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Synthesis and X-ray characterization of two isomeric dichloro bis-{1-(phenylazo)isoquinoline} complexes of ruthenium(II)

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Abstract

The azoimine functionalized ligand, 1-(phenylazo)isoquinoline (paiq) was synthesized and reacted with $RuCl_3$ in dry ethanol under nitrogen atmosphere to produce two isomeric dichloro bis-[1-(phenylazo)isoquinoline] ruthenium(II) complexes. They are green isomer (**a**) and blue isomer (**b**). In the X-ray crystal structure determination, the final reliability indices for isomers (**a**) and (**b**) are 0.0308 and 0.0448, respectively. Solvents for crystallization are found in both crystal structures. Of the five possible geometrical isomeric configurations of RuL_2Cl_2, L = 1-(phenylazo)isoquinoline, in order of the coordinating pairs: (Cl, Cl); (N,N); (N′,N′) where N represents N(isoquinoline), N′ represents N(azo), the two isomers isolated are *trans–cis–cis* (tcc, **a**) and *cis–cis–cis* (ccc, **b**). Both the green isomer (**a**) and the blue isomer (**b**) have six coordination. The coordination geometry of ruthenium(II) for the former (**a**) compound is distortedly octahedral with the surrounding four nitrogen atoms equatorial and two chlorine atoms axial. That for the latter isomer (**b**) is also a distorted octahedron with Cl2, N1, N3 and N6 atoms basal, and Cl1 and N4 atoms apical. The Ru–Cl distances for the green tcc-isomer (**a**) are shorter than those for the blue ccc-isomer (**b**). The Ru–N bond lengths in both isomer split into two categories.

Keywords: Phenylazoisoquinolin; Ruthenium(II) complexes; Isomers; X-ray structures

1. Introduction

The chemistry of ruthenium(II) complexes containing azoimine (–N=N–C=N–) and diimine (–N=C–N=C–) functional units have been reported elsewhere [1–6]. These two functions are isoelectronic and π-acidic in character. The advantage of the azoimine functional unit is that it has a strong ability to stabilize low valent metal redox states, such as Ru(II), Os(II), Pd(II), Pt(II), Ag(I), Cu(I) etc. Thus the chemistry of azoimine functionalized ligand complexes enamoured us to take an endeavor to develop a new ligand containing an azoimine unit. Our ligand skeleton is made up by an isoquinoline as an N-heterocycle with a pendant azo arm.

Isoquinoline was contemplated because of its potential application in medicinal alkaloids. The ring structure of isoquinoline is of great consequence in medicinal plant alkaloids and as a result has found application in chemotherapy [7]. Morphine and codeine are well known analgesics, emitine is an antiamoebic—all are regarded as tetrahydroisoquinoline derivatives. Berberin, a protoberberine dihydrodibenzoisoquinolizinium alkaloid containing the typical tetracyclic ring structure, has found applications as an antibacterial, antimalarial and antipyretic compound [8]. A small group of isoquinoline alkaloids, for example corydaldine, is known to have medicinal importance [8].

It is presumable that the coordination chemistry plays an important role in biological molecules such as hemoglobin [9], chlorophyll [10] and vitamin E [11,12]. The metal usually coordinates with oxygen, nitrogen

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and sulfur atoms in the coordination compound [13]. Several types of ruthenium metal complexes have shown high in vitro and in vivo antitumor activity and some compounds are in advanced stages of preclinical studies [14–17]. Although the mechanism of action of antitumor-active ruthenium compounds is not fully understood yet, it is thought that, similar to the platinum drugs [18–21], the chloride complexes can hydrolyze in vivo, allowing the Ru to finally bind to the nucleobases of the DNA. Very recently the remarkably different cytotoxicity data in vitro of a series of human tumor cell lines of the three isomers of dichloro bis-{2-(phenylazo) pyridine)} ruthenium(II) complexes has been investigated [22]. Crystal structures of these isomers are reported [22,23].

Our successfully synthesized new ligand (L), 1-phenylazoisoquinoline (Scheme 1), is an unsymmetrical *N*,*N′*-bidentate ligand, lacks a twofold symmetry axis and on complexation with ruthenium(II), affords pseudo-octahedral, RuL_2Cl_2 complexes.

Theoretically, the RuL_2Cl_2, complex formula bestows five geometrical isomers: *trans–cis–cis* (tcc); *trans–trans–trans* (ttt); *cis–trans–cis* (ctc); *cis–cis–trans* (cct); and *cis–cis–cis* (ccc) (Scheme 1). We were able to isolate only two isomers among the five isomers. In this paper we wish to describe the synthesis and X-ray characterization of tcc-(dichloro){bis-(1-phenylazoisoquinoline)}ruthenium(II) and ccc-(dichloro){bis-(1-phenylazoisoquinoline)}ruthenium(II) complexes. A study of some coordinated bond lengths of these ligand complexes with other similar ligand complexes of ruthenium(II) have been summarized and compared herein.

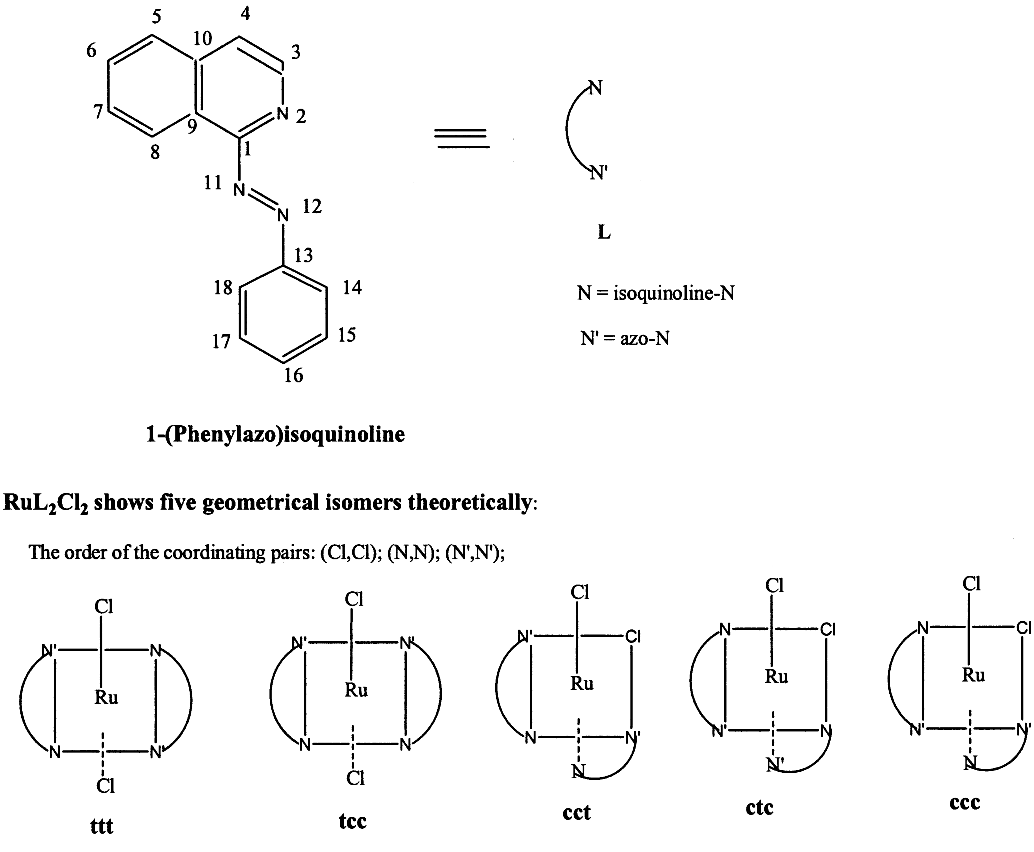
2. Experimental

2.1. Materials

1-Aminoisoquinoline, nitrosobenzene and $RuCl_3 \cdot xH_2O$ were purchased from Aldrich. Ruthenium trichloride hydrate was treated before use as earlier [1]. All other chemicals and solvents were of reagent grade and were used without further purification.

2.2. Preparation of the ligand 1-(phenylazo)isoquinoline (paiq)

To a solution of 1-aminoisoquinoline (1.0 g, 6.94 mmol) in dry benzene (25 ml) in the presence of molecular sodium (0.5 g), nitrosobenzene (0.75 g, 7.0 mmol) was added slowly in small portions for 2 h and



Scheme 1.

refluxed under nitrogen atmosphere. The reaction was further continued for 3 h and cooled to room temperature (r.t.). The dark red solution was then filtered and the filtrate was washed thoroughly with water three to four times. The solution was concentrated by vacuum distillation and then subjected to column chromatography (30 × 1 cm) on silica gel (60–120 mesh). The desired compound, a red band, was eluted with benzene and concentrated by distillation. A gummy mass of the ligand was obtained by evaporation of the solvent. The yield was 42%.

Table 1
Summarized crystallographic data for complexes **a** and **b**

Crystal parameters	Green tcc isomer (**a**)	Blue ccc isomer (**b**)
Formula	$C_{31}H_{24}Cl_4N_6Ru$	$C_{35}H_{23}Cl_2N_6O_2Ru$
M	723.43	731.56
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
a (Å)	10.213(2)	25.040(7)
b (Å)	11.616(2)	14.816(4)
c (Å)	14.297(3)	19.780(6)
α (°)	110.497(3)	90
β (°)	105.189(3)	113.873(5)
γ (°)	91.952(3)	90
V (Å^3)	1518.5(5)	6710(3)
Wavelength (Å)	0.71073	0.71073
ρ_{calc} (Mg m^{-3})	1.582	1.448
Z	2	8
Temperature (K)	294(2)	294(2)
μ (Mo Kα) (mm^{-1})	0.901	0.667
Refined parameters	385	384
R [a]	0.0308	0.0448
wR	0.0840	0.1403
Goodness-of-fit [b]	1.095	0.713

[a] $R = [\Sigma[F_o - F_c]/\Sigma\ F_o]$.

[b] GOF is defined as $[w(F_o - F_c)/(n_o - n_c)]^{1/2}$ where n_o and n_c denote the numbers of data and variables, respectively.

2.3. *Preparation of two complexes of isomeric $Ru(paiq)_2Cl_2$, trans–cis–cis-dichlorobis-{1-(phenylazo)isoquinoline}ruthenium(II) (green isomer, **a**) and cis–cis–cis-dichlorobis-{1-(phenylazo)-isoquinoline}ruthenium(II) (blue isomer, **b**)*

$RuCl_3 \cdot xH_2O$ (0.2 g, 0.76 mmol) was dissolved in 20 ml of dry ethanol and was refluxed with stirring for 5 h under nitrogen atmosphere. During this period the color of the solution changed from brown to green. Then 0.36 g (1.53 mmol) of the ligand, 1-(phenylazo)isoquinoline (paiq) in 5 ml dry ethanol was added and the mixture was refluxed for an additional 4 h. The color of the solution became bluish-green with a dark precipitate. The solution was cooled to r.t., filtered and washed thoroughly with water, ethanol and finally with diethylether. The precipitate was then dried in vacuum. The dried product was dissolved in small volume of CH_2Cl_2 and then subjected to column chromatography on alumina. A green band was eluted by 5:1 benzene–acetonitrile mixture and a blue band was eluted by 1:1 benzene–acetonitrile mixture. Crystals suitable for single X-ray diffraction were grown by slow evaporation of the eluted solution at r.t.

2.4. *X-ray crystallography*

Crystals suitable for X-ray work were cut into the size of 0.30 × 0.30 × 0.20 mm for green isomer (**a**) and 0.30 × 0.25 × 0.23 mm for blue isomer (**b**). X-ray diffraction data were collected on a Siemens SMART CCD diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 295 K. The crystal data and the collection parameters are listed in Table 1. The data were corrected for Lorentz-polarization factors and absorption effects. An empirical absorption was applied based on the azimuthal rotation from reflections [24]. Systematic absences led to the identification of space groups as shown in Table 1. Of the total measured 14 814 (**a**) and 19 731 (**b**) reflections, 6632 and 7488 are unique, 5911 and 5664 are significant ($I > 2\sigma(I)$) and used for structure determination, respectively. The initial phases for both isomers were determined by the conventional heavy atom method and checked by a direct method. Successively alternative difference Fourier synthesis and full-matrix least-squares fit were applied to solve the two whole structures [25]. Both structures contain solvent(s) in somewhat disorder, besides the expected model molecule. From the difference Fourier map by using the calculated structure factor for the model, residues higher than 3 e Å^{-3} were found. Judging from the solvents we added to synthesize the compound and to grow the crystals, the solvent(s) in the structures were located. They were CH_2Cl_2 (dichloromethane) for the green tcc isomer, and C_6H_6 (benzene), CH_3CH_2OH (ethanol) and H_2O (water molecule) for the blue ccc isomer. The structures were determined by using SHELX-97 [26] and their ORTEP were plotted by NRCVAX [27].

3. Results and discussion

3.1. *Synthesis*

1-(Phenylazo)isoquinoline (paiq, Scheme 1) was synthesized by condensing nitrosobenzene with 1-aminoisoquinoline in the presence of metallic sodium in dry benzene under refluxing conditions for 5 h. The ligand was purified by column chromatography on silica gel. The ligand is new and acted as an unsymmetrical bidentate *N*,*N*-chelating ligand. The donor centers are abbreviated as N(isoquinoline), N and N(azo), N′ and the atom numbering is shown in Scheme 1. Ru(II)-

complexes, $Ru(paiq)_2Cl_2$, were generated when $RuCl_3 \cdot xH_2O$ was refluxed in dry ethanol under N_2-atmosphere followed by the addition of the ligand via spontaneous reductive chelation. Upon cooling, mainly green isomer with a small amount of blue isomer were precipitated. The mother liquor provides mainly the blue isomer. Isomers were isolated by column chromatography on alumina.

3.2. Crystal structures

The molecular structures of green tcc isomer (**a**) and blue ccc isomer (**b**) are shown in Figs. 1 and 2, and selected bond parameters are listed in Tables 2 and 3, respectively. The coordination geometry around ruthenium is distortedly octahedral. The atomic arrangement in the green isomer (**a**) involves sequentially two *trans*-chlorine, *cis*-isoquinoline-N (N) and *cis*-azo-N (N′) and corresponds to a tcc configuration. Similarly, the arrangement in blue isomer is *ccc*.

3.3. Green tcc-isomer (**a**)

The ruthenium ion of the green crystal is six-coordinated. The coordination geometry of ruthenium(II) for this green isomer is distortedly octahedral with surrounding N1, N3, N4, N6 atoms equatorial (rms deviation of 0.068 Å) and Cl1, Cl2 atoms axial (−2.3798(12) and 2.3436(13) Å, respectively, from the basal plane). The two atomic groups Ru, Cl(1), Cl(2), N(3), N(4) and Ru, Cl(1), Cl(2), N(1), N(6) constitute two good planes (rms deviation, 0.09 Å) and are almost orthogonal to the third molecular plane, Ru, N(1), N(3),

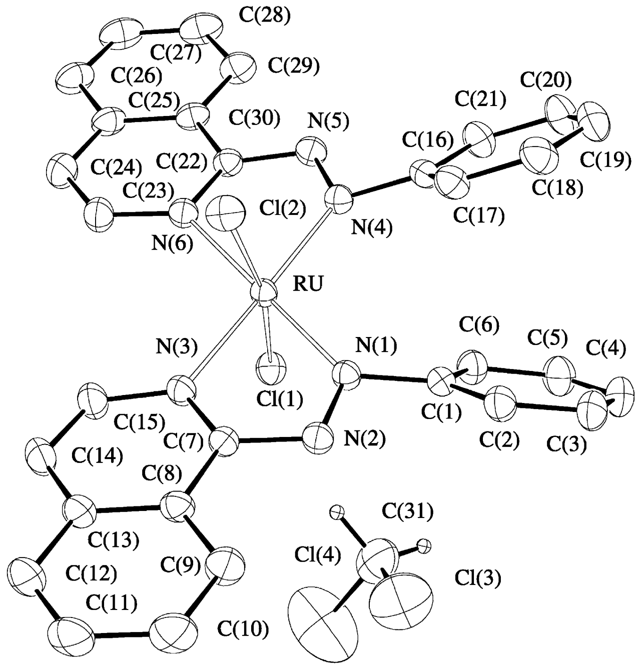


Fig. 1. Molecular structure and atom-labeling scheme for the crystal structure of green tcc-isomer (**a**), with solvent of dichloromethane.

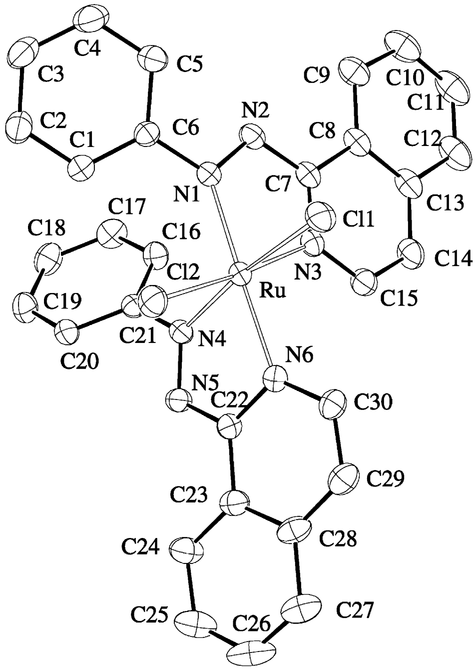


Fig. 2. Molecular structure and atom-labeling scheme for the crystal structure of blue ccc-isomer (**b**), excluding the solvents.

Table 2
Selected bond lengths (Å) and angles (°) for green tcc-isomer (**a**)

Bond lengths	
Ru–N(1)	1.9851(19)
Ru–N(4)	1.9952(19)
Ru–N(3)	2.1009(19)
Ru–N(6)	2.103(2)
Ru–Cl(2)	2.3640(7)
Ru–Cl(1)	2.3837(7)
N(1)–N(2)	1.295(3)
N(4)–N(5)	1.293(3)
Bond angles	
N(1)–Ru–N(4)	104.10(8)
N(1)–Ru–N(3)	75.36(8)
N(4)–Ru–N(3)	175.79(8)
N(1)–Ru–N(6)	176.41(7)
N(4)–Ru–N(6)	75.11(8)
N(3)–Ru–N(6)	105.69(8)
N(1)–Ru–Cl(2)	93.75(6)
N(4)–Ru–Cl(2)	93.14(6)
N(3)–Ru–Cl(2)	82.75(6)
N(6)–Ru–Cl(2)	89.80(6)
N(1)–Ru–Cl(1)	92.63(6)
N(4)–Ru–Cl(1)	93.83(6)
N(3)–Ru–Cl(1)	90.37(6)
N(6)–Ru–Cl(1)	83.95(6)
Cl(2)–Ru–Cl(1)	169.13(2)

Table 3
Selected bond lengths (Å) and angles (°) for blue ccc-isomer (**b**)

Bond lengths	
Ru–N(4)	1.968(3)
Ru–N(1)	2.003(3)
Ru–N(3)	2.018(3)
Ru–N(6)	2.055(3)
Ru–Cl(2)	2.3833(12)
Ru–Cl(1)	2.3997(12)
N(1)–N(2)	1.306(4)
N(4)–N(5)	1.298(4)
Bond angles	
N(4)–Ru–N(1)	102.50(12)
N(4)–Ru–N(3)	98.13(12)
N(1)–Ru–N(3)	77.17(12)
N(4)–Ru–N(6)	76.31(12)
N(1)–Ru–N(6)	176.73(11)
N(3)–Ru–N(6)	99.92(12)
N(4)–Ru–Cl(2)	87.56(9)
N(1)–Ru–Cl(2)	99.54(8)
N(3)–Ru–Cl(2)	173.91(9)
N(6)–Ru–Cl(2)	83.48(8)
N(4)–Ru–Cl(1)	170.99(9)
N(1)–Ru–Cl(1)	86.22(8)
N(3)–Ru–Cl(1)	85.91(9)
N(6)–Ru–Cl(1)	95.11(8)
Cl(2)–Ru–Cl(1)	88.77(4)

N(4), N(6) (rms deviation, 0.06 Å). The Ru atom is shifted by 0.005 Å from the third plane towards Cl(1). The N(1)–Ru–N(6) angle is 176.41(7)° which is distorted from linearity by 3.6°. This deviation is quite similar to that of tcc-Ru(aai)$_2$Cl$_2$ [1] and tcc-Ru(papm)$_2$Cl$_2$ [3] and the reason is undoubtedly from the acute (75.36(8)°) chelate bite angle [1]. The chelate ring, Ru, N(1), N(2), C(7), N(3), is planar (rms deviation, 0.083 Å) and is similar to the other planarity of Ru, N(4), N(5), C(22), N(6) (rms deviation, 0.086 Å) and their interplanar angle is 6.85°. The *trans*-chlorine angle is 169.13(2)° which is essentially equivalent to the reported values [1,3]. The structure of the molecule is shown in Fig. 1 and the geometrical parameters are listed in Tables 2 and 3 for isomers (**a**) and (**b**), respectively.

The Ru–N′[N(azo): N(1) or N(4)] bond length (average, 1.990(2) Å) is shorter than the Ru–N[N(isoquinoline): N(3) or N(6)] [average, 2.102(2) Å] bond distance by 0.112 Å. The shortening may be due to greater π-backbonding, $d(\mathrm{Ru}) \rightarrow \pi^*(\mathrm{azo})$ [1,3]. In this complex, the average N–N distance is 1.294(3) Å which is shorter than some reported values of free azo ligands [28,29] and essentially equivalent to that of tcc-Ru(aai)$_2$Cl$_2$ [1] and tcc-Ru(papm)$_2$Cl$_2$ [3]. The coordination leads to a decrease in the N–N bond order due to both σ-donor and π-acceptor character of the ligand, the later character having a more pronounced effect and possibly being the reason of elongation. The two *cis*-phenyl rings are planar (rms deviations of 0.006 and 0.005 Å) and intersect at an angle of 27.07(11)° to each other. The two *cis*-isoquinolines are planar (rms deviations of 0.0103 and 0.0273 Å) and are almost parallel to each other (dihedral angle, 2.89(14)°). The solvent of dichloromethane is disordered in this green crystal.

3.4. Blue ccc-isomer (*b*)

Similar to the green isomer, the ruthenium ion of the blue crystal is six-coordinated, and the coordination geometry of ruthenium(II) for the blue isomer is also distorted octahedron with Cl(2), N(1), N(3) and N(6) atoms basal (rms deviation of 0.0602 Å), and Cl(1) and N(4) apical (−2.3560(18) and 1.9500(32) Å, respectively, from the equatorial plane). The atomic groups Ru, N(1), N(3), Cl(2) (rms deviation, 0.041 Å) and Ru, N(4), N(6), Cl(1) (rms deviation, 0.022 Å) constitute two almost orthogonal (dihedral angle, 87.87(6)°) planes. The third plane, Ru, Cl(1), Cl(2), N(3), N(4) (rms deviation, 0.093 Å), is less orthogonal (dihedral angles, 84.73(10)° and 83.26(10)°, respectively, with the earlier two planes). The *trans* angles around the ruthenium center in the planes range from 170.99(9)° to 176.73(7)°, indicating distortion from rectilinear geometry. The chelate rings, Ru, N(1), N(2), C(7), N(3) (rms deviation, 0.062 Å) and Ru, N(4), N(5), N(6), C(22) (rms deviation, 0.076 Å), are planar and their dihedral angle is 76.67(10) Å. Their chelate angles are considerably deviated from ideal octahedral geometry. It is interesting that most of the distortions away from octahedral positions arising out of the larger angular distortions are associated with the azo nitrogens rather than the isoquinoline nitrogens, [N(3)–Ru–N(6), 99.92(12)°; N(1)–Ru–N(4), 102.50(12)°]. The *cis*-chloro angle of 88.77(4)° is very nearly the ideal octahedral angle and is comparable to reported values [1,3]. The N–N distances of 1.306(4) and 1.298(4) Å are longer than those in its green counterpart of 1.295(3) and 1.293(3) Å. The Ru–N(azo) distances (1.968(3), 2.003(3) Å) are shorter than those of Ru–N (isoquinoline) (2.018(3), 2.055(3) Å) and this is an indication of an M–L π-interaction that is localized in the M-azo fragment. The two pendant phenyl rings are planar (rms deviations of 0.009 and 0.003 Å) and intersect at an angle of 68.15(14)°. The two *cis*-isoquinolines are planar (rms deviations of 0.009 and 0.020 Å) and intersect at an angle of 68.95(10)°. It is interesting to note that this *ccc*-conformation is quite different from the *tcc* one on the planarity of both *cis*-isoquinolines and *cis*-phenyl rings. The *ccc* configuration has a greater dihedral angle than the tcc scheme for both isoquinolines. The dihedral angles between the chelate ring and the corresponding phenyl ring are 38.15(18)° and 47.31(13)°. The Ru–Cl distance is comparable with the reported values [1,3]. The solvents of water, benzene and ethanol exist in the blue crystal.

Table 4
Some selected bond lengths for related complexes

Compound	Ru–Cl(1)	Ru–Cl(2)	Ru–N_{azo}(1)	Ru–N_{azo}(2)	Ru–N(1)	Ru–N(2)
tcc-Ru(paiq)$_2$Cl$_2$ [a]	2.364(7)	2.384(7)	1.985(2)	1.995(2)	2.101(2)	2.103(2)
ccc-Ru(paiq)$_2$Cl$_2$ [a]	2.383(1)	2.399(1)	1.968(3)	2.003(3)	2.018(3)	2.055(3)
tcc-Ru(aai-Bz)$_2$Cl$_2$ [1]	2.382(2)	2.382(2)	2.016(3)	2.016(3)	2.063(3)	2.063(3)
ctc-Ru(aai-Me)$_2$Cl$_2$ [1]	2.392(2)	2.407(2)	1.991(4)	1.987(4)	2.033(4)	2.043(4)
tcc-Ru(papm)$_2$Cl$_2$ [3]	2.363(1)	2.401(1)	2.000(3)	2.005(3)	2.072(3)	2.093(3)
ccc-Ru(papm)$_2$Cl$_2$ [3]	2.394(1)	2.401(1)	1.971(3)	2.014(3)	2.027(3)	2.047(3)
tcc-Ru(azpy)$_2$Cl$_2$ [22]	2.368(2)	2.3768(1)	1.986(5)	1.988(5)	2.099(5)	2.116(5)
ctc-Ru(azpy)$_2$Cl$_2$ [23]	2.397(1)	2.401(1)	1.977(4)	1.984(4)	2.045(4)	2.051(4)
ccc-Ru(azpy)$_2$Cl$_2$ [23]	2.401(2)	2.410(3)	1.96(1)	1.9589(9)	2.028(9)	2.069(9)

[a] The present work.

There is one hydrogen bond between a water molecule and ethanol. Its bond distance and bond angle of O(1)–H(41)···Ow are 2.823 Å and 128.69°, respectively. The center of the benzene ring is located at an inversion center so that only three atoms of the ring have to be determined. Consequently, the six atoms of the ring are in a plane with rms deviation of 0.0066 Å. The temperature factors of the carbon atoms on the ring are high and reveal that the ring is disordered.

Some related Ru–Cl distances, Ru–N(azo) lengths and other Ru–N distances for several compounds are shown in Table 4. From this table, one can see that the *trans* Cl configuration for one isomer has usually shorter Ru–Cl lengths than that in the correspondent *cis* Cl configuration for the other isomer. This is due to the strong M–L interaction, observed in the isomer where two azo functions have *cis* orientation. One more noticeable clue is that the Ru–N(azo) distances are shorter than the other Ru–N(heterocycle) lengths in the same compound. The reason for the shorter distance is the greater π-back bonding d(Ru)-π*(azo).

4. Supplementary material

Supplementary data are available from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk), on request, quoting the deposition numbers CCDC 191090 (for green **a**) and CCDC 191089 (for blue **b**). Atomic coordinates and isotropic thermal parameters are available from authors upon request.

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