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Effect of the counter anion and solvate on the structure, stability and spectral properties of a ruthenium(II) complex containing group 15 donors and 2,2′:6′,2″-terpyridine

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Abstract

Ruthenium complexes $[Ru(\kappa^3-tpy)(AsPh_3)_2C1]PF_6 \cdot 0.42H_2O$ (tpy = 2,2′:6′,2″-terpyridine) *(1)* and a new crystal form of $[Ru(\kappa^3-tpy)(AsPh_3)_2Cl]BF_4$ *(2)*, which crystallized without water solvate, and their comparative studies on spectral, structure and stability aspects are reported. The complexes have been characterized by elemental analyses, FAB-MS, i.r., ^1H n.m.r. and electronic spectral studies. In these complexes weak C—H···π and face-to-face π–π interactions lead to a single helical motif while, C—H···*X* (*X* = F, Cl) interactions result in linear chains. Various studies on the stability of the complexes suggested that the compound containing the counter anion PF_6^- is more stable than the other containing BF_4^- as the counterpart.

Introduction

Coordination compounds of ruthenium(II) containing nitrogen donor ligands, particularly polypyridyl ligands, have attracted considerable interest due to their unique photophysical and redox characteristics [1a–c]. These ligands confer on the metal center extra stability by the π interaction with the metal ion. 2,2′:6′,2″-Terpyridine (tpy) is a versatile ligand in metallosupramolecular chemistry and has found application in many fields such as luminescent materials, medical diagnostics, molecular biology, sensors and molecular-scale wires [2a–f]. The terpyridine coordinates meridionally in most ruthenium complexes. During our studies concerning synthesis and characterization of Ru(II) polypyridyl complexes, a new series of complexes $[Ru(\kappa^3-tpy)(EPh_3)_2Cl]^+BF_4^-$ (E = P or As) was isolated from the reactions of hydrated ruthenium chloride or the complex $[RuCl_2(EPh_3)_3]$ (E = P or As) with terpyridine, and their DNA-binding behavior and substitution chemistry were studied [3]. There are only a few reports on ruthenium complexes containing group 15 donor ligands and tpy available in the literature [4, 5]. Furthermore, the counter ion plays an important role in intermolecular interaction in ionic species and in such systems the anion seems to control the chemistry [6a-b]. In organometallic chemistry PF_6^- and BF_4^- are used in many cases as counter ions because of their capabilities to form microcrystalline or crystalline materials with a variety of large complex cations. We describe herein synthesis and structure of the complexes $[Ru(\kappa^3-tpy)(AsPh_3)_2C1]^+ PF_6^-$ *(1)*, $[Ru(\kappa^3-tpy)(AsPh_3)_2Cl]^+ BF_4^-$ *(2)*, and compare their spectral, structure, and weak interaction studies.

Experimental

Materials

Analar grade chemicals were used throughout. All the synthetic manipulations were performed under an oxygen-free nitrogen atmosphere. Solvents were dried and distilled before use following standard literature procedures [7]. Hydrated ruthenium(III) chloride, 2,2′:6′,2″-terpyridine, Ph_3As, NH_4BF_4 and NH_4PF_6 were obtained from Aldrich Chemical Company, Inc., USA and were used without further purification. The precursor complex $[RuCl_2(EPh_3)_3]$ was prepared and purified by the literature procedure [8].

Physical measurements

Microanalytical data of the complexes were obtained from the microanalytical laboratory of the Sophisti-

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cated Analytical Instrument Facility, Central Drug Research Institute, Lucknow. I.r. spectra in nujol mulls in the 4000–400 cm^{-1} region and electronic spectra were recorded on a Shimadzu-8201 PC and Shimadzu UV-1601 spectrophotometer, respectively. ^1H n.m.r. spectra with Me_4Si as the internal reference at room temperature were obtained on a Bruker DRX-300 NMR machine. Fast atom bombardment (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 the spectra were recorded at room temperature using *m*-nitrobenzyl alcohol as the matrix.

Preparation of $[Ru(\kappa^3 - tpy)(AsPh_3)_2Cl]PF_6 \cdot 0.42H_20$ *(1)*

Complex *(1)* was prepared by either of the following two methods: (a) Hydrated ruthenium trichloride $RuC1_3 \cdot xH_2O$ (0.260 g, 1.0 mmol) dissolved in hot MeOH (10 cm^3) was added to a solution of $AsPh_3$ (1.836 g, 6.0 mmol) in refluxing MeOH (50 cm^3) and the solution was heated under reflux for 1 h. 2,2′:6′,2″-Terpyridine (0.233 g, 1.0 mmol) was added to the resulting suspension and the contents of the flask were heated under reflux for 8–10 h. The resulting purple red solution was cooled to room temperature and filtered to remove any solid residue. The filtrate was concentrated under reduced pressure to one fourth of its volume and a saturated solution of NH_4PF_6 dissolved in MeOH was added and left to slowly crystallize in the refrigerator. A microcrystalline product was gradually obtained, which was separated by filtration and washed repeatedly with MeOH and Et_2O and dried *in vacuo*. Dark red needle shaped X-ray suitable crystals were grown by the diffusion method from CH_2C1_2–petroleum ether solution. Yield: 70% (0.794 g). $As_2C_{51}ClF_6H_{40.8}N_3O_{0.42}Ru$ calcd. (this formula was established from the X-ray diffraction analysis): C, 53.9; H, 3.6; N, 3.7. Found: C, 53.4; H, 3.3; N, 3.85%. *m/z* (obs.; rel.int.; assignment): 982, 20 (M^+); 676, 50 (M^+-$AsPh_3$); 641, 25 (M^+-$ASPh_3$-Cl); 335, 15 (M^+-2$AsPh_3$-Cl). ^1H NMR ($CDC1_3$, δ): 9.05 (d, 2H, $J=5.4$), 8.04 (d, 2H, $J=7.8$), 7.83 (d, 2H, $J=7.8$), 7.75 (t, 2H, $J=7.8$), 7.59 (t, 1H, $J=8.1$), 7.26–6.96 (br, m., 30H, aromatic protons of $AsPh_3$), 7.09 (2H, overlapped with aromatic protons of $AsPh_3$). UV–Vis λ_{max}, nm (e): 494 (2292), 313 (16,266), 268 (29,138).

(b) A suspension of $RuCl_2(AsPh_3)_3$ (1.09 g, 1.0 mmol) in MeOH (50 cm^3) was treated with 2,2′:6′,2″-terpyridine (tpy) (0.233 g, 1.0 mmol) and the resulting solution was heated under reflux for 8 h whereupon a red-brown solution was obtained. After cooling to room temperature, the resulting solution was filtered through celite to remove any solid impurities. Saturated solution of NH_4PF_6 dissolved in MeOH was added to the filtrate and was left in the refrigerator to slowly crystallize. After a couple of days a red crystalline product separated. It was analyzed for $[Ru(\kappa^3 - tpy)(AsPh_3)_2Cl]PF_6$.

Preparation of $[Ru(\kappa^3 - tpy)(AsPh_3)_2Cl]BF_4$ *(2)*

Compound *(2)* was prepared following our earlier procedure mentioned above [3]. The dehydrated red complex was analyzed. $[Ru(\kappa^3 - tpy)(AsPh_3)_2Cl]BF_4$ Yield: 74% (0.791 g), $As_2BC_{51}Cl\ F_4H_{41}N_3Ru$ calcd: C, 57.2; H, 3.8; N, 3.9. Found: C, 57.2; H, 3.1; N, 3.9%. *m/z* (obs.; rel.int.; assignment): 982, 15 (M^+); 676, 64 (M^+-$AsPh_3$); 641, 25 (M^+-$AsPh_3$-Cl); 335, 25 (M^+-2$AsPh_3$-Cl). ^1H NMR ($CDC1_3$, δ); 9.04 (d, 2H, $J=5.4$), 8.12 (d, 2H, $J=7.8$), 7.82 (d, 2H, $J=7.8$), 7.75 (t, 2H, $J=7.8$), 7.59 (t, 1H, $J=8.1$), 7.26–6.90 (br, m., 30H, aromatic protons of $AsPh_3$), 7.10 (2H, overlapped with aromatic protons of $AsPh_3$). UV–Vis, λ_{max}, nm (e): 269 (43000), 312 (22000), 481 (3600).

Crystal structure determination

X-ray diffraction data for compound *(1)* and the dehydrated monoclinic form of *(2)* were collected on a Bruker SMART APEX 3-circle diffractometer (graphite-monochromated MoKα radiation, $\lambda=0.71073$Å, with CCD area detector at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz. Hemispheres of the reciprocal space were measured by omega scan frames with $\delta(\omega)$ 0.30 degrees. Correction for absorption and crystal decay (insignificant) were applied by a semiempirical method from equivalents using the program SADABS [9a]. The structures were solved by direct methods, completed by subsequent difference Fourier synthesis and refined on F^2 by full matrix least-squares procedures using the program SHELXTL [9b]. ORTEP3 for windows was used for molecular representation [9c]. A summary of crystal data and refinements is included in Table 1. CCDC 258130 & 258131 contains the supplementary crystallographic data for compounds *(1)* and *(2)*, respectively. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internet.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Results and discussion

Synthetic, spectral and structural studies

Treatment of the hydrated ruthenium(III) chloride with tpy in the presence of an excess of $AsPh_3$ in methanol under refluxing conditions afforded the complexes $[Ru(\kappa^3$-tpy)$(AsPh_3)_2Cl]^+$ in excellent yield (70%). The complex was isolated as its hexafluorophosphate

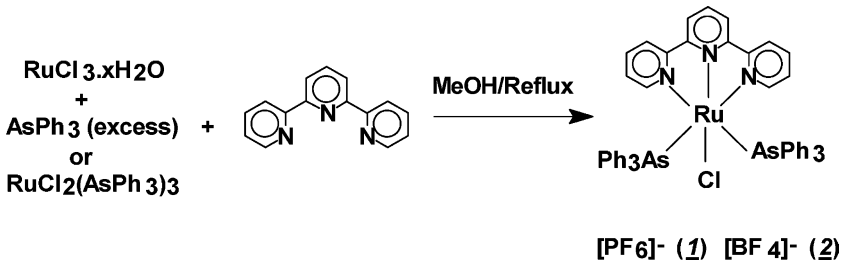
Table 1. Selected crystallographic data for complex *(1)* and complex *(2)*

	Complex *(1)*	Complex *(2)*
Empirical formula	As_2C_51ClF_6H_40.8N_3O_0.42Ru	C_51H_41As_2BCLF_4N_3Ru
Molecular weight	1136.21	1069.04
Color and habit	Dark red	Red
Crystal size/mm	0.23×0.20×0.15	0.51×0.28×0.09
Space group	**P21/c**	**C2/c**
System	Monoclinic	Monoclinic
Unit cell dimensions		
a/Å	9.8450(8)	23.962(5)
b/Å	19.9697(15)	9.8650(18)
c/Å	23.4491(18)	39.536(7)
α/Å	90.00	90.00
β/Å	94.1940(10)	95.663(5)
γ/Å	90.00	90.00
V/Å^3	4597.8(6)	9300(3)
Z	4	8
d_{calc}/mg m^{-3}	1.641	1.527
μ/mm^{-1}	1.928	1.862
Temperature/K	100	100
No. of reflections	6614	6617
No. of refined para	602	562
R factor all	0.0829	0.1016
R factor [$I>2\sigma(I)$]	0.0787	0.0899
wR2	0.1513	0.2092
wR2 [$I>2\sigma(I)$]	0.1488	0.2012
Goodness of fit	1.030	1.083

and tetrafluoroborate salts (Scheme 1). Only recently we have reported synthesis of a complex with similar composition as that of the compound *(1)* as its tetra fluoroborate salt and analogous triphenylphosphine complex [3].

Analytical data of the complexes *(1)* and *(2)* conformed well to the formulation of the respective complexes. Further information about composition of the complexes has been obtained from FAB-MS spectral studies. FAB-MS spectral data of the complexes are summarized in the experimental section. All the complexes gave easily interpretable fragmentation patterns with the tpy ligands remaining intact. The overall fragmentation pattern in the FAB-MS spectra of the respective complexes strongly supported the proposed formulation of the complexes.

The ^{1}H n.m.r. spectral data of the complexes is recorded in the experimental section. The complex *(1)* in its ^{1}H n.m.r. spectrum exhibited signals in the region 9.05 (d, 2H, $J=5.4$), 8.04 (d, 2H, $J=7.8$), 7.83 (d, 2H, $J=7.8$), 7.75 (t, 2H, $J=7.8$), 7.59 (t, 1H, $J=8.1$), 7.09 (2H, overlapped with aromatic protons of $AsPh_3$) associated with coordinated tpy. The aromatic protons of the $AsPh_3$ resonated in their usual position as a broad multiplet at 7.26–6.96 ppm. An analogous ^{1}H n.m.r. spectral pattern was observed in complex *(2)*. The electronic spectra of the complexes *(1)* and *(2)* were recorded in dichloromethane and resulting data were compared with the tetrafluoroborate salt of the same cationic moiety. Complex *(1)* exhibited bands at ~494, 313, 268 nm and complex *(2)* at ~481, 312, 269 nm. The low energy bands present in the spectra at 494 or 481 nm are assigned to the Ru(dp → tpyp*) (metal-to-ligand charge transfer) MLCT transition typical for ruthenium(II) complexes involving pyridyl components of the coordinated tpy ligands. The red shift in the MLCT transition in its hexafluorophosphate salt as compared to the tetrafluoroborate salt (~13 nm) may be due to greater stability of metal complex that depends on ion size or ion-pair dissociation energy. The intense higher energy bands, typically below 300 nm can be assigned to ligand



Scheme 1.

centered p $\rightarrow$ π^* and n $\rightarrow$ π^* transition and these are similar to the tetrafluoroborate salt of the same complex. Molecular structure of the complex *(1)* and *(2)* was determined crystallographically (Figure 1). Both complexes crystallize in the monoclinic system with $P2_1/c$ and C2/c space groups, for complex *(1)* and *(2)*, respectively. The coordination geometry about ruthenium in both the complexes is octahedral, which is covalently bound with all the three major coordination sites of tpy, two arsenic donor atoms from triphenylarsine and the chloro group [3]. The N—Ru—N bond angles and Ru—N distances in both complexes are consistent with those in other Ru(II) tpy complexes and strongly suggested that the usual meriodional mode of bonding of coordinated tpy is maintained [10a–b]. The Ru—N bond distances in complex *(1)* are shorter than Ru—N bond distances of tetrafluoroborate salt, complex *(2)*, which lead to strain intrinsic to the metalterpyridine moiety [3, 11]. The N—Ru—N angle in complex *(1)* is 159° formed by the terminal terpyridine nitrogens that are larger than tetrafluoroborate salt, complex *(2)*, reaches a typical value [12]. The triphenylarsine ligand in both complexes is *trans* disposed as indicated by As(l)—Ru(l)—As(2) bond angles, reaching a larger value in the tetrafluoroborate salt, complex *(2)*. The Ru—As distances in both complexes are normal and comparable with other Ru(II) complexes [13a–c]. These distances are normally larger than tetrafluoroborate salt [complex *(2)*]. The Ru—Cl distance in complex *(1)* is lower than that in tetrafluoroborate salt [complex *(2)*] and consistent to Ru—Cl distances in other complexes [14a–c].

Weak interaction studies

Weak interaction studies in complexes *(1)* and *(2)* with the analogous cationic moiety, but different counter anion, exhibited the presence of C—H···*X* (*X* = Cl, F) and π–π interactions. It is observed that, in general, a very soft C—H···F contact occurs if BF_4^- and PF_6^- are used as counter ion. The intermolecular C—H···F and C—H···Cl short distances in complex *(1)* are 2.408–2.627 Å and 2.729–2.888 Å. These distances fall in the same range as in the tetrafluoroborate salt [complex *(2)*] and are comparable with other C—H···F and C—H···Cl short distances in the literature [15a–c]. The intermolecular C—H···F and C—H···Cl weak interactions result in linear chain like structure, which expands the motif in the crystal lattice through these interactions (Figure 2). Complex *(1)* shows C—H···π type of intermolecular interaction and face-to-face π–π interactions leading to a single helical motif. However, in the tetraborate salt [complex *(2)*] face-to-face and edge-to-face π—π interactions lead to single helical motif (Figures 3 and 4). This observation is consistent with the literature reports [3, 16]. The respective helical motifs exhibited a pitch of 19.970 Å and void space of 12.980 Å for complex *(1)*, however, a smaller pitch of 9.865 Å and void space of 6.723 Å are found for complex *(2)* (Figure 5). Though no guest molecules are found included in the void space of the helical framework for any of these complexes, however, they may show prospects for guest inclusion. It is interesting to see that the two *trans* $AsPh_3$ molecules are fully eclipsed. (dihedral angle = 1.64°) in the complex *(1)* as

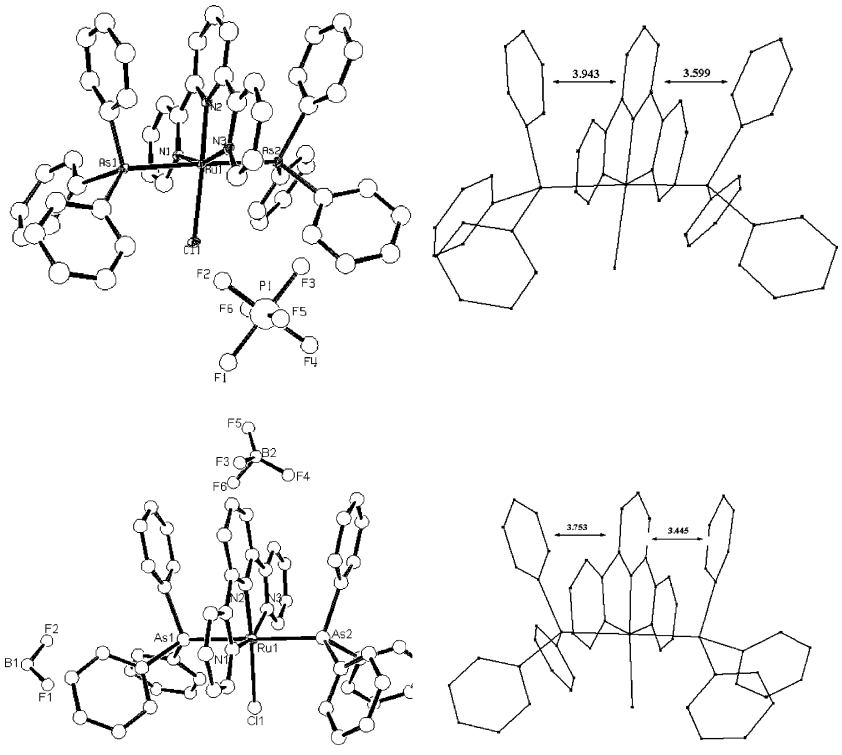


Fig. 1. Molecular representation of complexes *(1)* and *(2)*.

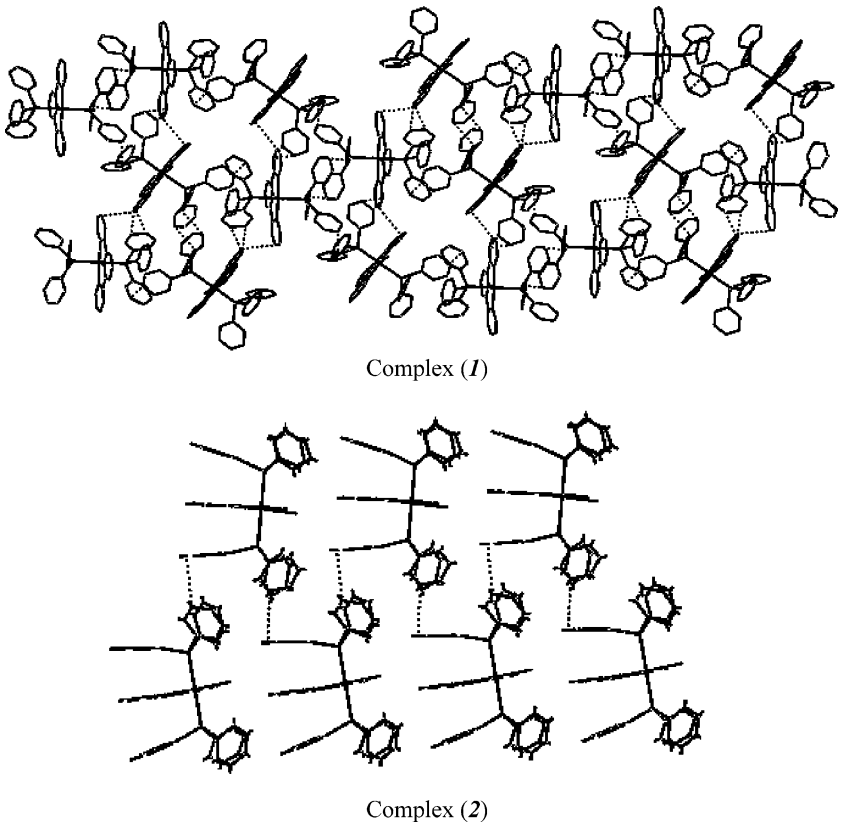


Fig. 2. Face-to-face π–π interactions in complex *(1)* and face-to-face and edge-to-face π–π interaction in complex *(2)*.

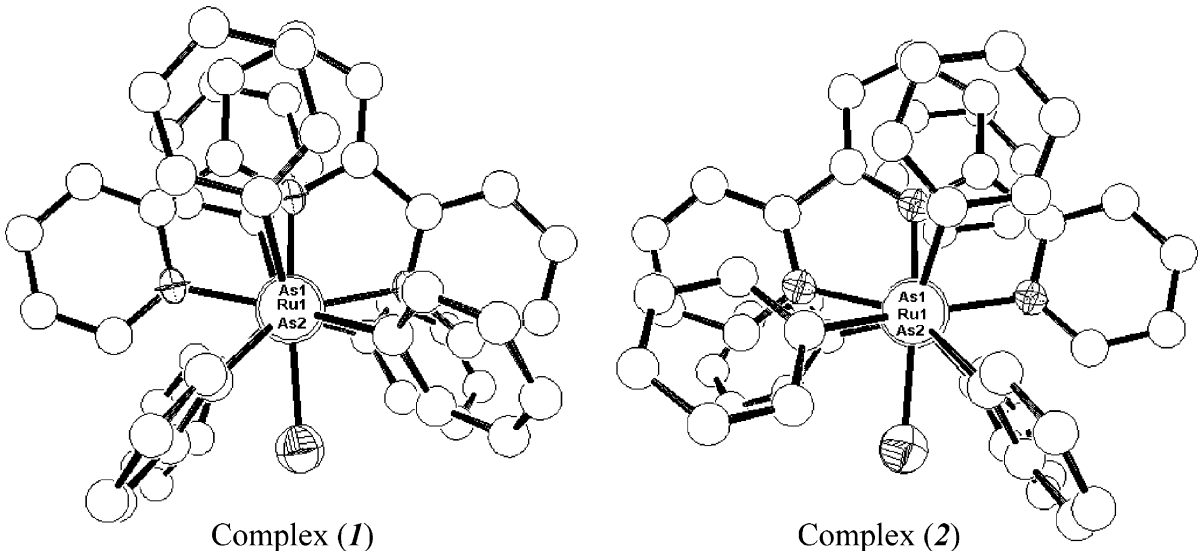


Fig. 3. As(1)–Ru(1)–As(2) axial view of the complexes *(1)* and *(2)* exhibiting different stacking arrangements of the phenyl rings to terpyridine.

compared to that in the tetrafluoroborate salt [complex *(2)*]. An almost fully eclipsed arrangement of complex *(1)* can be explained by a longer distances of phenyl rings with the pyridyl rings as compared to less distorded eclipsed arrangement of the complex *(2)* which, in turn leaves 66% of the terpyridine uncovered (Figure 6). These observations are consistent well with the results of Ye *et al.* [17]. Further, the importance of π–π stacking interactions between aromatic rings has widely been recognized in the intercalation of drugs with DNA especially in biological systems, which lie in the range 3.4–3.5 Å. The complex *(1)* and *(2)*

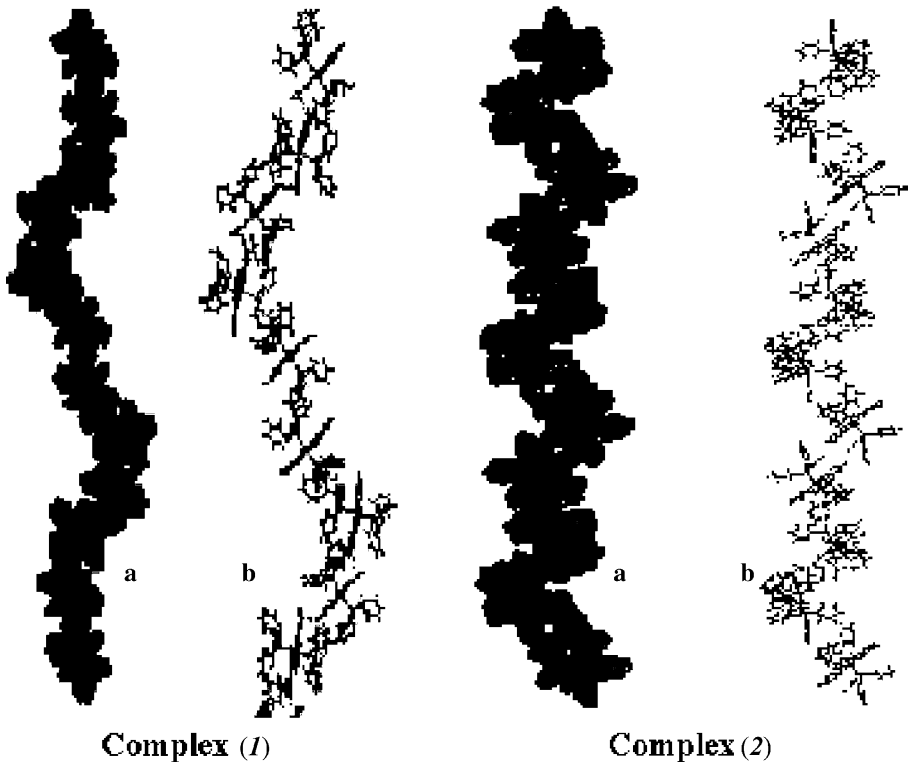


Fig. 4. Space filled (a) and Wireframe (b) single helix motif for complexes *(1)* and *(2)*.

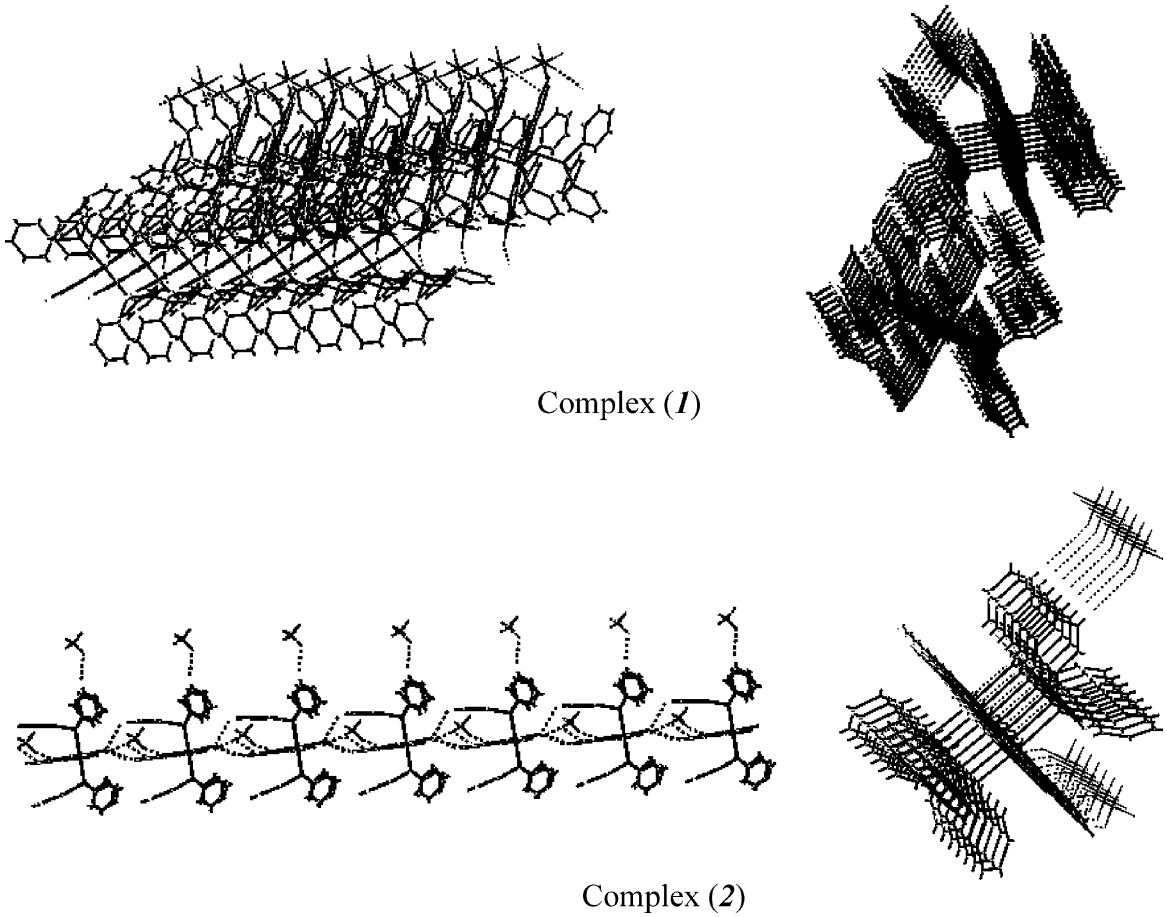


Fig. 5. Linear chains in complexes *(1)* and *(2)* made through intermolecular C—H···*X* (*X* = F, Cl) weak non-bonding interaction (top and side view).

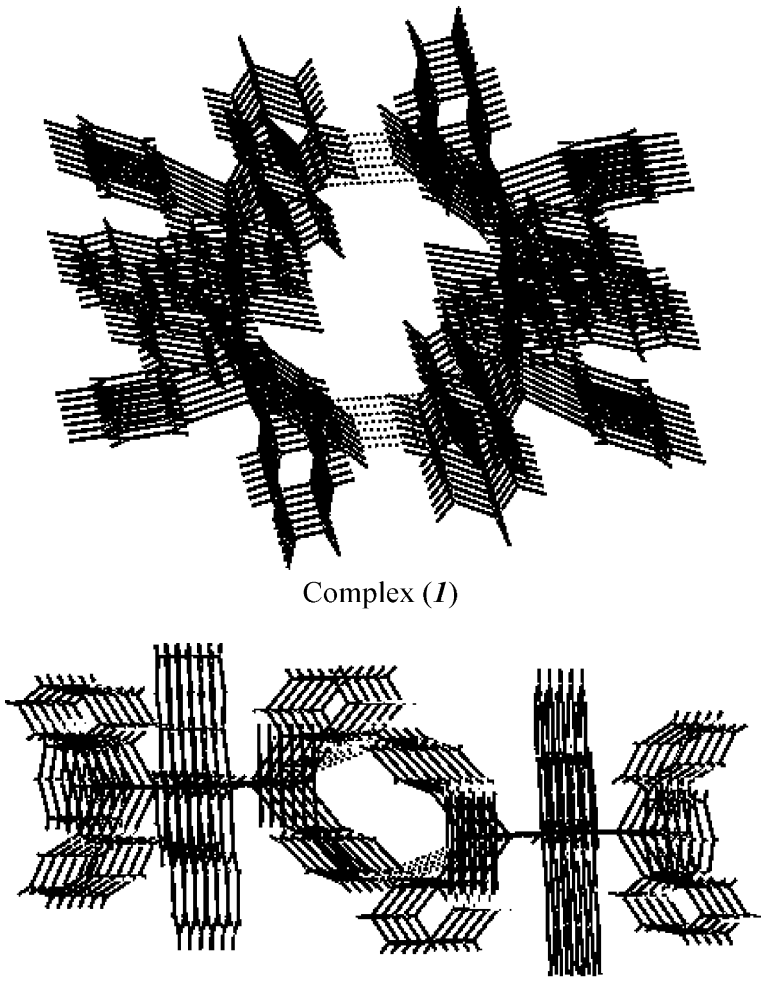


Fig. 6. Cavity developed by weak C—H···π interactions (top view) in complexes *(1)* and *(2)*.

Table 2. Selected bond lengths (Å) and bond angles (°) for the cation complex in *(1)* and *(2)*

	Complex*(1)*	Complex*(2)*
Ru(1)—N(1)	2.057(7)	2.074(9)
Ru(1)—N(2)	1.915(7)	1.948(8)
Ru(1)—N(3)	2.045(7)	2.086(9)
Ru(1)—As(1)	2.5519(12)	2.4679(13)
Ru(l)—As(2)	2.5574(12)	2.4655(13)
Ru(1)—Cl(1)	2.381(2)	2.432(3)
N(2)—Ru(1)—N(3)	82.6(3)	79.5(4)
N(2)—Ru(1)—N(1)	77.2(3)	79.4(4)
N(3)—Ru(1)—N(1)	159.8(3)	158.9(4)
N(2)—Ru(1)—Cl(1)	175.5(2)	175.0(3)
N(3)—Ru(1)—Cl(1)	101.9(2)	105.1(3)
N(1)—Ru(1)—Cl(1)	98.3(2)	96.0(2)
N(2)—Ru(1)—As(1)	100.2(2)	91.0(2)
N(3)—Ru(1)—As(1)	90.3(2)	89.4(2)
N(1)—Ru(1)—As(1)	91.8(2)	91.3(2)
Cl(1)—Ru(1)—As(1)	79.81(6)	87.21(7)
N(2)—Ru(1)—As(2)	82.0(2)	89.5(2)
N(3)—Ru(1)—As(2)	90.4(2)	87.4(2)
N(1)—Ru(1)—As(2)	88.3(2)	92.1(2)
Cl(1)—Ru(1)—As(2)	97.95(6)	92.53(7)
As(1)—Ru(1)—As(2)	177.75(4)	176.65(5)

Table 3. Matrices of intra and intermolecular interactions of complex in compound *(1)*

Complex *(1)*				
D—H···A	d(D—H)Å	d(H···A)Å	d(D···A)Å	<(DHA)°
C(2)···H(2)···F(4)[a]	0.9500	2.4100	3.117(13)	131.00
C(4)···H(4)···F(3)[b]	0.9500	2.5300	3.248(13)	132.00
C(21)···H(21)···C1(1)	0.9500	2.7600	3.512(10)	137.00
C(35)···H(35)···C1(1)	0.9500	2.7300	3.576(9)	149.00
C(43)···H(43)···C1(1)[c]	0.9500	2.7300	3.181(10)	110.00

[a] $1-x$, $1/2+y$, $1/2-z$; [b] $-x$, $1/2+y$, $1/2-z$; [c] $-1+x$, y, z.

(Figure 1) exhibits intermolecular (π)phenyl/(π)phenyl (ct/ct distances 3.334– 3.399 Å) and intramolecular π/π/π interactions of the phenyl rings of $AsPh_3$ with the central pyridyl ring of terpyridine ligand (ct/ct/ct 3.445–3.943 Å) [18, 19].

Conclusions

In summary, we have reported herein the synthesis of $[Ru(\kappa^3\text{-tpy})(AsPh_3)_2Cl]PF_6$ in excellent yields and

compared their spectral, structure and interaction aspects with its tetrafluoroborate counterpart. In addition to the counter anion, the presence of water in the crystal contributes to considerable differences in packing. Due to presence of labile groups it will be interesting to see role of counterion in binding of metals to nucleobases within DNA. More detailed work in this direction is in progress in our laboratory.

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