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Synthetic, spectral and structural studies of ruthenium(II) compounds based on 2,6-diacetylpyridinemonoxime

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Abstract

Reaction of the ruthenium complexes $[RuCl_2(EPh_3)_3]$ (E = P, As), $[(\eta^5\text{-}C_5H_5)RuCl(EPh_3)_2]$ (E = P, As), $[(\eta^5\text{-}C_5Me_5)RuCl(PPh_3)_2]$ and $[(\eta^5\text{-}C_9H_7)RuCl(PPh_3)_2]$ with 2,6-diacetylpyridinemonoxime (dapmoH) have been investigated. Compounds with the formulations $[Ru(\kappa^3\text{-dapmoH})Cl(PPh_3)_2]PF_6$ (**1**), $[Ru(\kappa^3\text{-dapmoH})Cl(PPh_3)_2]BF_4$ (**2**) and $[Ru(\kappa^3\text{-dapmoH})Cl(AsPh_3)_2]Cl$ (**3**) have been isolated and fully characterized by elemental analyses, IR, NMR, electronic, emission spectral and electrochemical studies. Molecular structures of the complexes $[Ru(\kappa^3\text{-dapmoH})Cl(PPh_3)_2]PF_6 \cdot H_2O$ (**1**) and $[Ru(\kappa^3\text{-dapmoH})Cl(PPh_3)_2]BF_4 \cdot 1.5H_2O$ (**2**) have been determined by single crystal X-ray diffraction studies. A structural feature of interest for both the compounds is that the counter anions in **1** and **2** play vital role in the self-assembly of cages through intermolecular weak interactions in which water dimers or trimers are encapsulated. Compounds **1** and **2** strongly emit upon excitation at their respective MLCT transitions.

Keywords: Ruthenium; Tertiary phosphines; dapmoH; X-ray; Weak interactions; Luminescence

1. Introduction

Considerable attention has been paid towards the construction of molecules and molecular assemblies of different size and shapes to encapsulate guest molecules because of their potential use as selective hosts for anion sensing [1], separation and selective recognition [2], catalysis [3] and gas sorption and storage [4]. The self-assembly of relatively small molecules, through covalent or hydrogen-bonding interactions has proved to be very useful in forming large capsular cavities [5]. Furthermore, use of the functional groups such as oxime to bridge metal centres is also an interesting area as they are easy to prepare and such systems can take advantage of site-preference for metal ions according to Pearson's hard–soft Lewis acid–base index [6]. In the oxime-bridging mode metal binds with the ligand 2,6-diacetylpyridinemonoxime (dapmoH) in κ^3-manner. The major coordination site in this molecule consists of two nitrogen and an oxygen atom and should show preference for softer Lewis acids, while deprotonation of OH group generates an oxide-like species which prefers to bind a hard Lewis acid. Although, a number of first row transition metal complexes containing 2,6-diacetylpyridinedioxime ($dapdoH_2$) are reported in the literature, complexes containing 2,6-diacetylpyridinemonoxime (dapmoH) have scarcely been studied and to our knowledge structural data on any such complex is yet to be reported [7]. On the other hand, water clusters have been extensively studied both theoretically and experimentally, in attempts to provide insight into the structure and properties of liquid water or ice [8]. A variety of water clusters, such as dimers, trimers, tetramers and pentamers having cyclic and quasi-planar minimum energy structures are

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particularly interesting among the possible clusters. A number of reports dealing with water clusters of different nuclearities and structures have been reported in the literature [9,10].

During our studies devoted in this direction ruthenium(II) compounds with the formulations $[Ru(\kappa^3\text{-dapmoH})Cl(PPh_3)_2]PF_6$ (**1**), $[Ru(\kappa^3\text{-dapmoH})Cl(PPh_3)_2]BF_4$ (**2**) and $[Ru(\kappa^3\text{-dapmoH})Cl(AsPh_3)_2]Cl$ (**3**) were isolated from the reactions of $[RuCl_2(EPh_3)_3]$ (E = P, As), $[(\eta^5\text{-}C_5H_5)RuCl(EPh_3)_2]$ (E = P, As), $[(\eta^5\text{-}C_5Me_5)RuCl(PPh_3)_2]$ and $[(\eta^5\text{-}C_9H_7)RuCl(PPh_3)_2]$, respectively, with dapmoH in methanol under refluxing conditions. In this paper, we present reproducible syntheses and spectral characterization of ruthenium compounds with the general formulations $[Ru(\kappa^3\text{-dapmoH})Cl(EPh_3)_2]^+$ (E = P, As). We also describe herein the crystal structures of representative compounds **1** and **2** and encapsulation of water dimer in D2 pattern and trimer in D3 pattern in the molecular cages of **1** and **2** assisted by counter ions.

2. Experimental

2.1. Materials and physical measurements

All the synthetic manipulations were performed under nitrogen atmosphere. The solvents were of AR grade and were purified rigorously by standard procedures prior to their use [11]. Ammonium hexafluorophosphate, ammonium tetrafluoroborate, 2,6-diacetylpyridine, ruthenium(III) chloride hydrate (all Aldrich) were used as received without further purifications. The precursor complexes $[RuCl_2(EPh_3)_3]$ (E = P, As), $[(\eta^5\text{-}C_5H_5)RuCl(EPh_3)_2]$ (E = P, As), $[(\eta^5\text{-}C_5Me_5)RuCl(PPh_3)_2]$ and $[(\eta^5\text{-}C_9H_7)RuCl(PPh_3)_2]$ were synthesized following the literature methods [12]. 2,6-diacetylpyridinemonoxime (dapmoH) was synthesized following the method of Turnbull et al., using 2,6-diacetylpyridine and hydroxylamine hydrochloride [13].

Elemental analyses were performed by Micro-analytical section of the Sophisticated Analytical Instrumentation Centre, Central Drug Research Institute, Lucknow. IR in KBr discs and electronic spectra were recorded on a Shimadzu-8201PC and Shimadzu-UV-1601 spectrophotometers, respectively. ^1H and ^{31}P NMR spectra were acquired on a Bruker DRX-300 NMR instrument. FAB mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer using Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature with *m*-nitrobenzyl alcohol as the matrix. Electrochemical data were acquired on a BAS-100 Epsilon Electrochemical Analyzer using TBAP as a supporting electrolyte. The three electrode measurement was carried out under nitrogen atmosphere with a platinum working electrode, platinum wire auxiliary electrode and calomel reference electrode. Luminescence spectra in the solid state and solution were recorded on a Perkin-Elmer LS-45 luminescence spectrophotometer.

2.2. General synthesis of the complexes

2.2.1. $[Ru(\kappa^3\text{-dapmoH})Cl(PPh_3)_2]PF_6 \cdot H_2O$ (1)

To a suspension of $[RuCl_2(PPh_3)_3]$ (0.958 g, 1.0 mmol) in methanol (25 mL) dapmoH (0.178 g, 1.0 mmol) was added and the resulting solution was heated under reflux for 4 h. The brown solution thus obtained was cooled to room temperature and filtered through Celite to remove any solid impurity. The filtrate was concentrated to one third of its volume under vacuum and a solution of NH_4PF_6 (0.200 g, 1.22 mmol) dissolved in methanol (5 mL) was added to it and left for slow crystallization at ~4 °C. In a couple of days crystalline product appeared which was separated by filtration and washed twice with methanol, diethyl ether and dried *in vacuo*. Yield: 0.80 g (80%). Anal. Calc. for $C_{45}F_6H_{42}ClN_2O_3P_3Ru$ (1002): C, 53.89; H, 4.19; N, 2.79%. Found: C, 53.86; H, 4.17; N, 2.81%. IR (KBr): ν/cm^{-1} 3400(b), 1675(w), 1590(m), 1458(s), 1430(m), 1350(m), 1253(w), 1165(w), 1145(s), 1090(s), 1018(s), 961(w), 845(m), 670(m), 660(w), 630(m), 355(m) cm^{-1}. δ_H (300 MHz; $CDCl_3$; Me_4Si) 10.06 (s, 1H, N—OH), 7.41 (d, J = 6.0 Hz, 2H, Py-3H and 5H), 7.52 (d, J = 9.0 Hz, 1H, Py-4H), 7.36–6.98 (br m aryl protons, PPh_3), 2.22 (s, 2H, H_2O), 1.57 (s, 3H, CH_3), 1.25 (s, 3H, CH_3). δ_P (300 MHz; $CDCl_3$; PCl_3) 27.12 (s, PPh_3), −141.22 (PF_6^-). $^{13}C\{^1H\}$ NMR (d_6-acetone): 155.97 [—C=NOH], 154.50 [py-1(6C)], 137.74 [py-4C], 130.09 [—C—PPh_3] 120.50[py-3(5C)], 10.09 [—CH_3]. FAB-MS: *m/z* 839(838), 29, $[Ru(\kappa^3\text{-dapmoH})Cl(PPh_3)_2]^+$, 577(577), 54, $[Ru(\kappa^3\text{-dapmoH})Cl(PPh_3)]^+$, 315(316), 35, $[Ru(\kappa^3\text{-dapmoH})Cl]^+$. UV/vis: λ_{max} (CH_2Cl_2, ε[dm^3 mol^{-1} cm^{-1}]) 406 (7202), 236 (44980).

Compound **1** was also obtained from the reactions of ruthenium arene complexes $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$, $[(\eta^5\text{-}C_5Me_5)RuCl(PPh_3)_2]$ and $[(\eta^5\text{-}C_9H_7)RuCl(PPh_3)_2]$ with 2,6-diacetylpyridinemonoxime following the above procedure.

2.2.2. $[Ru(\kappa^3\text{-dapmoH})Cl(PPh_3)_2]BF_4 \cdot 1.5H_2O$ (2)

The compound **2** was prepared following the above procedure for **1** using NH_4BF_4 instead of NH_4PF_6. Yield: 0.74 g (78%). Anal. Calc. for $BC_{45}F_4H_{40}ClN_2O_{3.50}P_2Ru$ (950): C, 56.84; H, 4.21; N, 2.94%. Found: C, 56.86; H, 4.17; N, 2.88%. IR (KBr): ν/cm^{-1} 3404(b), 1678(w), 1596(m), 1454(s), 1432(m), 1358(m), 1248(w), 1161(w), 1142(s), 1094(s), 1045(s), 963(w), 818(m), 674(m), 662(w), 634(m), 356(m) cm^{-1}. δ_H (300 MHz; $CDCl_3$; Me_4Si) 10.16 (s, 1H, N—OH), 7.44 (d, J = 6.0 Hz, 2H, Py-3H and 5H), 7.56 (d, J = 9.0 Hz, 1H, Py-4H), 7.36-6.98 (br m aryl protons, PPh_3), 2.21 (s, 2H, H_2O), 1.59 (s, 3H, CH_3), 1.22 (s, 3H, CH_3). δ_P (300 MHz; $CDCl_3$; PCl_3) 27.02 (s, PPh_3). $^{13}C\{^1H\}$ NMR (d_6-acetone): 155.97 [—C=NOH], 154.71 [py-1(6C)], 137.62 [py-4C], 130.09 [—C—PPh_3] 120.50 [py-3(5C)], 10.09 [—CH_3]. FAB-MS: *m/z* 839(838), 24, $[Ru(\kappa^3\text{-dapmoH})Cl(PPh_3)_2]^+$, 577(577), 50, $[Ru(\kappa^3\text{-dapmoH})Cl(PPh_3)]^+$, 315(316), 32, $[Ru(\kappa^3\text{-}$

dapmoH)Cl]$^+$. UV/vis: λ_{max} (CH_2Cl_2, ε[$dm^3\ mol^{-1}\ cm^{-1}$]) 404(7412), 232(43680).

2.2.3. [Ru(κ^3-dapmoH)Cl($AsPh_3$)$_2$]Cl·H_2O (3)

It was prepared following the above procedure for **1** except that [$RuCl_2(AsPh_3)_3$] (1.090 g, 1.0 mmol) was used in place of [$RuCl_2(PPh_3)_3$] and was isolated as chloride salt. Yield: 0.85 g (78%). Anal. Calc. for $As_2C_{45}H_{42}ClN_2O_3Ru$ (980): C, 55.10; H, 4.28; N, 2.85%. Found: C, 55.47; H, 4.78; N, 2.52. IR (KBr): ν/cm^{-1} 3395(b), 1675(w), 1590(m), 1454(s), 1438(m), 1350(m), 1240(w), 1155(w), 1140(s), 1090(s), 1018(s), 961(w), 810(m), 675(m), 650(w), 620(m), 360(m) cm^{-1}. δ_H (300 MHz; $CDCl_3$; Me_4Si) 10.24 (s, 1H, N—OH), 8.41 (d, $J = 6.0$ Hz, 2H, Py-3H & 5H), 7.78 (d, $J = 9.0$ Hz, 1H, Py-4H), 7.35–7.07 (br m aryl protons, $AsPh_3$), 2.28 (s, 2H, H_2O), 1.77 (s, 3H, CH_3), 1.45 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (d_6-acetone): 155.80 [—C=NOH], 154.65 [py-1(6C)], 137.62 [py-4C], 128.20 [—C—PPh_3] 120.50 [py-3(5C)], 10.19 [—CH_3]. FAB-MS: m/z 927(926), 25, [Ru(κ^3-dapmoH)Cl($AsPh_3$)$_2$]$^+$, 891(890), 30, [Ru(κ^3-dapmoH)($AsPh_3$)$_2$]$^+$. UV/vis: λ_{max} (CH_2Cl_2, ε[$dm^3\ mol^{-1}\ cm^{-1}$]) 438(6286), 232(29805).

Compound **3** was also synthesized by reaction of [(η^5-C_5H_5)RuCl($AsPh_3$)$_2$] with 2,6-diacetylpyridinemonoxime following the above procedure.

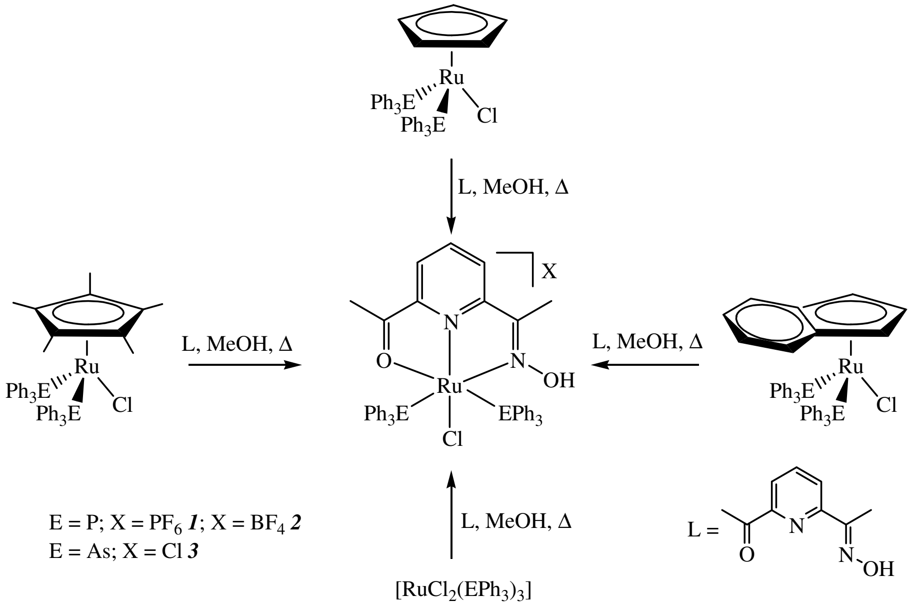
2.3. X-ray crystallographic study

Crystals suitable for single crystal X-ray diffraction analyses for **1** and **2** were obtained from CH_2Cl_2/petroleum ether (60–80°) at room temperature. Intensity data were collected at 293(2) K on Enraf-Nonius CAD 4 diffractometer using graphite monochromatised Mo-Kα radiation ($\lambda = 0.70930$) from plate-like crystals with the dimensions 0.35 × 0.30 × 0.25 (**1**) and 0.40 × 0.30 × 0.25 (**2**) in the $\omega - 2\theta$ scanning technique with 2θ range 4.0–50.0°, respectively. Intensities of these reflections were measured periodically to monitor crystal decay. The structure was solved by direct methods and refined by full matrix least squares on F2 (SHELX-97) [14]. In the final cycles of refinement all the non-H atoms were treated anisotropically. The contribution due to H-atoms attached to carbon atoms was included as fixed contribution. Final value of $R_1 = 0.0433$, GOF = 1.043 for **1** and $R_1 = 0.0631$, GOF = 1.031 for **2**.

3. Results and discussion

3.1. Synthesis

[$RuCl_2(EPh_3)_3$] (E = P, As) reacted with 2,6-diacetylpyridinemonoxime (dapmoH) in methanol under refluxing conditions to afford compounds **1**–**3** as shown in Scheme 1. Furthermore, reactions of the ruthenium complexes containing η^5-bonded hydrocarbon ligands with dapmoH were also examined under analogous conditions. Surprisingly, reactions of the ruthenium η^5-C_5H_5, η^5-C_5Me_5 and η^5-C_9H_7 complexes [(η^5-C_5H_5)RuCl(PPh_3)$_2$], [(η^5-C_5Me_5)RuCl(PPh_3)$_2$] and [(η^5-C_9H_7)RuCl(PPh_3)$_2$] with dapmoH also led to the formation of compound **1** in good yield, while reaction of [(η^5-C_5H_5)RuCl($AsPh_3$)$_2$] gave compound **3**. Interestingly, in these reactions rather strong ruthenium to η^5-C_5H_5, η^5-C_5Me_5 or η^5-C_9H_7 bonds were broken and dapmoH interacted with the metal centre through the major coordination sites in the κ^3-mode. Substitution of the η^5-bonded C_5H_5, C_5Me_5 and C_9H_7 groups by dapmoH may be attributed to the stronger σ donor ability of the latter as compared to the η^5-bonded



Scheme 1.

hydrocarbon ligands. This observation is consistent with earlier reports [15].

3.2. Characterization

Compounds **1**–**3** are air stable solids and does not show any signs of decomposition in solution even exposure to air for several days. These were fully characterized by IR, NMR (^{1}H, ^{13}C and ^{31}P), UV–vis, FAB-MS spectroscopy. Analytical data of the compounds (recorded in Section 2) corroborated well to their formulations. FAB-MS spectra of the compounds corresponded to their respective formulations. Infrared spectra of the compounds in Nujol displayed bands due to oxime ν(C═N) and ν(N—O) at 1590–1596 cm^{-1} and 1090–1094 cm^{-1}, while the band due to carbonyl ν(C═O) appeared at 1675–1678 cm^{-1}. This indicated coordination of dapmoH ligand with the metal centre in κ^3-mode through its major coordination sites. Broad bands in the region 845 and 1045 cm^{-1} have been assigned to counter anion PF_6^- and BF_4^-.

^{1}H and ^{13}C NMR spectra gave expected integration patterns and suggested coordination of dapmoH with ruthenium in the κ^3-manner. $^{31}P\{^1H\}$ NMR spectra of **1** and **2** showed a single resonance at ~27 ppm assignable to the metal-bound ^{31}P nuclei. It suggests that both the ^{31}P nuclei are chemically equivalent and triphenylphosphine ligands are *trans* disposed [16]. The signal associated with ^{31}P nuclei of the counter anion PF_6^- appeared at −141.22 ppm in its characteristic septet pattern. Electrochemical behavior of **1** and **2** were followed by cyclic voltammetry in acetonitrile solutions containing 0.1 M TBAP at 27 °C. Both the compounds displayed quasi-reversible redox waves corresponding to Ru(II)/Ru(III) oxidation couple at 1.23 and 1.20 V with peak-to-peak separation of 51 and 76 mV, respectively, for **1** and **2**. The ligand based quasi-reversible reduction couples were observed at −1.38, 0.75 and −1.38, 0.78 V vs. SCE in **1** and **2**, respectively. In the electronic absorption spectrum of **1**, **2** and **3**, the MLCT transitions appeared in visible region at 406, 404 and 438 nm and the ligand-centred transitions were observed at 236, 232 and 232 nm, respectively.

3.3. X-ray crystallography

The molecular structures of **1** and **2** were determined crystallographically.Perspective view of the cations of **1** and **2** with the atomic labels are shown in Fig. 1. Details about the data collection, solution and refinement are enlisted in Table 1 and selected bond lengths and angles are recorded in Table 2. Compounds **1** and **2** crystallize in monoclinic crystal systems, but with different space groups $P2_1/c$ and $C2/c$, respectively. The Ru(II) centres in both the **1** and **2** adopted distorted octahedral geometry by coordinating to dapmoH ligand in NNO κ^3-mode, two triphenylphosphine and a Cl atom. The angles N(1)—Ru(1)—N(2) and N(1)—Ru(1)—O(1) in **1** are 79.26(15)° and 75.92(14)°, while those in **2** are 78.0(2)° and 77.7(2)°, respectively. The N(2)—Ru(1)—O(1) angles in **1** and **2** are 155.18(15)° and 155.7(2)°, respectively, and the Ru—P distances and P—Ru—P angles in **1** and **2** are essentially equal and comparable to the reported ones [16]. Ruthenium to pyridyl nitrogen Ru(1)—N(1) bonds

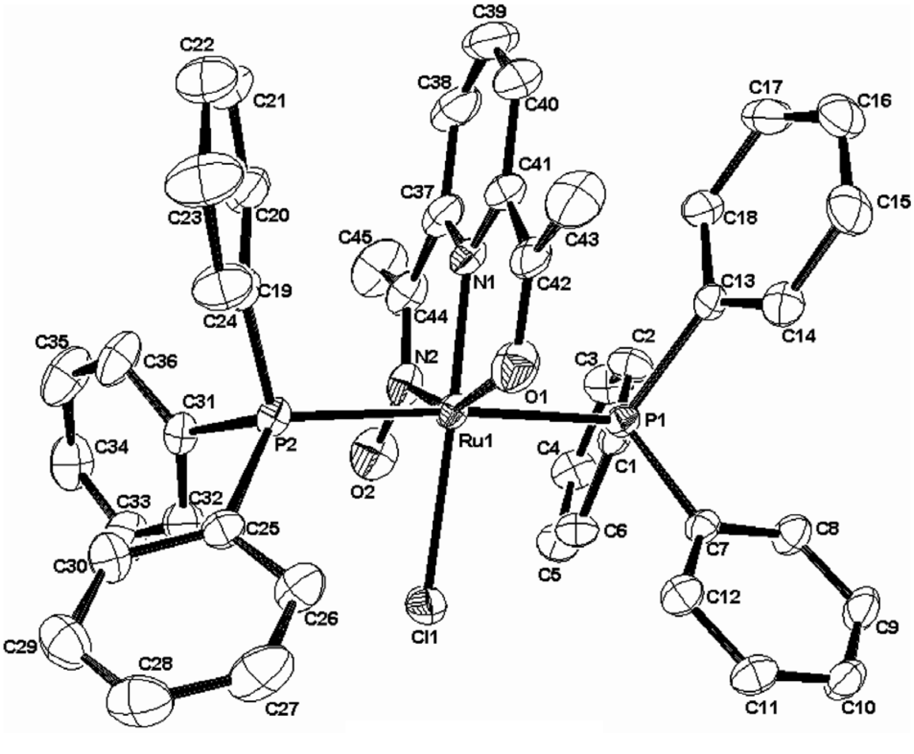


Fig. 1. ORTEP view of the complex cation of **1** with thermal ellipsoids shown at the 30% level; hydrogen atoms were omitted for clarity.

Table 1
Crystallographic data and refinement parameters for **1** and **2**

	1	**2**
Empirical Formula	$C_{45}H_{42}ClF_6N_2O_3P_3Ru$	$C_{45}H_{40}BClF_4N_2O_{3.5}P_2Ru$
Molecular weight	1002.24	950.06
Color and habit	Brown, needles	Brown, blocks
Crystal size (mm)	0.35 × 0.30 × 0.25	0.40 × 0.30 × 0.20
Space group	*P*21/*c*	*C*2/*c*
System	Monoclinic	Monoclinic
a (Å)	11.672(2)	21.851(2)
b (Å)	20.189(4)	11.916(2)
c (Å)	19.576(4)	35.414(3)
β (°)	104.71(3)	101.707(7)
V (Å^3)	4462.0(15)	9029.2(13)
Z	4	8
d_{calc} (g cm^{-3})	1.492	1.398
μ (mm^{-1})	0.586	0.536
Temperature (K)	293 (2)	293 (2)
Reflections collected/unique	8206/7806	8080/7937
R_1 factor $[I > 2\sigma(I)]$	0.0443	0.0631
wR_2	0.1068	0.1809
wR_2 $[I > 2\sigma(I)]$	0.1310	0.1535
Goodness of fit	1.043	1.031

Table 2
Selected bond length (Å), bond angles (°) and torsion angles (°) in **1** and **2**

	1	**2**
Ru(1)—Cl(1)	2.4920(14)	2.4630(17)
Ru(1)—P(1)	2.3402(12)	2.391(2)
Ru(1)—P(2)	2.3711(12)	2.3768(19)
Ru(1)—N(1)	1.970(4)	1.935(5)
Ru(1)—N(2)	2.025(3)	2.011(5)
Ru(1)—O(1)	2.104(3)	2.096(5)
O(2)—N(2)	1.398(5)	1.391(7)
N(2)—Ru(1)—N(1)	79.26(15)	78.0(2)
O(1)—Ru(1)—N(1)	75.92(14)	77.7(2)
N(2)—Ru(1)—O(1)	155.18(15)	155.7(2)
N(2)—Ru(1)—Cl(1)	92.20(12)	93.53(16)
N(1)—Ru(1)—Cl(1)	171.44(11)	171.51(16)
O(1)—Ru(1)—Cl(1)	112.61(11)	110.73(17)
P(2)—Ru(1)—Cl(1)	92.48(5)	88.81(6)
P(1)—Ru(1)—Cl(1)	83.07(5)	87.69(6)
P(2)—Ru(1)—P(1)	175.05(4)	175.60(6)

are 1.970(4) and 1.935(5) Å and ruthenium oxime nitrogen Ru(1)—N(2) bonds are 2.025(3) and 2.011(5) Å, respectively. All Ru—N, Ru—O and Ru—Cl bonds fall into normal ranges [17,18].

Directionality and specificity of hydrogen bonding recognized it as a powerful tool for designing molecular frameworks. In addition to traditional hydrogen bonding, charge-assisted co-operative interactions have inherent effect on overall geometry of the framework. Such interactions are strong and occur in ionic or zwitterionic systems. Compounds **1** and **2** exhibit strong intra- and intermolecular C—H···X (F, Cl, O, N or π) interactions [19]. PF_6^- ions in **1** undergo bifurcated C—H···F interactions with the phenyl hydrogen atoms to form a compact rectangular cavity where four cationic units are head-to-tail linked [20], while compound **2** displays interlocking of two cationic moieties by strong C—H···π intermolecular interactions where the molecular cavity is located in the space of these dimeric cations and BF_4^- ions do not participate in active interactions. It should be noted that, although most of fluoride atoms of PF_6^- ions in **1** participated in non-covalent interactions, two distinct bifurcated C—H···F interactions incurred by two *trans*-fluoride atoms (F2 and F4) determine the geometry of observed cavity in **1**.

Interestingly, the guest water molecules trapped in the molecular cavity of **1** are congregated together to form a water dimer in D2 pattern with intermolecular O—H···O hydrogen-bonding interactions [O1WA—H1-WA···O1W#1] but, lacking any interaction with the host cations. Geometrical parameters of the water dimer are recorded in Table 3. It should be noted that the O···O separation in the dimer is 2.808 Å, which is comparable to that in regular ice (2.74 Å), liquid water (2.85 Å) and in the vapor phase (2.89 Å) [9a]. Theory and calculations are in fairly good agreement with the *trans*-linear structure of water dimer determined by Dyke et al. [10a,10b]. The water dimer in **1** has (Fig. 2a) a cyclic structure (D2 pattern) similar to the one reported for water polymers $(H_2O)_n$ wherein each monomer acts both as single donor and acceptor, and the two free hydrogen atoms oriented above and below the ring, respectively [10]. It is well established that by judicious choice of the counter ion, distinct framework geometries can be designed [20a,20b]. The hydrogen-bonding strength for PF_6^- is slightly higher than BF_4^-, it corresponds well with the observed compactness in **1** [20a,20b,20c]. Replacing anion PF_6^- of **1** by BF_4^- leads to a completely different motif in **2**. In absence of any bridging co-operative interaction, compound **2** shows the formation of a loose cavity, encapsulating linear water trimers (D3 pattern) (Fig. 2b). Closer look revealed an absolute linear arrangement (180°) in D3 pattern for three of the water molecules with the central water molecule, keeping it as the symmetry centre to two terminal water mole-

Table 3
Hydrogen bond distances [Å] and angles [°] for **1** and **2**

D—H···A	d(H···A)	d(D···A)	<(DHA)
1			
O(1W)—H(1WA)···O(1W)#1	2.69	2.808(9)	90
C(35)—H(35)···F(2)#2	2.42	3.216(6)	144
C(39)—H(39)···F(1)#3	2.65	3.206(7)	119
C(43)—H(43A)···F(2)	2.48	3.428(8)	170
C(40)—H(40)···F(4)	2.52	3.053(6)	117
C(11)—H(11)···F(4)	2.64	3.075(6)	110
O(2)—H(2A)···Cl(1)	2.64	3.286(4)	137
2			
C(5)—H(5)···π^A	2.73	3.571(3)	151
O(1W)^a···O(2W)···O(1W)^b	2.82	5.651(4)	180

Symmetry operations for **1**: #1 x,y,z; #2 $-x+1,-y+1,-z+2$; #3 $-x+1,y+1/2,-z+1/2$; #4 $x,-y+3/2,z+1/2$; **2**: $^a -x+3/2, -y+3/2, -z+1$; $^b x,y,z-1$.

^{A} Centroid of the phenyl ring represented by C(25)—C(26)—C(27)—C(28)—C(29)—C(30).

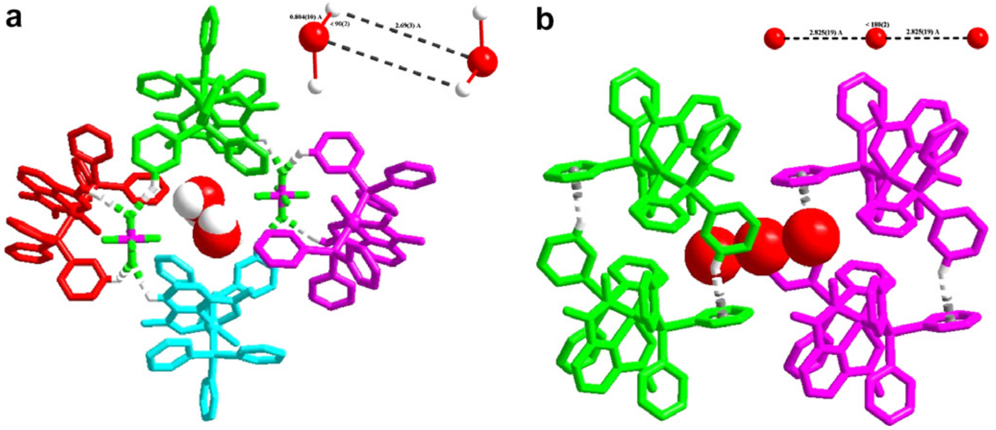


Fig. 2. (a) Encapsulated water dimer in **1** and its close view, and (b) water trimer in **2** and its close view.

cules. In this trimer the O···O separation is 2.825(19) Å [21]. Similar to the water dimer in **1**, the water molecules from the trimer also lack any intermolecular interactions with its host. The shortening of O···O distance indicated stronger H-bonding interactions due to the co-operative nature of hydrogen bonding [9a]. The O···O distance of water dimer in **1** is lower than water trimer in **2**, indicated that the water dimers are more stable because of tightly held hydrogen bonding than the water trimers in compound **2** (O···O 2.808 Å vs. 2.825 Å).

3.4. Luminescence properties

Compounds **1** and **2** are luminescent at room temperature both in the solid state and in solution. In the solid state **1** and **2** shows a yellow-orange emission at λ_{em} 566 nm ($\lambda_{ex} = 404$ nm) (Fig. 3a) which is significantly blue shifted by ~56 nm in solution (Fig. 3b). The non-structured solid state emission band can be attributed to the metal to ligand (MLCT) electron transition and the blue-green emission of **1** and **2** in solution is believed to be associated with deactivation of the intermolecular interactions and segregation of superstructure into individual molecules [22]. Furthermore, it is interesting to observe the solid state emission intensity of 79.8 a.u. for **1** is significantly reduced to 53.7 a.u. for **2** suggesting that the crystal packing in **1** is more tightly held than in **2** [23]. In addition to the compactness of the framework, the encapsulated water trimer in the loosely bound framework of **2** induces solvent quenching in a more pronounced way than that of the compact framework for **1**. To have an idea about the solvent dependency, emission spectra were acquired in the solvents of varying polarity viz., methanol, dimethylsulfoxide, acetonitrile, acetone and chloroform. Excitation and emission spectra of **1** and **2** in dichloromethane is shown in Fig. 3b. A distinct bathochromic shift of the emission bands were observed in polar solvents. Furthermore, along-with the generation of a secondary peak, emission intensity quenched with an increase in the solvent polarity. It is concluded that position of the emission peak and emission intensity in **1** and **2** strongly depends on polarity of the solvent. The solvent effect varies not only with

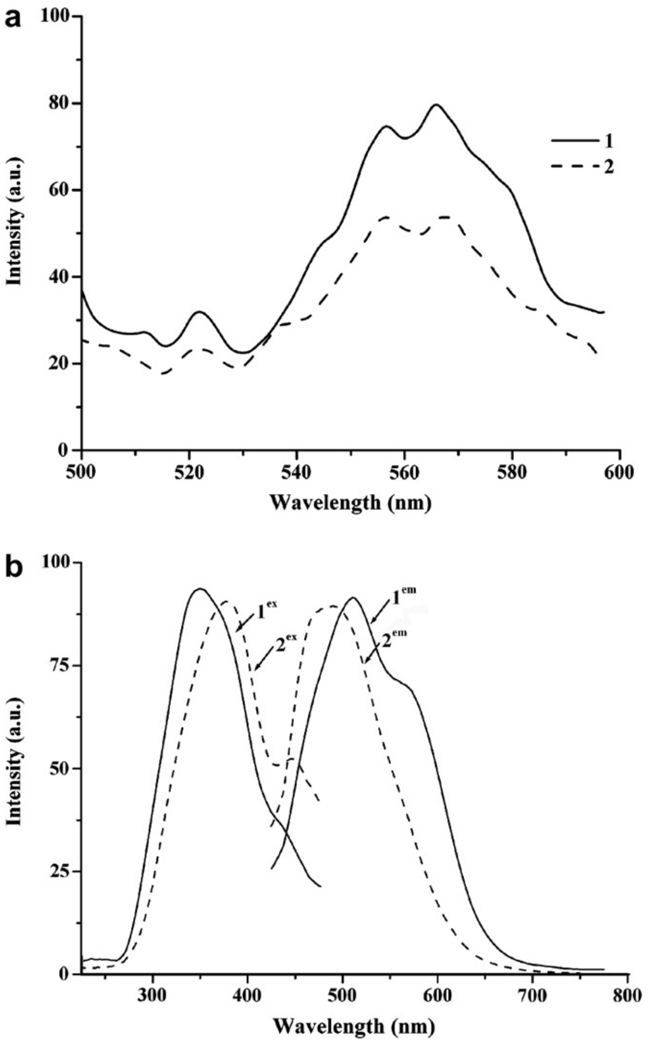


Fig. 3. (a) Emission spectra of **1** and **2** in the solid state (λ_{ex} 404 nm), and (b) excitation spectra and emission (λ_{ex} 404 nm) for **1** (λ_{em} 510 nm) and **2** (λ_{em} 490 nm) in dichloromethane.

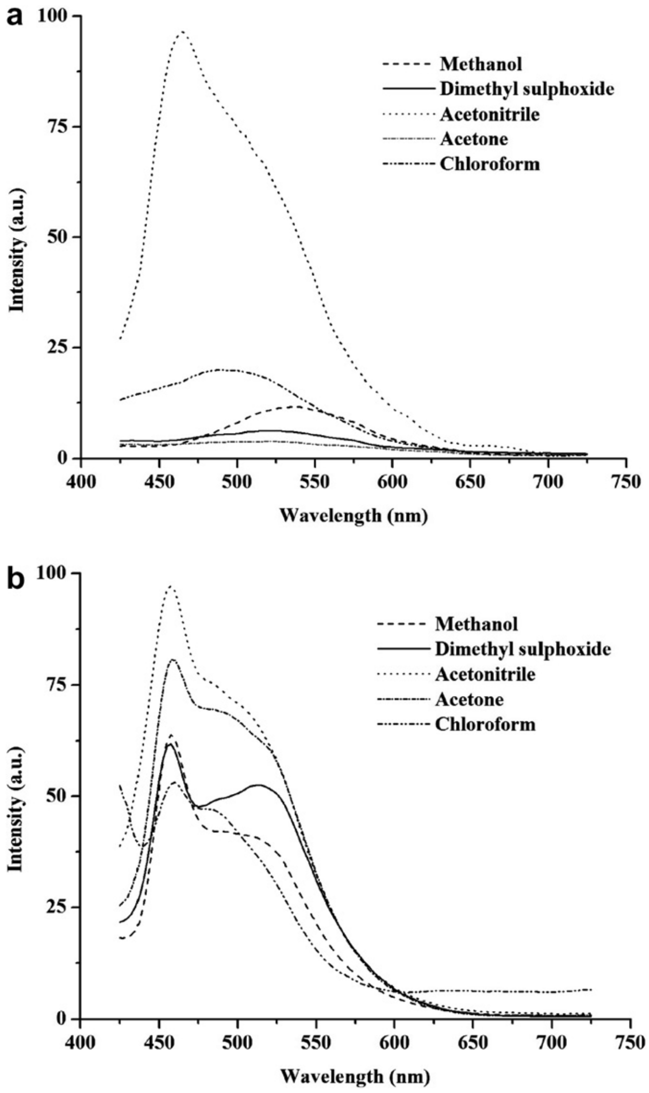


Fig. 4. Emission spectra of **1** (a) and **2** (b) in different solvents.

the dielectric constant of the solvent but, also with polarity and protic nature of the solvent. This observation is in keeping with earlier reports [24]. The quenching effect with the solvent observed in present study can be generalized as: MeOH > DMSO > CH_3CN > CH_3COCH_3 > $CHCl_3$. Quenching of the emission band in **1** is not very distinct, however for compound **2**, appearance of a secondary peak at around 530 nm with an increase of solvent polarity is very clear (Fig. 4).

4. Conclusions

In conclusion, two Ru(II) compounds with respective water dimer and trimer have been reported. The result shows that the counter anions play vital roles to tune the packing formations for such coordination compounds through intra- and intermolecular weak interactions. Further investigations to elucidate encapsulation of other guest molecules and role of the counter anions in molecular construction is in progress.

5. Supplementary data

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC numbers 623811 (**1**) and 623812 (**2**). Copies of this information can be had free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.com.ac.uk or www: http://www.ccdc.com.ac.uk).

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