = 507 $[M]^+$, 472 $[M - Cl]^{2+}$, 237 $[M - Cl - dpp]^{2+}$. UV/Vis: λ_{max} (ε, $dm^3\,mol^{-1}\,cm^{-1}$) = 396 (2.4×10^3), 328 (1.2×10^4), 286 (1.7×10^4), 237 (3.3×10^4) nm.

Synthesis of $[(\eta^5\text{-}C_5Me_5)RhCl(\kappa^2\text{-}tptz)]BF_4$ (2): This was prepared from $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl\}_2]$ (0.618 g, 1.0 mmol) in methanol following the above procedure for **1** but using tptz (0.624 g, 2.0 mmol) in place of dpp. Bright yellow solid, yield 0.417 g (62%). $C_{28}H_{27}BClF_4N_6Rh$ (673.72): calcd. C 49.92, H 4.04, N 12.47; found C 49.97, H 3.98, N 12.31. IR (nujol): $\tilde{\nu}$ = 1083 cm^{-1} (B–F). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.79 (s, 15 H, C_5Me_5), 7.61 (t, J = 7.2 Hz, 2 H), 7.95 (t, J = 5.4 Hz, 2 H), 8.03 (m, 2 H), 8.22 (t, J = 7.8 Hz, 1 H), 8.95 (m, 4 H), 9.19 (d, J = 7.8 Hz, 1 H). FAB-MS: m/z = 585 $[M]^+$, 550 $[M - Cl]^{2+}$, 238 $[M - Cl - tptz]^{2+}$. UV/Vis: λ_{max} (ε, $dm^3\,mol^{-1}\,cm^{-1}$) = 370 (5.4×10^3), 273 (1.5×10^4), 235 (2.7×10^4) nm.

Synthesis of $[(\eta^5\text{-}C_5Me_5)IrCl(\kappa^2\text{-}dpp)]BF_4$ (3): This was prepared by following the same procedure as for **1** but using $[\{(\eta^5\text{-}C_5Me_5)Ir(\mu\text{-}Cl)Cl\}_2]$ (0.796 g, 1.0 mmol) in methanol (30 mL) and 2,3-di(2-pyridyl)pyrazine (0.468 g, 2.0 mmol). Yellow-orange solid, yield 0.451 g (66%). $C_{24}H_{25}BClF_4N_4Ir$ (683.94): calcd. C 42.11, H 3.65, N 8.19; found C 42.20, H 3.50, N 8.26. IR (nujol): $\tilde{\nu}$ = 1081 cm^{-1} (B–F). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.75 (s, 15 H, C_5Me_5), 7.20 (d, J = 3.2 Hz, 1 H), 7.58 (t, J = 5.9 Hz, 1 H), 7.76 (t, J = 4.1 Hz, 2 H), 8.11 (m, 2 H), 8.66 (d, J = 4.3 Hz, 1 H), 8.79 (t, J = 3.3 Hz, 1 H), 8.93 (d, J = 3.2 Hz, 1 H), 9.08 (d, J = 3.1 Hz, 1 H). FAB-MS: m/z = 596 $[M]^+$, 560 $[M - Cl]^{2+}$, 326 $[M - Cl - dpp]^{2+}$.

Table 3. Crystallographic data and refinement parameters for **1**, **2** and **3**.

	1	**2**·CH_2Cl_2	**3**·0.5H_20
Formula	$C_{24}H_{25}BClF_4N_4Rh$	$C_{29}H_{29}BCl_3F_4N_6Rh$	$C_{24}H_{27}BClF_4IrN_4O0.5$
Formula weight	594.65	757.65	693.96
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1$	$P2_12_12_1$	$P2_1/n$
a [Å]	11.354(3)	7.6390(10)	11.3600(8)
b [Å]	15.797(3)	19.6490(10)	15.8850(12)
c [Å]	15.019(5)	21.5380(10)	15.0970(15)
β [°]	111.88(2)	90.00	111.618(7)
V [$Å^3$]	2499.9(11)	3232.8(5)	2532.7(4)
Z	4	4	4
$D_{calcd.}$ [$mg\,m^{-3}$]	1.580	1.557	1.820
Radiation (λ [Å])	Mo-K_α (0.71073)	Cu-K_α (1.54180)	Mo-K_α (0.70930)
Reflections:			
Collected/unique	4783/4557	3259/3259	4654/4417
R_1, wR_2 [$I > \sigma(I)$]	0.0487, 0.1525	0.0713, 0.1989	0.0550, 0.1366
GOF	1.335	1.245	1.010

UV/Vis: λ_{max} (ε, $dm^3 mol^{-1} cm^{-1}$) = 452 (6.3×10^2), 380 (4.0×10^3), 326 (1.2×10^4), 290 (1.8×10^4), 233 (1.9×10^4) nm.

Synthesis of [(η^5-C_5Me_5)IrCl(κ^2-tptz)]BF_4 (4): This was prepared following the above procedure for **3** but using tptz (0.624 g, 2.0 mmol) in place of dpp. Red-brown solid, yield 0.480 g (63%). $C_{28}H_{27}BClF_4N_6Ir$ (763.02): calcd. C 44.09, H 3.54, N 11.02; found C 44.15, H 3.68, N 11.10. IR (nujol): $\tilde{\nu}$ = 1084 cm^{-1} (B–F). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.69 (s, 15 H, C_5Me_5), 7.68 (t, J = 7.1 Hz, 2 H), 7.91 (t, J = 5.5 Hz, 2 H), 8.10 (m, 2 H), 8.27 (t, J = 7.5 Hz, 1 H), 9.01 (m, 4 H), 9.23 (d, J = 7.6 Hz, 1 H). FAB-MS: m/z = 675 $[M]^+$, 639 $\{M - Cl\}^{2+}$, 327 $[M - Cl - tptz]^{2+}$. UV/Vis: λ_{max} (ε, $dm^3 mol^{-1} cm^{-1}$) = 455 (2.5×10^3), 366 (6.0×10^3), 265 (1.9×10^4), 233 (2.2×10^4) nm.

X-ray Crystallography: Suitable crystals of **1**, **2** and **3** for X-ray crystallographic studies were obtained from CH_2Cl_2/petroleum ether by diffusion. X-ray data for **1** and **3** were collected on an automatic Enraf–Nonius MACH 3 diffractometer using graphite-monochromated Mo-K_α radiation at 293(2) K. For **2**, X-ray data were collected at 293(2) K on an Enraf–Nonius CAD-4 diffractometer using monochromated Cu-K_α radiation, λ = 1.54180 Å. The structures were solved by direct methods and refined by using MAXUS-99 and SHELX-97.[16] The non-hydrogen atoms had anisotropically refined thermal parameters. All hydrogen atoms were geometrically fixed and were refined using a riding model. The computer program PLATON was used for analysing the interactions and stacking distances.[16] All the pertinent crystallographic data are listed in Table 3.

CCDC-604770 to -604772 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.

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