New Multifunctional Complexes $[Ru(\kappa^3\text{-}L)(EPh_3)_2Cl]^+$ [E = P, As; L = 2,4,6-Tris(2-pyridyl)-1,3,5-triazine] Containing both Group V and Polypyridyl Ligands

Sanjeev Sharma,[a] Manish Chandra,[a] and Daya Shankar Pandey*[a]

Keywords: Ruthenium / Tertiary phosphanes / 2,4,6-Tris(2-pyridyl)-1,3,5-triazine / DNA / Topoisomerase II

Synthesis, structure, reactivity and enzyme inhibitory activity of the new cationic ruthenium complexes $[Ru(\kappa^3\text{-}L)(EPh_3)_2Cl]BF_4$ [L = 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz); E = P (**1**), As (**2**)] and their substitution products $[Ru(\kappa^3\text{-}tptz)(PPh_3)(dtc)]Cl$ (**3**), $[Ru(\kappa^3\text{-}tptz)(PPh_3)(CN)_2]$ (**4**), $[Ru(\kappa^3\text{-}tptz)(AsPh_3)(dtc)]BF_4$ (**5**), and $[Ru(\kappa^3\text{-}tptz)(AsPh_3)(CN)_2]$ (**6**) are reported. The complexes were characterized by analytical and spectroscopic methods and the structures of the complexes **1**, **2** and **3** determined by X-ray diffraction studies. C–H···X (X = Cl, F and S), C–H···π and π–π interactions were observed in these complexes. Further studies indicated that the complexes $[Ru(\kappa^3\text{-}L)(EPh_3)_2Cl]^+$ could find application as precursors in the synthesis of other ruthenium complexes or as metallo-ligands. The complexes also interact with DNA, which was illustrated by absorption titration studies with CT-DNA and inhibition of topoisomerase II of the filarial parasite *Setaria cervi*.

Introduction

Recently, (polypyridyl)Ru^{II} complexes have received considerable attention owing to their possible application in conversion of solar energy to electrical energy,[1] in long-range electron and energy transfer,[2] molecular electronic devices,[3] self-assembly processes[4] and as photoprobes for DNA.[5] Polypyridyl bridging ligands containing a delocalized π-electron system have drawn special attention in this regard. Using such ligands, many luminescent and redox-active compounds have been synthesized and studied extensively.[6] During the past few years, we have been interested in the synthesis and characterization of metallo-ligands/synthons based on organometallic systems containing organonitriles and polypyridyl ligands.[7] During our studies on the reactivity of hydrated Ru^{III} chloride in the presence of excess EPh_3 or $[RuCl_2(PPh_3)_3]$ with 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz), we have isolated a completely new series of cationic complexes $[Ru(\kappa^3\text{-}L)(EPh_3)_2Cl]^+$. These compounds are examples of ruthenium complexes containing both Group V and polypyridyl ligands, which are associated with classical coordination chemistry.

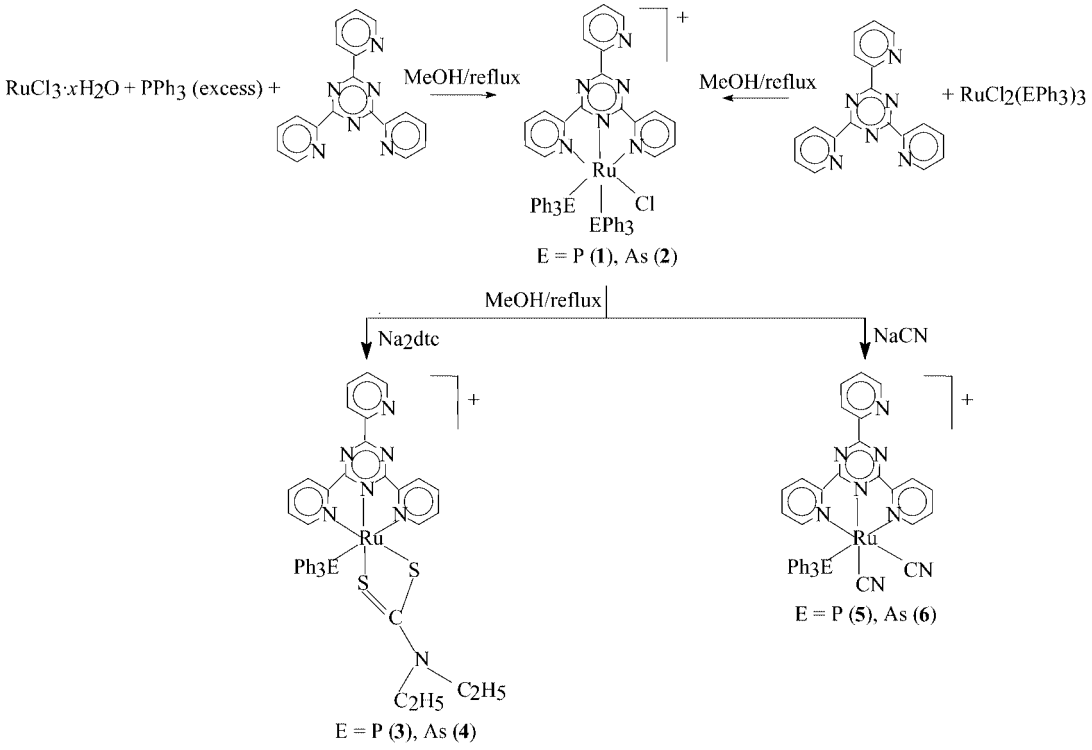
The new cationic complexes $[Ru(\kappa^3\text{-}L)(EPh_3)_2]Cl]^+$ all possess κ^3-bonded tptz, two tertiary phosphane or arsane ligands, a labile chloro group, and have the potential to exhibit rich chemistry. The ligand tptz primarily acts as a tridentate ligand similar to terpyridine (tpy), but is more versatile than tpy. The complexes under study offer a unique opportunity to behave as metallo-ligands because of the presence of vacant donor sites at the tptz ligand and, thus, could find applications in the synthesis of homo-, hetero di- or polynuclear systems. Furthermore, DNA binding studies have shown that ruthenium complexes containing polypyridyl ligands are of significant importance.[5] It was felt that the new complexes of the series $[Ru(\kappa^3\text{-}L)(EPh_3)_2Cl]^+$ could be used as DNA probes. Although, a number of reports dealing with DNA binding and inhibition activity of (polypyridyl)Ru^{II} complexes are available in the literature, activity of the complexes incorporating triphenylphosphane or triphenylarsane and a polypyridyl ligand have yet to be examined. We report herein, on the reactivity, absorption titration studies and inhibitory activity against DNA topo II of the filarial parasite *Setaria cervi* of the new, air-stable mononuclear complexes $[Ru(\kappa^3\text{-}tptz)(L_2)Cl]^+$.

Results and Discussion

The air-stable cationic complexes **1**, **2** and their representative substitution products $[Ru(\kappa^3\text{-}tptz)(PPh_3)(dtc)]Cl$ (**3**), $[Ru(\kappa^3\text{-}tptz)(PPh_3)(CN)_2]$ (**4**), $[Ru(\kappa^3\text{-}tptz)(AsPh_3)(dtc)]BF_4$ (**5**), and $[Ru(\kappa^3\text{-}tptz)(AsPh_3)(CN)_2]$ (**6**) were obtained in excellent yield as shown in Scheme 1. The compounds were characterized spectroscopically and gave satisfactory elemental analyses. The microanalyses, FAB-MS and NMR (^1H and ^{31}P) data of the complexes correspond to their respective formulas.

^1H NMR spectroscopic data of the complexes are given in the Exp. Sect. The positions and integrated intensities of

[a] Department of Chemistry, Awadhesh Pratap Singh University, Rewa 486003 (M.P.), India
E-mail: dsprewa@yahoo.com



Scheme 1

the signals corresponding to tptz corroborated well with a system containing two magnetically equivalent coordinated pyridyl rings and one uncoordinated pyridyl ring. This observation indicated coordination of the tptz to Ru in a κ^3-manner. The aromatic protons of the PPh_3 and $AsPh_3$ ligands gave a broad multiplet in the usual region with δ = 7.26−7.07 ppm. Integrated intensities and positions of the signals were consistent with the respective formulas of the complexes. The main feature of the ^1H NMR spectra of the diethyl dithiocarbamate containing complexes **3** and **4** is the presence of multiplet signals at high field with chemical shifts characteristic of methyl and methylene protons. In the complexes **3** and **4**, these appeared at δ = 4.10 (q, J = 7.2 Hz, 2 H), 3.62 (q, J = 6.9 Hz, 2 H), 1.52 (t, J = 7.2 Hz, 3 H), 1.13 (t, J = 6 Hz, 3 H) and 4.03 (q, J = 7.2 Hz, 2 H), 3.55 (q, J = 7.2 Hz, 2 H), 1.50 (t, J = 7.2 Hz, 3 H), 1.10 (t, J = 6.1 Hz, 3 H) ppm, respectively. The presence of signals in this region strongly suggests coordination of the diethyl dithiocarbamate to the metal center. In the $^{31}P\{^1H\}$ NMR spectra of the complexes **1**, **3** and **5**, single sharp resonances were observable at δ = 16.24, 37.81 and 32.89 ppm, respectively. The presence of a single sharp peak in the $^{31}P\{^1H\}$ NMR spectrum of complex **1** suggests that both the ^{31}P nuclei are chemically equivalent and that the triphenylphosphane ligands are *trans*-disposed in this complex.

Electrochemical properties of the new complexes were observed by cyclic voltammetry. The cyclic voltammogram of complex $[Ru(\kappa^3\text{-tptz})(AsPh_3)_2Cl]BF_4$ (**2**) is shown in Figure 1. The ruthenium complexes with the tptz ligand $[Ru(\kappa^3\text{-tptz})(PPh_3)_2Cl]BF_4$ and $[Ru(\kappa^3\text{-tptz})(AsPh_3)_2Cl]BF_4$ exhibited reversible ($Ru^{II/III}$) metal-based oxidation couples at 1.05 (70) V and 1.02 (50) V, respectively.[8] In the cathodic potential window, three ligand-based reversible and quasi-reversible reduction couples were observed in the range 0.89−1.50 V for the tptz ligand.

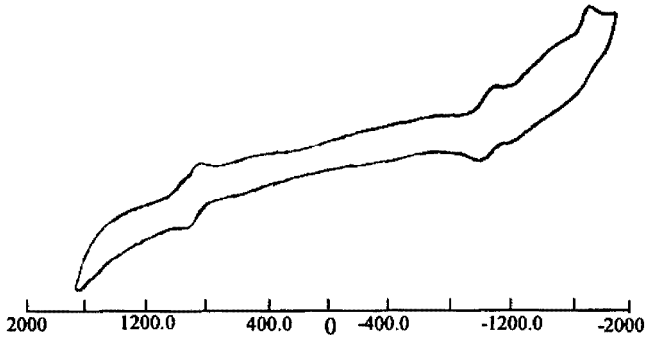


Figure 1. Cyclic voltammogram of the complex **2**

In the electronic absorption spectra of complexes **1** and **2**, the MLCT transitions appeared in the visible region at λ (ε) = 472 (24022) and 489 (6930) nm, respectively, while the ligand-centered transitions were observed at λ (ε) = 309 (63759), 273 (149195) (for **1**) and 342 (7250), 271.5 (21355) (for **2**) nm. Complexes **3**−**6** exhibited red-shifted absorptions when compared with complexes **1** and **2**. The complexes do not luminesce in air at room temperature.

Molecular structures of complexes **1**−**3** were established crystallographically.[9] Both complexes **1** and **2** crystallize in the $P2_1/c$ space group, while complex **3** crystallizes in a very rare $F2dd$ space group (Table 3). In all the complexes, Ru is

bonded covalently within the major coordination sites of tptz in a κ^3-manner by two phosphorus or arsenic atoms from the triphenylphosphane or arsane ligand and a chloro group in complex **1** and **2** and one phosphorus atom from the triphenylphosphane ligand and a dithiolato group in complex **3**. There is a distorted octahedral coordination geometry about the ruthenium center. The N(1)−Ru(1)−N(2) and N(2)−Ru(1)−N(3) angles in complex **1** are essentially equal with 78.77(12) and 78.47(11)°, while in complexes **2** and **3** these angles are 78.91(13) and 78.44(12)° and 76.9(5) and 77.1(5)°, respectively. This suggests some inward bending of the coordinated pyridyl group and may be the reason for the observed distortion. The bond length of Ru(1) to the central triazine nitrogen atom Ru(1)−N(2) in complex **1** is 1.936(3) Å, which is shorter than the bond of Ru(1) to the coordinated pyridyl nitrogen atom Ru(1)−N(1) [2.110(3) Å] and Ru(1)−N(3) [2.103(3) Å]. Similarly, in complexes **2** and **3** Ru(1)−N(2) is 1.931(3) and 1.968(13) Å, and the Ru(1)−N(1) and Ru(1)−N(3) distances are 2.098(3), 2.099(3) Å and 2.099(17), 2.076(13) Å, respectively. The Ru−N bond lengths are consistent with a κ^3-coordination of tptz and similar to those reported for other $(tptz)Ru^{II}$ complexes.[10] The triphenylphosphane ligands in complex **1** and the triphenylarsane ligands in complex **2** are *trans*-disposed as indicated by the P(1)−Ru(1)−P(2) angle of 178.52(3)° and As(1)−Ru(1)−As(2) angle of 178.26(2)°. The Ru(1)−P(1) and Ru(1)−P(2) distances are 2.4130(11) and 2.4264(11) Å in complex **1**, while in complex **2** the Ru(1)−As(1) and Ru(1)−As(2) distances are 2.481(6) and 2.491(6) Å, respectively. In complex **3**, the Ru1−S1 and Ru1−S2 distances are 2.427(4) and 2.407(4) Å, respectively. These are essentially equivalent or similar to those in related complexes.[11] The Ru−Cl distances in both complexes **1** and **2** are normal and are similar to Ru−Cl distances in other complexes (Table 1).[12]

The triazine ring from tptz and the coordinated pyridyl rings are almost coplanar. In complexes **1** and **2**, the uncoordinated pyridyl ring is inclined from the coordinated part of the ligand tptz by 25.9 and 23.3°, respectively. In complex **3**, which is obtained by replacement of one PPh_3 ligand and the chloro group of complex **1** by a dithiocarbamate ligand, the tptz ligand has regained its planarity. This is suggested by the angle of inclination (2.4°).

Selection of ligands plays an important role amongst the factors that induce the self-assembly processes. The ligands EPh_3 and triazine are expected to show different propensities for molecular arrangement based on the stacking arrangement of phenyl or triazine rings. The X-ray structure for complexes **1**−**3** revealed intermolecular C−H···X (X =

Table 2. Selected hydrogen bond lengths [Å] and angles [°] for the complex **1**−**3**

D−H−A	*d*(D−H)	*d*(H−A)	*d*(D−A)	∠(DHA)
1				
C(8)−H(8)−Cl(1)	0.93	2.69	3.536(4)	151.9
C(14)−H(14)−Cl(1)	0.93	2.72	3.566(4)	152.3
C(24)−H(24)−Cl(1)	0.93	2.71	3.411(5)	132.7
C(26)−H(26)−Cl(1)	0.93	2.81	3.669(4)	153.7
C(39)−H(39)−F(3)[a]	0.93	2.51	3.041(8)	116.1
C(43)−H(43)−F(2)[b]	0.93	2.53	3.443(7)	165.7
2				
C(39)−H(39)−F(1)[a]	0.84(7)	2.44(7)	3.084(9)	134(6)
C(8)−H(8)−Cl(1)	0.93	2.82	3.671(5)	151.8
3				
C(15)−H(15)−N(4)	0.93	2.47	2.79(2)	100.4
C(20)−H(20A)−S(1)	0.97	2.53	3.10(2)	117.3
C(22)−H(22B)−S(2)	0.97	2.61	2.98(2)	103.0
C(25)−H(25)−S(2)	0.93	2.70	3.477(19)	142.0
C(37)−H(37)−S(2)	0.93	2.77	3.615(19)	151.0

[a] x, y, z. [b] $x, y, z + 1$.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **1**−**3**

1		**2**		**3**	
Ru(1)−Cl(1)	2.4473(11)	Ru(1)−Cl(1)	2.443(11)	Ru(1)−N(1)	2.099(17)
Ru(1)−P(1)	2.4130(11)	Ru(1)−As(1)	2.481(6)	Ru(1)−N(2)	1.968(13)
Ru(1)−P(2)	2.4264(11)	Ru(1)−As(2)	2.491(6)	Ru(1)−N(3)	2.076(13)
Ru(1)−N(1)	2.110(3)	Ru(1)−N(1)	2.098(3)	Ru(1)−P(1)	2.323(4)
Ru(1)−N(2)	1.936(3)	Ru(1)−N(2)	1.931(3)	Ru(1)−S(1)	2.427(4)
Ru(1)−N(3)	2.103(3)	Ru(1)−N(3)	2.099(3)	Ru(1)−S(2)	2.407(4)
N(2)−Ru(1)−N(1)	78.77(12)	N(2)−Ru(1)−N(1)	78.91(13)	S(1)−C(19)	1.758(18)
N(3)−Ru(1)−N(2)	78.47(11)	N(3)−Ru(1)−N(2)	78.44(12)	S(2)−C(19)	1.66(2)
N(1)−Ru(1)−Cl(1)	103.31(9)	N(1)−Ru(1)−Cl(1)	102.45(10)	N(7)−C(19)	1.37(2)
N(2)−Ru(1)−Cl(1)	177.16(9)	N(2)−Ru(1)−Cl(1)	178.15(9)	N(1)−Ru(1)−N(2)	76.9(5)
N(3)−Ru(1)−Cl(1)	99.48(8)	N(3)−Ru(1)−Cl(1)	100.21(9)	N(2)−Ru(1)−N(3)	77.1(5)
P(1)−Ru(1)−Cl(1)	91.21(4)	As(1)−Ru(1)−Cl(1)	91.14(3)	N(2)−Ru(1)−P(1)	94.4(4)
P(2)−Ru(1)−Cl(1)	89.44(4)	As(2)−Ru(1)−Cl(1)	90.40(3)	S(1)−Ru(1)−S(2)	72.54(15)
P(2)−Ru(1)−P(1)	178.52(3)	As(2)−Ru(1)−As(1)	178.26(2)	P(1)−Ru(1)−S(2)	94.09(14)
N(4)−C(49)−C(50)−N(6)	154.1(4)	N(4)−C(49)−C(50)−N(6)	−156.7(4)	S(1)−Ru(1)−N(2)	98.9(4)
				S(2)−C(19)−S(1)	113.6(11)
				C(22)−N(7)−C(19)−S(2)	−3(3)
				N(4)−C(13)−C(14)−N(6)	177.6(15)

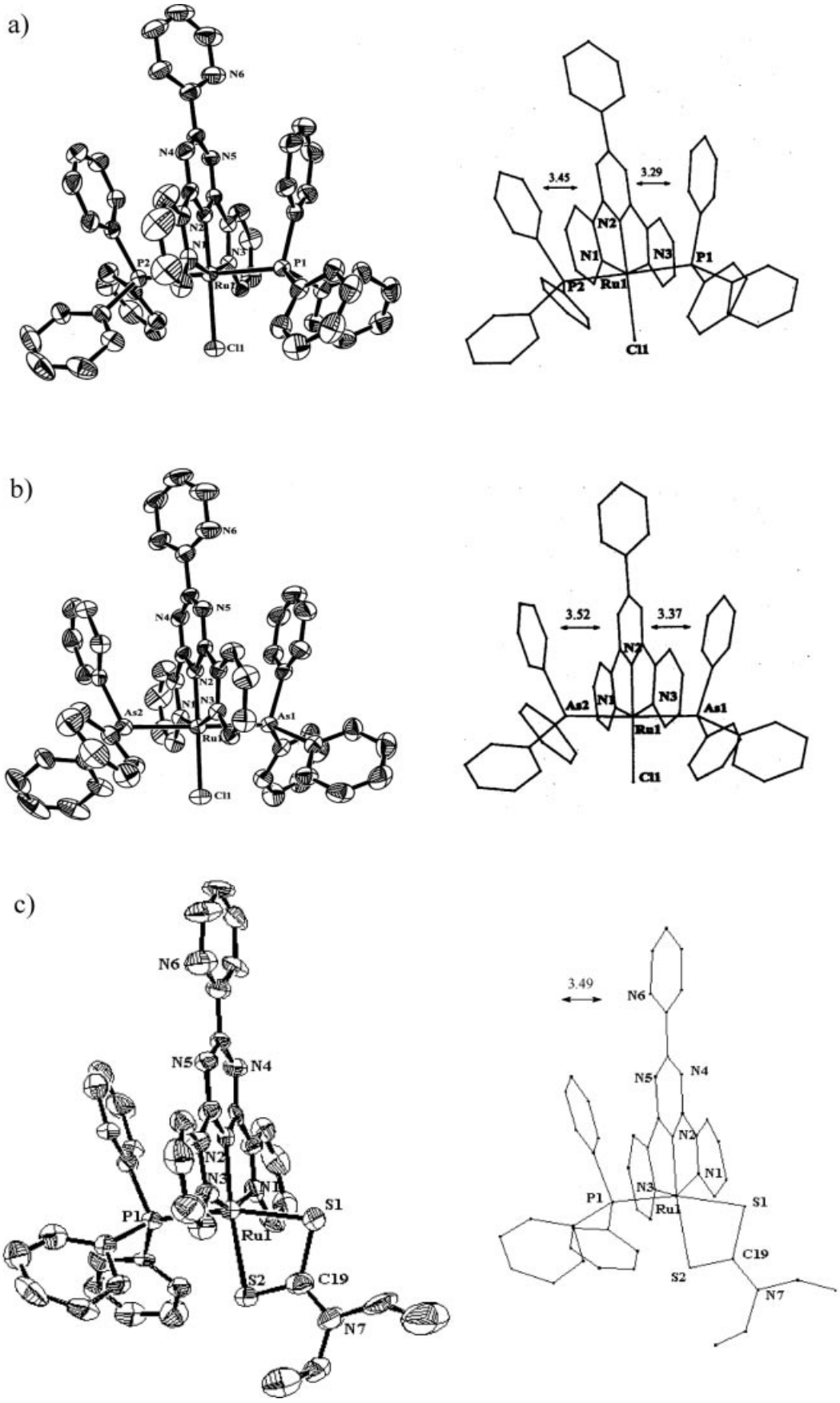


Figure 2. (a) Molecular structure of $[Ru(\kappa^3\text{-tptz})(PPh_3)_2]Cl]^+$ (**1**); (b) molecular structure of $[Ru(\kappa^3\text{-tptz})(AsPh_3)_2]Cl]^+$ (**2**); (c) molecular structure of $[Ru(\kappa^3\text{-tptz})(PPh_3)(dtc)]^+$ (**3**)

F, N, S and Cl) and π−π interactions. (Table 2) Complex **1** shows C−H···Cl intramolecular interactions, which involve Cl and an adjacent hydrogen atom attached to the phenyl (PPh_3) rings. However, this type of interaction is not apparent in complex **2** which has an analogous structure. The absence of a C−H···Cl type interaction is probably due to the longer Ru−As bond in complex **2** when compared with the Ru−P distance in complex **1**. The importance of π−π stacking interactions between aromatic rings, which lie in the range 3.4−3.5 Å, has widely been recognized in the intercalation of drugs with DNA[13] in biological systems. In all the complexes **1**−**3**, intramolecular π−π interactions have been found with the interaction distances in the range 3.29−3.52 Å (see a, b and c in Figure 2). In complexes **1** and **2**, the intermolecular π−π stacking interaction [distance 3.42 Å (**1**) and 3.67 Å (**2**)] results in a single helical motif (see a in Figure 3), while C−H···π, C−H···S−C and π−π stacking (3.39 Å) interactions in complex **3** lead to a double helical network (b in Figure 3).[13]

Interaction of the complexes with DNA is supported by the results from absorption titration studies with calf thymus DNA and inhibition studies (gel electrophoresis) of topoisomerase II of the filarial parasite *S. cervi*. Chloride salts of the complexes were used for DNA binding and inhibition studies. It is well documented that nonplanar octahedral complexes can partially intercalate with the DNA helix or they can show groove binding interactions with the major or minor groove of the helix.[14] Fixed amounts of metal complexes [13.3 μM (**1**) and 40 μM (**2**)] were titrated with an increasing amount of CT-DNA over a range of DNA concentrations from 0 to 112 μM.[15] Absorption spectra were measured after equilibration and the binding constants of the complexes with CT-DNA were determined by monitoring the decay in absorbance with increasing DNA concentration. The model of Bard and Thorp for noncooperative and nonspecific binding was used.[16] Figure 4 depicts the UV/Vis spectra of complex **1** for a solution buffered at pH = 7.1 in the presence of increasing quantities of CT-DNA. Absorption spectra exhibited an average decrease in absorption (hypochromism) of 29% and 42% and bathochromic shifts of 7.5 and 6.5 nm for complexes **1** and **2**, respectively. These observations are consistent with the values reported for other polypyridyl transition metal complexes.[17,18] Binding constants for complexes **1** and **2** are 2.5×10^4 M^{-1} ($s = 0.25$) and 2.1×10^4 M^{-1} ($s = 0.21$), respectively. The value for $s < 1$ is similar to other re-

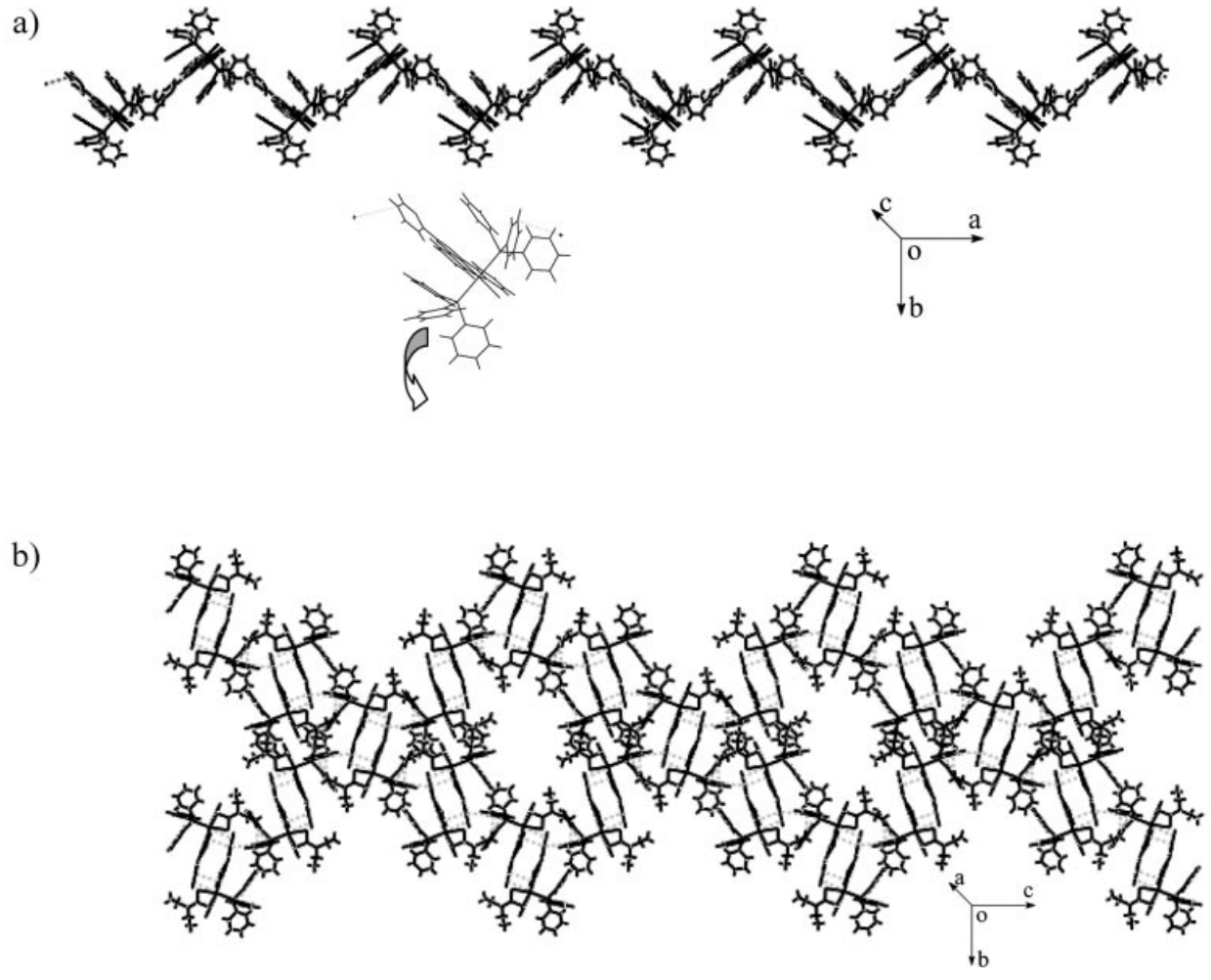


Figure 3. (a) An intermolecular π−π stacking interaction results in a single helical network for complex **1**; (b) intermolecular C−H···π, C−H···S−C and π−π stacking interactions result in a double helical network for complex **3**

ports.[17] The binding strength of the compounds **1** and **2** to nucleotides is relatively poor. This may be due to the presence of the bulky EPh_3 groups *trans* to each other, which causes steric hindrance. Also, the phenyl rings of EPh_3 restrict further the intercalating properties of the complexes. The six-coordinate ruthenium center does not intercalate with the nucleotide and the absorption titration data supports that tptz is stacking with other tptz ligands of nearby complexes bound on the surface of the DNA.[17] Further addition of a 12-fold excess of CT-DNA after saturation of a 13.3 μM solution of complex **1** or addition of a 16-fold excess of CT-DNA to a 40 μM solution of complex **2** caused no changes in the absorption spectra of the final equilibrium mixtures over a period of 48 h. This indicates a strong interactive binding mode of (κ^3- tptz)Ru^{II} complexes.

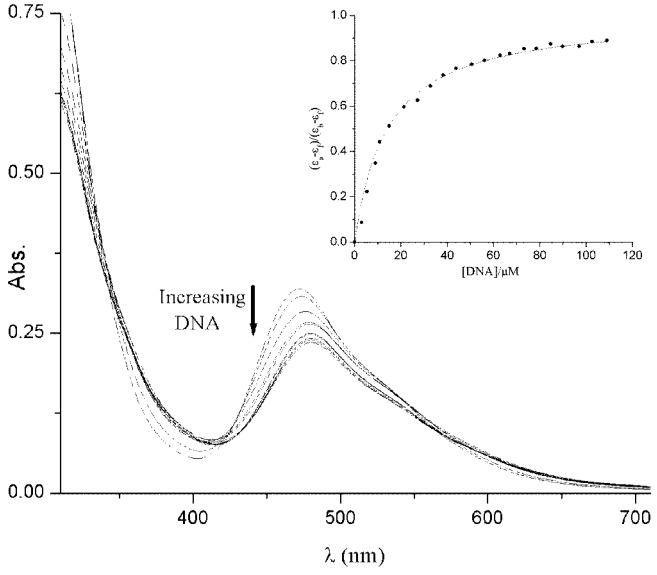


Figure 4. Absorption spectra of $[Ru(\kappa^3\text{-tptz})Cl(PPh_3)_2]^+$ (13.3 μM), in buffer A in the presence of an increasing amount of CT DNA (0−112 μM); inset represents a plot of $(\varepsilon_a - \varepsilon_f)/(\varepsilon_b - \varepsilon_f)$ vs. [DNA] in μM for $[Ru(\kappa^3\text{-tptz})Cl(PPh_3)_2]^+$; the best-fit line is superimposed on the data according to the model of Bard and Thorp[17] for the absorption titration [$K_b = 2.5 \times 10^4$ M^{-1} ($s = 0.25$)]

Efficacy of complexes **1** and **2** against DNA topoisomerase II (topo-II) of the filarial parasite *S. cervi* was examined. The interaction behavior is supported by the inhibitory effect of the metal complexes on DNA topoisomerase II of the filarial parasite. Potential antifilarial agents act either on membrane receptors or on metabolic enzymes. DNA topoisomerases are cellular enzymes that are intricately involved in the topographic structure of DNA transcription and mitosis.[18] In general, inhibition depends upon the availability of binding sites for the enzyme on DNA. Topoisomerase has been identified as an important biochemical target in chemotherapy and microbial infections. Complexes **1** and **2** are potential inhibitors of DNA topo-II of the filarial parasite *S. cervi* with 86% and 93% inhibition at a 10 μM concentration (Figure 5).

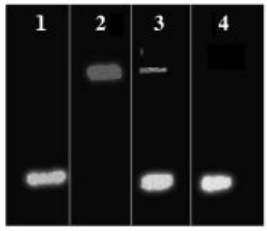


Figure 5. Inhibition of *S. cervi* topoisomerase II by complexes **1** and **2**; lane 1: pBR322 alone; lane 2: DNA + *S. cervi* topo II; lanes 3 and 4 correspond to complex $[Ru(\kappa^3\text{-tptz})Cl(PPh_3)_2]^+$ and $[Ru(\kappa^3\text{-tptz})Cl(AsPh_3)_2]^+$ (10 μM) and the inhibition percentage is 86% and 93%, respectively

Conclusions

In this work, we have presented the synthesis of the (polypyridyl)Ru^{II} complexes $[Ru(\kappa^3\text{-tptz})(PPh_3)_2Cl]^+$, which have many potential uses. We have shown that they can be employed as precursors of other Ru^{II} complexes, as metalloligands or as biocatalysts. Detailed studies of the structure, reactivity and assembling capability of the substituted complexes is in progress in our laboratory.

Experimental Section

General: All reactions were carried out under nitrogen and in deaerated solvents. The solvents were of AR grade and were purified rigorously by standard procedures[19] prior to use. Triply distilled and deionized water was used for the preparation of the various buffers. 2,4,6-Tris(2-pyridyl)-1,3,5-triazine (tptz), ammonium tetrafluoroborate, ruthenium(III) chloride hydrate (all Aldrich) and tetrabutylammonium perchlorate (Fluka) were used as received. Calf thymus (CT) DNA, supercoiled pBR322 DNA, bovine serum albumin (BSA), ATP, dithiothreitol (DTT), agarose, ethidium bromide, sodium dodecyl sulfate (SDS) and proteinase were procured from Sigma Chem. Topoisomersase II from filarial parasite *Setaria cervi* was partially purified according to the method by Pandeya et al.[20] The complex $RuCl_2(PPh_3)_3$ was prepared by a literature method.[21]

Physical Measurements

Spectroscopy and Electrochemistry: Microanalyses were performed by the microanalytical section of the Sophisticated Analytical Instrumentation Centre, Central Drug Research Institute, Lucknow. IR and electronic spectra were recorded with Shimadzu 8201PC and Shimadzu UV-1601 spectrophotometers, respectively. Electronic absorption spectra were measured in a quartz cuvette with a path length of 1 cm. ^1H, ^1H-^1H COSY, ^{13}C and ^{31}P NMR spectra were recorded with a Bruker DRX-300 NMR instrument. FAB mass spectra were recorded with 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. Thermal denaturation analyses were conducted with a DU-640 spectrophotometer. Electrochemical data were acquired with a PAR model 273A electrochemistry system at a scan rate of 50 mVs^{-1}. The sample solutions (10^{-3} M) were prepared in purified acetonitrile containing $Et_4N^+ClO_4^-$ (0.1 M) as the supporting electrolyte. Solutions were

deoxygenated by bubbling dinitrogen for about 20 min before each experiment. The platinum wire working and auxiliary electrodes, and an aqueous saturated calomel reference electrode were used in a three-electrode configuration.

X-ray Crystallography: Suitable crystals for X-ray crystallographic studies for the complexes **1**−**3** were obtained from CH_2Cl_2/petroleum ether (60−80°C) at room temperature over a period of 3 d. All the pertinent crystallographic data are recorded in Table 3. Intensity data were collected at 293(2) K with an Enraf−Nonius CAD 4 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.70930) from plate-like crystals with dimensions 0.22 × 0.22 × 0.17 (**1**), 0.4 × 0.35 × 0.35 (**2**) and 0.25 × 0.35 × 0.41 mm (**3**) in the ω-2θ scan mode in the range from 1.51 to 24.92°. Intensities of these reflections were measured periodically to monitor crystal decay. The structures were solved by direct methods and refined by full-matrix least squares on F^2 (SHELX-97).[10] 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 a fixed contribution. Final residual values and goodness-of-fit were $R1$ = 0.0405, $wR2$ = 0.1132, GOF = 1.104 (**1**), $R1$ = 0.0343, $wR2$ = 0.0803, GOF = 1.063 (**2**) and $R1$ = 0.0673, $wR2$ = 0.1968, GOF = 1.066 (**3**). CCDC-229719 (**1**), -229720 (**2**) and -233890 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

DNA Binding and Cleavage Studies

DNA Topoisomerase II Estimation: For activity measurements, the reaction was carried out (10 μL) in a mixture containing buffer B, 10 mM $MgCl_2$, 1 mM ATP, 0.1 mM EDTA, 0.5 mM DTT, 30 μg/mL BSA and enzyme protein. The reaction was started by incubation at 37 °C for 30 min and stopped by addition of 5 μL of loading dye. The samples were electrophoresed on 1% agarose gel in tris-acetate buffer at 20 V for 18 h. Gels were stained with ethidium bromide (0.5 μg/mL) visualized and photographed on a UVP GDS 7500 UV trans-illuminator. The percentage relaxation was measured by micro densitometry of gel using the Gel base/Gel blot Pro Gel analysis software programme. ^{1}H-NMR and UV/Vis spectral analyses were used to check the stability of the complexes towards the solvent (water and DMSO) and no change was observed. Buffer A (5 mM Tris-HCl, pH = 7.1, 50 mM NaCl) was used for absorption titration and buffer B (50 mM tris-HCl, pH = 7.5, 50 mM KCl) was used for inhibition studies.

Preparation of $[Ru(\kappa^3\text{-tptz})(PPh_3)_2]Cl]BF_4\cdot H_2O$ (1): Complex **1** was prepared by either of the following two methods.

Method (a): Hydrated ruthenium trichloride $RuCl_3\cdot xH_2O$ (0.260 g, 1.0 mmol), dissolved in hot methanol (10 mL), was added to a refluxing solution of triphenylphosphane (PPh_3; 1.578 g, 6.0 mmol) in methanol (50 mL) and the solution was heated under reflux for 1 h. Ligand tptz (0.312 g, 1.0 mmol) was added to the resulting suspension and the contents of the flask were heated under reflux for 8−10 h. After the resulting purple solution was cooled to room temperature, any solid residue was filtered and the filtrate was concentrated under reduced pressure to one fourth of its volume. A saturated solution of ammonium tetrafluoroborate, dissolved in methanol, was added to the concentrated solution and the mixture left for slow crystallization in a refrigerator at 8 °C. The microcrystalline product, which slowly deposited, was separated by filtration and washed repeatedly with methanol and diethyl ether and then dried in vacuo. Yield 73% (0.786 g). $C_{54}H_{44}BClF_4N_6OP_2Ru$ (1078.3): calcd. C 60.11, H 4.08, N 7.79; found C 60.08, H 4.12, N 7.74. FAB-MS: *m/z* obsd. (calcd.), rel. int., [assignm.]: 973 (973), 29, $[Ru(\kappa^3\text{-tptz})(PPh_3)_2Cl]^+$; 711 (711), 69, $[Ru(\kappa^3\text{-tptz})(PPh_3)Cl]^+$; 675 (675), 25, $[Ru(\kappa^3\text{-tptz})(PPh_3)]^{+2}$; 413 (414), 12, $[Ru(\kappa^3\text{-tptz})]^{+2}$. ^{1}H NMR: δ = 9.12 (d, J = 4.80 Hz, 2 H), 8.92 (d, J = 3.00 Hz), 1 H, 8.74 (d, J = 7.8 Hz, 1 H), 8.57 (d, J = 6.5 Hz, 1 H), 8.12 (t,

Table 3. Crystal data for complexes **1**−**3**

	1	**2**	**3**
Empirical formula	$C_{54}H_{44}BClF_4N_6OP_2Ru$	$C_{54}H_{44}As_2BClF_4N_6ORu$	$C_{41}H_{43}ClN_7O_{2.50}PRuS_2$
Formula mass	1078.22	1166.12	905.43
Color and habit	purple-black block	violet-black block	black plate
Crystal size [mm]	0.22 × 0.22 × 0.17	0.4 × 0.35 × 0.35	0.25 × 0.35 × 0.41
Space group	$P2_1/c$	$P2_1/c$	$F2dd$
System	monoclinic	monoclinic	orthorhombic
Unit cell dimensions			
a [Å]	12.338(3)	12.439(8)	13.9940(13)
b [Å]	24.823(5)	25.127(3)	30.5770(19)
c [Å]	16.291(4)	16.399(13)	40.295(3)
β [Å]	101.16(2)	101.27	90.00
V [Å^3]	2532.4(4)	3753.0(12)	17242(2)
Z	4	4	16
$d_{calcd.}$ [mg/m^3]	1.463	1.541	1.395
μ [mm^{-1}]	0.502	1.732	0.604
Temperature [K]	293(2)	293(2)	293(2)
No.of reflections	7469	7220	3157
No. of refined parameters	639	807	505
R factor all	0.0515	0.0496	0.0907
R factor [$I > 2\sigma(I)$]	0.0405	0.0343	0.0673
$wR2$	0.1132	0.0803	0.1968
$wR2$ [$I > 2\sigma(I)$]	0.1045	0.0727	0.1716
Goodness of fit	1.104	1.063	1.066

J = 7.5 Hz, 2 H), 8.00 (t, J = 7.8 Hz, 2 H), 7.58 (t, J = 5.1 Hz, 1 H), 7.38 (t, J = 6.3 Hz, 2 H) and 7.26−7.07 (br. m, aromatic protons of PPh_3) ppm. $^{31}P\{^1H\}$ NMR: δ = 16.24 (s) ppm. UV/Vis: λ_{max} (ε [dm^3 $mol^{-1}cm^{-1}$]) = 472 (24022), 309(63759), 273 (149195) nm.

Method (b): A suspension of $[RuCl_2(PPh_3)]$ (0.982 g, 1.0 mmol) in methanol (50 mL) was treated with tptz (0.312 g, 1.0 mmol) and the resulting solution was heated under reflux for 8.0 h resulting in a purple solution. After cooling to room temperature, the resulting solution was filtered through Celite to remove any solid impurities. A saturated solution of ammonium tetrafluoroborate, dissolved in methanol, was added to the filtrate and it was left in the refrigerator for slow crystallization. After several days, a purple-black crystalline product had separated. Analytical and spectroscopic data were identical to those of the previous method but the yield was higher.

Preparation of $[Ru(\kappa^3\text{-tptz})(AsPh_3)_2Cl]BF_4\cdot H_2O$ (2): This complex was prepared by a similar method (complex **1**) except that $AsPh_3$ (1.836 g, 6.0 mmol) was used in place of PPh_3. A violet-black complex was obtained. Yield 71% (0.827 g). $C_{54}H_{44}As_2BClF_4N_6ORu$ (1166.1): calcd. C 55.57, H 3.77, N 7.20; found C 55.62, H 3.68, N 7.12. FAB-MS: *m*/*z* obsd. (calcd.), rel. int., [assignm.]: 1061 (1061), 19, $[Ru(\kappa^3\text{-tptz})(AsPh_3)_2Cl]^+$; 755 (755), 54, $[Ru(\kappa^3\text{-tptz})(AsPh_3)Cl]^+$; 449 (449), 35, $Ru(\kappa^3\text{-tptz})Cl]^+$. ^1H NMR: δ = 9.26 (d, J = 5.1 Hz, 2 H), 8.93 (d, J = 3.6 Hz, 1 H), 8.69 (d,, J = 8.1 Hz 1 H), 8.65 (d, J = 7.8 Hz, 1 H), 8.11 (m, J = 7.5 Hz, 4 H), 7.59 (t, J = 5.1 Hz, 1 H), 7.51 (t, J = 6.3 Hz, 2 H) and 7.23−7.03 (br. m, aromatic protons of $AsPh_3$) ppm. UV/Vis: λ_{max} (ε [dm^3 $mol^{-1}cm^{-1}$]) = 489 (6930), 342 (7250), 271.5 (21355) nm.

Preparation of $[Ru(\kappa^3\text{-tptz})(PPh_3)(dtc)]Cl$ (3): Complex **3** was prepared by the reaction of $[Ru(\kappa^3\text{-tptz})(PPh_3)_2Cl]Cl$ (0.501 g, 0.5 mmol) with sodium diethyldithiocarbamate (0.112 g, 0.5 mmol) in methanol in the same way as Method (b) for complex **1**. Yield 75% (0.322 g). $C_{41}H_{37}ClN_7PRuS_2$ (859.4): calcd. C 57.24, H 4.30, N 11.40; found C 57.46, H 4.17, N 11.21. FAB-MS: *m*/*z* obsd. (calcd.), rel. int., [assignm.]: 824 (823), 100, $[Ru(\kappa^3\text{-tptz})(PPh_3)dtc]^+$; 561 (562), 94, $[Ru(\kappa^3\text{-tptz})(dtc)]^+$; 414 (413), 38, $[Ru(\kappa^3\text{-tptz})]^{+2}$. ^1H NMR: δ = 9.00 (d, J = 5.4 Hz, 2 H), 8.94 (d, J = 3.9 Hz, 1 H), 8.80 (d, J = 7.8 Hz, 1 H), 8.73 (t, J = 7.5 Hz, 2 H), 8.09 (m), 7.77 (t, J = 6 Hz, 2 H) 7.60 (t, J = 2.7 Hz, 1 H) 7.16 (m), 7.003 (t, J = 7.5 Hz, 6 H), 4.10 (q, J = 7.2 Hz, 2 H), 3.62 (q, J = 6.9 Hz, 2 H), 1.52 (t, J = 7.2 Hz, 3 H), 1.13 (t, J = 6 Hz, 3 H) ppm. $^{31}P\{^1H\}$ NMR: δ = 37.81 (s) ppm. UV/Vis: λ_{max} (ε [dm^3 $mol^{-1}cm^{-1}$]) = 245 (60488), 289 (49367), 387 (16805), 485 (13173) nm.

Preparation of $[Ru(\kappa^3\text{-tptz})(PPh_3)(CN)_2]$ (4): Complex **4** was prepared by the reaction of $[Ru(\kappa^3\text{-tptz})(PPh_3)_2(Cl)]BF_4$ (0.539 g, 0.5 mmol) with a slight excess of sodium cyanide according to the procedure of Method (b) for complex **1**. Yield 63% (0.229 g). $C_{38}H_{27}N_8PRu$ (727.7): calcd. C 62.72, H 3.71, N 15.40; found C 62.69, H 3.65, N 15.38. FAB-MS: *m*/*z* obsd. (calcdd), rel. int., [assignm.]: 701 (702), 31, $[Ru(\kappa^3\text{-tptz})(PPh_3)(CN)]^+$; 675 (676), 33, $[Ru(\kappa^3\text{-tptz})(PPh_3)]^{2+}$; 413 (414), 35, $Ru(\kappa^3\text{-tptz})]^{2+}$. ^1H NMR: δ = 9.04 (d, J = 3.0 Hz, 1 H), 8.92 (d, J = 3.9 Hz, 1 H), 8.71 (d, J = 7.5 Hz, 1 H), 8.63 (t, J = 7.5 Hz, 1 H), 8.16 (m, 4 H), 7.75 (m, 2 H), 7.22 (m), 7.09 (t, J = 5 Hz, 1 H) ppm. $^{31}P\{^1H\}$ NMR: δ = 32.89 (s) ppm. UV/Vis: λ_{max} (ε [dm^3 $mol^{-1}cm^{-1}$]) = 233 (31663), 247 (35003), 372 (1489), 522 (1722) nm.

Preparation of $[Ru(\kappa^3\text{-tptz})(AsPh_3)(dtc)]BF_4$ (5): Complex **5** was prepared by the reaction of $[Ru(\kappa^3\text{-tptz})(AsPh_3)_2(Cl)]BF_4$ (0.583 g, 0.5 mmol) with sodium diethyldithiocarbamate (0.112 g, 0.5 mmol) in methanol according to the procedure for complex **2**. Yield 70% (0.334 g). $C_{41}H_{38}AsBF_4N_7Ru$ (891.6): calcd. C 51.51, H 3.97, N 10.26; found C 59.20, H 3.49, N 14.53. FAB- MS: *m*/*z* obsd. (calcd.), rel. int., [assignm.]: 868 (867), 60, $[Ru(\kappa^3\text{-tptz})(AsPh_3)(dtc)]^+$; 562 (561), 100, $[Ru(\kappa^3\text{-tptz})(dtc)]^+$; 413 (414), 36, $Ru(\kappa^3\text{-tptz})]^{2+}$. ^1H NMR: δ = 9.26 (d, J = 5.1 Hz, 1 H), 9.05 (d, J = 5.4 Hz, 2 H), 8.94 (t, J = 4.2 Hz, 1 H), 8.80 (dd, J = 5.4 Hz, 3 H), 8.66 (d), 8.09 (t, J = 7.8 Hz, 4 H) 7.79 (t, J = 6.3 Hz, 2 H) 7.58 (m), 7.17 (m), 6.83 (d, J = 7.1 Hz, 3 H), 4.10 (q, J = 7.2 Hz, 2 H), 3.55 (q, J = 7.2 Hz, 2 H), 1.50 (t, J = 7.2 Hz, 3 H), 1.10 (t, J = 6.1 Hz, 3 H) ppm. UV/Vis: λ_{max} (ε [dm^3 $mol^{-1}cm^{-1}$]) = 229 (11600), 277 (11500), 343 (2500), 493 (2100) nm.

Preparation of $[Ru(\kappa^3\text{-tptz})(AsPh_3)(CN)_2]$ (6): Complex **6** was prepared by the reaction of $[Ru(\kappa^3\text{-tptz})(AsPh_3)_2(Cl)]BF_4$ (0.583 g, 0.5 mmol) with a slight excess of sodium cyanide according to the procedure for complex **2**. Yield 62% (0.239 g). $C_{38}H_{27}AsN_8Ru$ (771.7): calcd. C 59.14, H 3.50, N 14.52; found C 59.20, H 3.49, N 14.53. FAB-MS: *m*/*z* obsd. (calcd.), rel. int., [assignm.]: 745 (745), 43, $[Ru(\kappa^3\text{-tptz})(AsPh_3)(CN)]^+$; 719 (720), 35, $[Ru(\kappa^3\text{-tptz})(AsPh_3)]^{2+}$; 413 (414), 41, $[Ru(\kappa^3\text{-tptz})]^{2+}$. ^1H NMR: δ = 9.21 (d, J = 4.6 Hz, 2 H), 9.05 (d, J = 3.9 Hz, 1 H), 8.79 (d, J = 6.5 Hz, 1 H), 8.43 (t, J = 7.5 Hz, 2 H), 8.25 (m, 4 H), 7.86 (m, 2 H), 7.27 (m), 7.13 (t, J = 5.3 Hz, 2 H) ppm. UV/Vis: λ_{max} (ε [dm^3 $mol^{-1}cm^{-1}$]) = 231 (12786), 320 (11607), 504 (1982) nm.

Acknowledgments

Thanks are due to the Department of Science and Technology, Ministry of Science and Technology, New Delhi for providing financial assistance [SP/S1/F-04/2000] and the National Single Crystal X-ray Diffraction Laboratory, Indian Institute of Technology, Mumbai, for providing single-crystal X-ray data.

[1] [1a] J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**. [1b]E. Amouyal, *Sol. Energy Matter. Sol. Cells* **1995**, *38*, 249. [1c] V. Balzani, P. Ceroni, A. Juris, M. Venturi, F. Puntariero, S. Campagna, S. Serroni, *Coord. Chem. Rev.* **2001**, *545*, 219. [1d] A. Beyeler, P. Belser, *Coord. Chem. Rev.* **2002**, *230*, 29. [1e] S. Campagna, P. D. Pietro, F. Loiseau, B. Maubert, N. McClenaghan, R. Passalacqua, F. Puntoriero, V. Ricevuto, S. Serroni, *Coord. Chem. Rev.* **2002**, *229*, 67.

[2] [2a] K. D. Demadis, C. M. Hartshorn, T. J. Meyer, *Chem. Rev.* **2001**, *101*, 2655. [2b] B. S. Brunschwig, C. Creutz, N. Sutin, *Chem. Soc. Rev.* **2002**, *31*, 168.

[3] [3a] N. H. Dam-Rauer, G. Cerullo, A. Yeh, T. R. Boussie, C. V. Shank, J. K. McCusker, *Science* **1997**, *275*, 54. [3b] F. L. Carter, R. E. Siatkowski, *Molecular Electronics Devices* (Ed.: H. Wohltjn), North Holland, Amsterdam, The Netherlands, **1998**.

[4] [4a] F. Bargiletti, L. Flamigni, *Chem. Soc. Rev.* **2000**, *29*, 1. [4b] S. S. Sun, A. J. Lees, *Inorg. Chem.* **2001**, *41*, 3154. [4c] K. Chichak, U. Jacquremard, N. R. Branda, *Eur. J. Inorg. Chem.* **2002**, 357. [4d] T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48 and refrences therein.

[5] [5a] N. Gupta, N. Grover, G. A. Neyhart, P. Singh, H. H. Thorp, *Inorg. Chem.* **1993**, *32*, 310. [5b] K. E. Erkkila, D. T. Odom, J. K. Barton, *Chem. Rev.* **1999**, *29*, 2777. [5c] J. Kelly, A. Tossi, D. McConnel, C. Ohuigin, *Nucleic Acids Res.* **1985**, *13*, 6017. [5d] A. Ambroise, B. G. Maiya, *Inorg. Chem.* **2000**, *39*, 4264.

[6] [6a] S. W. Keller, S. A. Johnson, E. S. Brigham, E. T. Yonemoto, T. E. Mallouk, *J. Am. Chem. Soc.* **1995**, *117*, 12879. [6b] B. E. Buchanan, R. Wang, G.V. Johannes, R. Hage, J. G. Hassnoot, J. Reedijk, *Inorg. Chem.* **1995**, *34*, 3358. [6c] E. Brauns, W. Sumner, J. A. Clark, S. M. Molnar, Y. Kawanishi, K. J. Brewer, *Inorg. Chem.* **1997**, *36*, 2861. [6d] J. -D. Lee, L. M. Vrana, E. R. Bullock, K.J. Brewer, *Inorg. Chem.* **1998**, *37*, 3575. [6e] C. Ceroni, F. Paolucci, S. Roffia, S. Serroni, S. Campagna, A. J.

Bard, *Inorg. Chem.* **1998**, *37*, 2829. [6f] D. J. Chesnut, A. Kusnetzow, R. R. Birgeard, J. Zubieta, *Inorg. Chem.* **1999**, *38*, 2663. [6g] G. Albano, P. Belser, C. Dual, *Inorg. Chem.* **2001**, *40*, 1408. [6h] C. Metcalfe, S. Spey, H. Adams, J. A. Thomas, *J. Chem. Soc., Dalton Trans.* **2002**, 4732.

[7] [7a] A. Singh, A. N. Sahay, D. S. Pandey, M. C. Puerta, P. Valerga, *J. Organomet. Chem.* **2000**, *613*, 250. [7b] A. N. Sahay, D. S. Pandey, M. G. Walwalkar, *J. Organomet. Chem.* **2000**, *605*, 74. [7c] A. Singh, N. Singh, D. S. Pandey, *J. Organomet. Chem.* **2002**, *642*, 48. [7d] M. Chandra, A. N. Sahay, S. M. Mobin, D. S. Pandey, *J. Organomet. Chem.* **2002**, *658*, 43−49.

[8] B. P. Sullivan, D. J. Salmon, T. J. Meyer, *Inorg. Chem.* **1978**, *17*, 3334.

[9] [9a] S. Mackay, W. Dong, C. Edwards, A. Henderson, C. Gilmox, N. Stewart, K. Shankland, A. Donald, University of Glasgow, Scotland, **1999**. [9b] G. M. Sheldrick, *SHELXS-97: Program for structure solution and refinement of crystal structures*, University of Göttingen, Germany, **1997**. [9c] G. M. Sheldrick, *SHELXL-97: Program for structure refinement*, University of Göttingen, Germany, **1997**. [9d] C. K. Johnson, *ORTEP III*, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, **1976**. [9e]*PLATON:* A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, C31.

[10] [10a] P. Paul, B. Tyagi, A. K. Bilakhia, D. Parthsarthi, E. Suresh, *Inorg. Chem.* **2000**, *39*, 14 and references cited therein. [10b] M. Chandra, A. N. Sahay, D. S. Pandey, M. C. Puerta, P. Valerga, *J. Organomet. Chem.* **2002**, *648*, 39.

[11] [11a] M. R. Churchill, K. M. Keil, F. V. Bright, S. Pandey, G. A. Baker, J. B. Keister, *Inorg. Chem.* **2000**, *39*, 5807. [11b] P. Ghosh, A. Chakravorty, *Inorg. Chem.* **1997**, *36*, 64. [11c] H. Sugimoto, K. Tsuge, K. Tanaka, *J. Chem. Soc., Dalton Trans.* **2001**, 57.

[12] [12a] M. I. Bruce, F. S. Wong, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **1981**, 1398. [12b] R. O. Gould, C. L. Jones, R. D. Robertson, T. A. Stephenson, *J. Chem. Soc., Dalton Trans.* **1981**, 129. [12c] T. Hayashida, H. Nagashima, *Organometallics* **2002**, *21*, 3884. [12d] H. Nishiyama, M. Konno, K. Aoki, H. M. L. Davies, M. L. Huw, *Organometallics* **2002**, *21*, 2536.

[13] [13a] E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem. Int. Ed.* **2003**, *11*, 42. [13b] D. Braga, P. J. Dyson, F. Grepioni, B. F. G. Johnson, *Chem. Rev.* **1994**, *94*, 1585.

[14] [14a] J. K. Barton, *Science* **1986**, *233*, 727. [14b] J. K. Barton, J. J. Dannesberg, A. L. Raphael, *J. Am. Chem. Soc.* **1982**, *104*, 4967. [14c] J. K. Barton, A. T. Danishefsky, J. M. Goldberg, *J. Am. Chem. Soc.* **1984**, *106*, 2172.

[15] The concentration of CT DNA was determined spectroscopically by using the molar extinction coefficient $\varepsilon(\lambda = 260\ nm) = 6600\ M^{-1}\cdot cm^{-1}$. [15a] M. E. Reichmann, S. A. Rice, C. A. Thomas, P. Doty, *J. Am. Chem. Soc.* **1954**, *76*, 3074. Solutions of DNA in an appropriate buffer A gave a ratio of UV absorption at 260 and 280 nm of $A_{260/280} \approx 1.8-1.9$, indicating that the DNA was sufficiently free of protein. [15b] J. Marmur, *J. Mol. Biol.* **1961**, *3*, 208.

[16] [16a] M. T. Carter, M. Rodriguez, A. J. Bard, *J. Am. Chem. Soc.* **1989**, *111*, 8901. [16b] S. R. Smith, G. A. Neyhart, W. A. Kalsbeck, H. H. Thorp, *New J. Chem.* **1994**, *18*, 397.

[17] Setting the value of $s > 1$ makes our fit unusual. It is consistent with other reports and suggests that it may be due to stacking of intercalculator molecules on the DNA surface. [17a] A. M. Pyle, J. P. Rehmann, R. Meshoyrer, C. V. Kumar, N. J. Turro, J. K. Barton, *J. Am. Chem. Soc.* **1989**, *111*, 3051. [17b] R. B. Nair, E. S. Teng, S. L. Kirkland, C. J. Murphy, *Inorg. Chem.* **1998**, *37*, 139. [17c] J.-G. Liu, Q.-L. Zhang, X.-F. Shi, L.-N. Ji, *Inorg. Chem.* **2001**, *40*, 5045. [17d] A. Frodl, D. Herebian, W. S. Sheldrick, *J. Chem. Soc., Dalton Trans.* **2002**, 3664.

[18] J. C. Wang, *J. Biol. Chem.* **1991**, *266*, 6659.

[19] D. D. Perrin, W. L. F. Armango, D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, Oxford, U. K., **1986**.

[20] [20a] U. Pandya, J. K. Saxena, S. M. Kaul, P. K. Murthy, R. K. Chatterjee, R. P. Tripathi, A. P. Bhaduri, O. P. Shukla, *Med. Sci. Res.* **1999**, *27*, 103−106. [20b] R. P. Tripathi, S. K. Rastogi, B. Kundu, J. K. Saxena, V. J. M. Reddy, S. Shrivastav, S. Chandra, A. P. Bhaduri, *Comb. Chem. High Throughput Screening* **2001**, *4*, 237.

[21] P. S. Hallman, T. A. Stephenson, G. Wilkinson, *Inorg. Synth.* **1970**, *12*, 238.

Received January 28. 2004
Early View Article
Published Online July 7, 2004

