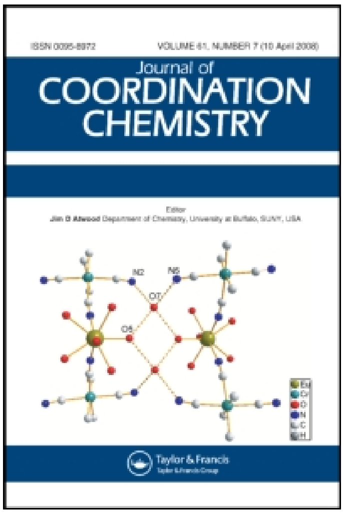

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The synthesis and structural analysis of <i>cis</i>-β-{(1,6-di(2'-pyridyl)(2,5-dibenzyl-2,5-diazahexane O(1,2-diazahexane))(1,2-benzoquinone diimine))ruthenium(II)} and related complexes

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The synthesis and structural analysis of *cis*-*β*-{(1,6-di(2′-pyridyl)(2,5-dibenzyl-2,5-diazahexane O(1,2-diazahexane))(1,2-benzoquinone diimine))ruthenium(II)} and related complexes

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Several isomers are possible when N_4-tetradentate ligands coordinate to form metal complexes. Here we report the synthesis and structural analysis of *cis*-*β*-{[1,6-di(2′-pyridyl)(2,5-dibenzyl-2,5-diazahexane)(1,2-benzoquinone diimine)]ruthenium(II)} formed exclusively from the *β*-precusor, *β*-{[1,6-di(2′-pyridyl)(2,5-dibenzyl-2,5-diazahexane) (dimethylsulfoxide)chloride] ruthenium(II)} hexaflourophosphate. Ruthenium(II) complexes synthesised from 1,6-di (2′-pyridyl)-2,5-dibenzyl-2,5-diazahexane, produce only two isomers which can be separated by recrystallisation into *α*- and *β*-[Ru(picenbz$_2$)(dmso)Cl]PF$_6$ (where picenbz$_2$ is 1,6-di(2′-pyridyl)-2,5-dibenzyl-2,5-diazahexane). The distinctively different proton NMR spectra of the isomers are an especially convenient feature with which to assess separation. Isomeric structure of the precursor, *α* or *β*, is conserved upon coordination of a bidentate ligand, such as benzene-1,2-diamine, 4,5-dimethyl-benzene-1,2-diamine, naphthalene-2,3-diamine, 2,2′-bipyridine, 1,10-phenanthroline or dipyrido[3,2-d:2′3′-*f*]quinoxaline, to produce complexes of the type *α*- or *β*-[Ru(picenbz$_2$)(bidentate)](PF$_6$)$_2$. The synthesis, separation and characterisation of the *α*- and *β*-precursors and the *α*- and *β*-[Ru(picenbz$_2$)(bidentate)](PF$_6$)$_2$ complexes are reported. Moreover, the crystal structures have been determined for *β*-[Ru(picenbz$_2$)(dmso)Cl]PF$_6$.0.5H$_2$O ($C_{30}H_{37}N_4O_{1.5}F_6PSClRu$); it is triclinic, space group $P\bar{1}$, $a = 9.987$, $b = 12.883$, $c = 14.287$ Å, $\alpha = 72.11$, $\beta = 78.65$, $\gamma = 88.39°$ and $Z = 2$ and *β*-[Ru(picenbz$_2$)(bqdi)](PF$_6$)$_2$, ($C_{34}H_{38}N_6F_{12}P_2Ru$) which is triclinic, space group $P\bar{1}$, with $a = 10.129$, $b = 10.338$, $c = 19.587$ Å, $\alpha = 104.42$, $\beta = 93.36$, $\gamma = 92.00°$ and $Z = 2$. The structures were determined at room temperature and refined by least-squares methods to $R = 0.044$ for 5109 and $R = 0.075$ for 3057 non-zero diffractometer data, respectively, for the dmso and bqdi species above.

Keywords: Ruthenium complexes; Stereospecific synthesis; N_4-tetradentate; 1,6-Di(2′-pyridyl)-2,5-dibenzyl-2,5-diazahexane; 1,2-Benzoquinone diamine; X-ray structure

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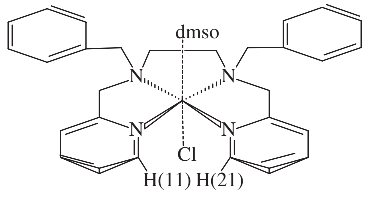
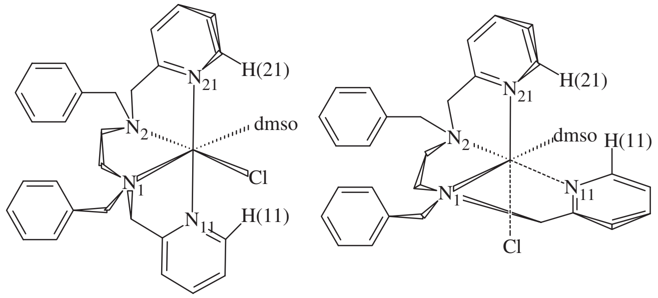
1. Introduction

There are many examples of molecular recognition in the fields of chemistry and biology based on non-covalent intermolecular bonding and shape complementarity, where selection of one molecule over another is afforded through thermodynamically preferred interactions. If the energetic preference for one of these molecules is sufficiently large, then the process is specific and the ensuing recognition unambiguous. An excellent example is the pivotal role played by DNA in orchestrating transcription and replication processes through its various molecular recognition functions. The field of coordination chemistry provides ready application to this highly active and rapidly expanding area of scientific research [1]. As a consequence, chiral metal complexes of the type $[M(pp)_3]^{n+}$ [2, 3], $[M(pp)_2(pp')]^{n+}$ [4–6] and $[M(tetradentate)(pp')]^{n+}$ [pp = bidentate polypyridyl ligands, such as 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) while pp′ = dipyrido[3,2-a:2′3′-c]phenazine (dppz), 9,10-phenanthrolinequinonediimine (phi), dipyrido[3,2-d:2′3′-f]quinoxaline (dpq)], have found uses as metalloprobes for DNA [6–8].

In particular, complexes derived from tetradentates such as 1,6-di(2′-pyridyl)-2,5-diazahexane (picen) have a number of potential advantages for discriminatory purposes. These derive from the increased isomeric range afforded by stereoisomeric products accessible when a linear N_4-tetradentate binds to an octahedral metal ion. These are the *trans* (planar), the dissymmetric (C_2) α- and the asymmetric (C_1) β-forms (figure 1) [9]. Moreover, if the remaining two coordination sites of the metal ion in



trans



α β2

Figure 1. The *trans* (planar), the dissymmetric (C_2) *cis*-α and the asymmetric (C_1) *cis*-β_1 isomer forms of $[Ru(picenbz_2)(dmso)Cl]^+$ (**5**, **6**); the β-isomers are differentiated with respect to the coordination positions of the dmso and chloride ligands. The β_1 isomer has the Cl *trans* to N(1) whereas for β_2 the Cl is *trans* to N(21).

β complexes are occupied by two different monodentate ligands, or by an unsymmetrical bidentate ligand, then those sites are diastereotopic and it becomes necessary to distinguish further between the possible β_1 or β_2 forms [9, 10].

Intramolecular parameters, which determine the choice between these geometries have been intensively studied [11, 12]. The synthesis of the archetypical tetradentate ligand picen was first described by Goodwin and Lions [13] following a reduction of the Schiff-base diimine derived from 1,2-diaminoethane and pyridine-2-carboxaldehyde. Modified forms of this general method have been utilised successfully with a number of diamines to produce a broad set of homologues [8]. The stereochemistries adopted by these tetradentate ligands upon coordination are due in part to torsional strain and steric constraints [9], but kinetic effects are sometimes manifested. The existence of an important unfavourable intermolecular steric interaction between the α-protons of the terminal groups (H(11) and H(21)) in the *trans* complex, defined as a B-strain [12] was identified as a reason for the dominant presence of *cis* geometries and observed with these ligands on octahedral metal complexes. These same protons remain significant when considering likely interligand and intermolecular steric interactions which could influence molecular recognition functions.

Stereoselective coordination behaviour can be enhanced by further substitution at the inner secondary nitrogen atoms of these tetradentate ligands, which is a prime stereochemical determinant [14]. Cobalt(III) complexes of *N*,*N*′-dimethyl-substituted isomers of 1,4,7,10-tetraazadecane (trien) and *N*,*N*′-dimethyl-*N*,*N*′-*bis*(2-picolyl)-1*R**,2*R**-diaminocyclohexane (picchxnMe$_2$) have been shown to adopt a largely α-configuration [14, 15]. The Δ-α-stereochemistry which *R**,*R**-picchxnMe$_2$ enforces, stereospecifically at Co(III) has been established by spectroscopic techniques and confirmed by single-crystal X-ray studies of several of its ternary α-aminoacidate complexes [8]. This degree of stereochemical control, however, has not been demonstrated with ruthenium. The picen precursor species, *cis*-[Ru(picen)(dmso)Cl]$^+$, is readily obtained through a general method under mild conditions using *cis*-[Ru(dmso)$_4$(Cl)$_2$] [16] as a starting material. The two monodentate ligands in these cations may then be replaced by a bidentate ligand usually with retention of stereochemistry, due to the kinetic inertness of Ru(II), but are obtained as mixtures of α- and β-forms, which require separation [8, 16]. Limited control over coordination geometry with Ru(II) complexes has impeded the development of tetradentate metal complexes for use as structural probes for DNA.

With respect to the *N*,*N*′-dibenzyl-substituted tetradentate 1,6-di(2′-pyridyl)-2,5-dibenzyl-2,5-dibenzyl,2,5-diazahexane (picenbz$_2$, **3**); a detailed investigation is described here exploring the possible synthetic utility of *N*,*N*′-benzylation on the stereoisomeric ratio. While it is expected that *cis*-[Ru(dmso)$_4$(Cl)$_2$] [16] and picenbz$_2$ will react under mild reaction conditions to produce α- and β-[Ru(picenbz$_2$)(dmso)Cl]$^+$ this has not been previously explored. A method for the isolation of the different stereoisomeric products (α, β_1 or β_2) of the precursor, [Ru(picenbz$_2$)(dmso)Cl]$^+$ was investigated. Further, the metal complexes produced after coordination to α- or β-[Ru(picenbz$_2$)(dmso)Cl]$^+$ by a bidentate ligand such as benzene-1,2-diamine (opda), 4,5-dimethyl-benzene-1,2-diamine (opdaMe$_2$), naphthalene-2,3-diamine (2,3-dnap), 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) or dpq [6] were examined with respect to retention of stereochemistry.

2. Experimental

2.1. *Materials*

A.R. grade reagents, metal salts and solvents were used for synthetic work as supplied. The reagents pyridine-2-carboxaldehyde, chloromethylbenzene, 2,3-dnap, benzene-1,2-diamine (opda), opdaMe$_2$, ethane-1,2-diamine (en), phen were obtained from Aldrich Chemical Company, Inc. Both pyridine-2-carboxaldehyde and en were freshly distilled prior to use. 1,10-Phenanthroline-5,6-dione (phendo) was synthesised by the method of Yamada [17].

2.2. *Synthesis*

2.2.1. Dipyrido[3,2-d:2′3′-f]quinoxaline • 2.5H$_2$O (dpq 1). A mixture of phendo [17] (0.41 g, 1.9 mmol) and en (0.74 g, 4.1 mmol) in ethanol (120 cm^3) was refluxed for 1 h, and the resulting orange solution concentrated at 50°C under reduced pressure. The residue was dissolved in propan-2-ol (100 cm^3) and the volume reduced again to 10 cm^3. This process was repeated until a cream solid formed. This was filtered off, washed with water (3 × 25 cm^3) and recrystallised from methanol to give cream colored needles. Yield: 0.41 g (92%). ^{1}H NMR (d$_6$ DMSO/TMS) δ 9.44 (H4, 2H, dd, $J = 8.2$, 1.8 Hz), 9.21, (H2, 2H, dd, $J = 4.3$, 1.8 Hz), 9.12 (H7, 2H, s), 7.92 (H3, 2H, dd, $J = 4.4$, 8.2 Hz). ^{13}C NMR (d$_6$ DMSO/TMS) δ 151.8 (C2), 146.6 (C6), 145.2 (C7), C1, 139.3 (C1), 132.4 (C4), 125.4 (C5), 124.1 (C3). Anal. Calcd for $C_{14}H_{13}N_4O_{2.5}$: C, 56.9; H, 5.1. Found: C, 56.8; H, 4.2%. M.p.: 331°C (uncorr).

2.2.2. 1,6-di(2′-pyridyl)-2,5-diazahexane (picen 2). The N$_4$-tetradentate ligand was prepared by a method similar to that reported by Goodwin and Lions [13]. A mixture of en (1.20 g, 20 mmol) and pyridine-2-carboxaldehyde (4.29 g, 40 mmol) in benzene (150 cm^3) was stirred for 15 min. This solution immediately became turbid due to the release of water on formation of the Schiff base. The azeotrope (benzene/water) was removed at 50°C under reduced pressure and the resulting oil was dissolved in absolute ethanol (150 cm^3). Palladium on charcoal catalyst (10% on charcoal; 0.5 g) was added and the mixture was then hydrogenated under a pressure of 3 atm. The reaction solution was filtered through a small celite pad under suction and subsequent solvent removal at 50°C under reduced pressure produced a yellow oil. Yield: 6.5 g (82%). ^{1}H NMR (d$_6$ DMSO/TMS) δ 8.82 (H(21), 2H, d, $J = 6.5$ Hz), 8.52 (H(23), 2H, t, $J = 7.5$, 7.5, 1.7 Hz), 8.12 (H(24), 2H, d, $J = 7.8$ Hz), 8.02 (H(22), 2H, t, $J = 6.9$, 6.9, 1.2 Hz), 4.66 (H(26ab), 4H, s), 3.61 (H(2ab), 4H, s). NMR was used to authenticate this compound [6].

2.2.3. 1,6-di(2′-pyridyl)-2,5-dibenzyl-2,5-diazahexane (picenbz$_2$ 3). Substitution at the nitrogen atoms of the secondary amines by benzyl groups was accomplished by adaptation of the method of Balakrishnan *et al.* [18]. A solution of chloromethylbenzene (8.9 g, 70 mmol) in dichloromethane (25 cm^3) was added slowly to a stirred solution of **2** (6.46 g, 17 mmol) in dichloromethane (25 cm^3) then 0.3 M sodium hydroxide (100 cm^3) was added. The mixture was flushed with N$_{2(g)}$, sealed securely and stirred.

Table 1. Summary of synthetic results.

No.	Complex	Molecular formula	Yld (%)	Calculated (%) C	Calculated (%) H	Calculated (%) N	Found (%) C	Found (%) H	Found (%) N
3	Picenbz$_2$	$C_{28}H_{30}N_4$	91	79.6	7.2	13.3	79.7	7.2	13.2
4	α-[Co(picenbz$_2$)Cl$_2$]	$C_{28}H_{30}N_4F_6PCl_2Co$	74	48.1	4.6	8.0	48.2	4.4	8.0
5	α,β-[Ru(picenbz$_2$)(dmso)Cl]PF$_6\cdot$2H$_2$O	$C_{30}H_{40}N_4F_6PClSO_3Ru$	91	44.0	4.9	6.9	43.9	4.7	6.8
6									
7	α-[Ru(picenbz$_2$)(dpq)](PF$_6$)$_2\cdot$4H$_2$O	$C_{42}H_{46}N_8O_4P_2F_{12}Ru$	84	45.1	4.1	10.0	45.1	3.7	9.7
8	β-[Ru(picenbz$_2$)(bqdi)](PF$_6$)$_2$	$C_{34}H_{38}N_6F_{12}P_2Ru$	95	44.3	4.2	9.1	44.8	4.1	9.6
9	β-[Ru(picenbz$_2$)(bqdiMe2)](PF$_6$)$_2$	$C_{36}H_{40}N_6F_{12}P_2Ru$	95	45.6	4.2	8.9	46.9	4.4	8.7
10	β-[Ru(picenbz$_2$)(2,3-dnap)](PF$_6$)$_2\cdot$2H$_2$O	$C_{38}H_{44}N_6O_2F_{12}P_2Ru$	63	45.3	4.4	8.3	45.3	4.3	8.1
11	β-[Ru(picenbz$_2$)(phen)](PF$_6$)$_2\cdot$5H$_2$O	$C_{40}H_{48}N_6O_5F_{12}P_2Ru$	71	44.3	4.5	7.8	44.4	3.9	7.4

After 24 h the dichloromethane layer was removed and stored and the remaining aqueous reaction mixture was extracted further with dichloromethane (2 × 25 cm^3). These extracts and the original dichloromethane layer were combined, washed with water (25 cm^3), and extracted with 1 M hydrochloric acid (3 × 50 cm^3). The combined acid extracts were washed with dichloromethane (50 cm^3) to remove any unreacted benzyl chloride, the pH was adjusted to 10 and again the mixture was extracted with dichloromethane (3 × 50 cm^3). These final dichloromethane extracts were dried over anhydrous sodium sulphate, treated with activated charcoal, filtered and evaporated to dryness to yield a pale yellow solid. The yield and microanalysis are given in table 1. ^{1}H NMR data are given in table 2.

2.2.4. α-[Co(picenbz$_2$)Cl$_2$]PF$_6$ (4). Compound **3** (0.22 g, 0.52 mmol) was dissolved in ethanol (25 cm^3), and to this was added, dropwise, a solution of cobalt chloride hexahydrate (0.12 g, 0.48 mmol) in ethanol (25 cm^3). Hydrochloric acid (1 cm^3) and 30% hydrogen peroxide (2 cm^3) were added and the mixture stirred for 1 h. The mixture was reduced in volume and a saturated solution of potassium hexafluorophosphate (2 cm^3) was added. The green solid, α-[Co(picenbz$_2$)Cl$_2$]PF$_6$, which immediately formed, was filtered off, washed with water (2 cm^3), then diethyl ether (2 cm^3) and dried under suction. Yield and microanalysis are given in table 1. ^{1}H NMR data are given in table 2.

2.2.5. α- and β$_1$-[(Ru(picenbz$_2$)(dmso)Cl]PF$_6$ · 2H$_2$O (5 and 6). A solution of *cis*-[Ru(dmso)$_4$]Cl$_2$ [19] (1.36 g, 2.8 mmol) dissolved in a small amount of water (5 cm^3) and ethanol (30 cm^3) was added dropwise to a warm, stirred solution of **3** (0.68 g, 1.6 mmol) in ethanol (50 cm^3). The khaki-green mixture was refluxed on a water bath for 2 h, filtered and a saturated solution of potassium hexafluorophosphate (1 cm^3) added, producing an immediate precipitate. The pale green product was collected by filtration, washed with water (2 × 5 cm^3), then diethyl ether (2 × 5 cm^3) and air-dried. The product was recrystallised from an acetone (15 cm^3)/methanol (15 cm^3)/water (5 cm^3) mix. Three crops of crystal were collected, each differing in its isomeric mix and appearance. Crop 1: (yellow-green) yield: 0.46 g (β); crop 2: (dark khaki-green) yield: 0.17 g (α);

Table 2. Chemical shifts[a] (δ), multiplicities, integration and coupling constants (Hz) for picenbz$_2$, α-[Co(picenbz$_2$)Cl$_2$], α-[Ru(picenbz$_2$)(dmso)(Cl)]$^+$ and α-[Ru(picenbz$_2$)(dpq)]$^{2+}$ in dmso-d_6.

Proton	Picenbz$_2$ (**3**)	α-[Co(picenbz$_2$)Cl$_2$]$^+$ (4)	α-[Ru(picenbz$_2$)(dmso)Cl]$^+$ (**5**)	α-[Ru(picenbz$_2$)(dpq)]$^{2+}$ (**7**)
CH$_3$ dmso			2.50, s, 6H	
CH$_3$ dmso				
H(1ab)/H(2ab)	3.46, s, 4H	3.20, m, 4H		
H(1a)			2.59, m, 1H	
H(1b)			2.74, m, 1H	
H(2a)			2.93, m, 1H	2.78, d, 2H, 10.5 Hz
H(2b)			2.59, m, 1H	2.75, d, 2H, 10.5 Hz
H(16a)			5.18, d, 1H, 14.8 Hz	
H(16b)			3.82, d, 1H, 14.8 Hz	
H(26a)		5.28, d, 2H, 15.7 Hz (exo)	3.78, d, 1H, 15.5 Hz	5.43, d, 2H, 16.8 Hz
H(26b)	3.69, s, 2H	3.60, d, 2H, 15.7 Hz (endo)	4.64, d, 1H, 15.5 Hz	4.03, d, 2H, 16.8 Hz
H(110a)			3.53, d, 1H, 13.6 Hz	
H(110b)			3.32, d, 1H, 13.6 Hz	
H(220a)		4.57, d, 2H, 13.3 Hz (exo)	4.76, d, 1H, 13.5 Hz	4.89, d, 2H, 14.0 Hz
H(220b)	3.55, s, 2H	3.66, d, 2H, 13.3 Hz (endo)	4.52, d, 1H, 13.5 Hz	3.81, d, 2H, 14.0 Hz
H(114)/H(224)			7.32, m, 2H	
ArH	7.31–7.11, m, 10H	7.50, m, 10H	7.42, m, 8H	7.55, m, 10H
H(11)			9.23, t, 1H, 6.6, 6.7, 1.3 Hz	
H(12)			7.59, t, 1H, 6.7, 6.7, 1.3 Hz	
H(13)			9.03, t, 1H, 7.7, 7.7, 1.4 Hz	
H(14)			7.71, d, 1H, 7.7 Hz	
H(21)	8.41, d, 2H, 5.8 Hz	9.68, d, 2H, 6.0 Hz	9.23, t, 1H, 6.6, 6.7, 1.3 Hz	7.81, d, 2H, 5.1 Hz
H(22)	7.31–7.11, m, 2H	7.80, m, 2H	7.59, t, 1H, 6.7, 6.7, 1.3 Hz	7.06, t, 2H, 7.2, 7.2, 1.7 Hz
H(23)	7.64, t, 2H, 8.2, 8.2, 1.8 Hz	8.24, t, 2H, 7.7, 7.6, 1.2 Hz	7.93, t, 1H 7.7, 7.7, 1.4 Hz	7.77–7.67, m, 2H
H(24)	7.40, t, 2H, 7.8, 7.4 Hz	7.80, m, 2H	7.76, d, 1H, 7.7 Hz	7.77–7.67, m, 2H
Diimine H(32)				10.06, d, 2H, 5.4 Hz
Diimine H(33)				8.37, dd, 2H, 8.1, 5.4 Hz
Diimine H(34)				9.60, d, 2H, 7.5 Hz
Diimine H(37)				9.34, s, 2H

[a] Chemical shifts in ppm (±0.01); [b] relative to TMS as an internal standard and coupling constants in Hz (±0.1); s: singlet d: doublet; dd: doublet of doublets; m: multiplet.

crop 3: (green) yield: 0.52 g (75% α, 25% β). Yield and microanalysis are given in table 1. ^{1}H NMR data are given in tables 2 and 3.

2.2.6. α-[(Ru(picenbz$_2$)(dpq)](PF$_6$)$_2\cdot$4H$_2$O (7). A solution of α-[(Ru(picenbz$_2$)(dmso)Cl]PF$_6\cdot$2H$_2$O (0.12 g, 0.15 mmol) in methanol (30 cm^3) was added to a stirred solution of dpq (**1**) (0.07 g, 0.30 mmol) in methanol (30 cm^3). This solution was gently refluxed on a steam bath for 2 h, filtered and a saturated solution of potassium hexafluorophosphate (1 cm^3) was added. The resulting product was collected by filtration and washed with cold water (2 × 5 cm^3), diethyl ether (2 × 5 cm^3), dried under suction and recrystallised from 50/50 (v/v) methanol/water. Yield and microanalysis are given in table 1. ^{1}H NMR data are given in table 2. Numbering conventions are illustrated in figure 2.

2.2.7. β-[(Ru(picenbz$_2$)(bidentate)](PF$_6$)$_2$ (8–11). A solution of β-[(Ru(picenbz$_2$)(dmso)Cl]PF$_6$ (0.15 mmol) in either methanol or ethanol (30 cm^3) was added to a stirred solution of the chosen bidentate ligand (opda, opdaMe$_2$, 2,3-dnap or phen) (0.30 mmol) in the same solvent (30 cm^3). This mixture was refluxed gently on a steam bath for 2 h until the colour changed from yellow to deep orange then a saturated solution of potassium hexafluorophosphate (1 cm^3) was added. The resulting products were collected by filtration and washed with cold water (2 × 5 cm^3), diethyl ether (2 × 5 cm^3), dried under suction and recrystallised from a 50/50 (v/v) methanol/water. Yields and microanalysis are given in table 1. ^{1}H NMR data are given in table 3.

2.3. *X-ray crystallography*

2.3.1. β_1-[(Ru(picenbz$_2$)(dmso)Cl]PF$_6\cdot$0.5H$_2$O (6). β_1-[(Ru(picenbz$_2$)(dmso)Cl]PF$_6\cdot$0.5H$_2$O (C$_{30}$H$_{36}$N$_4$O$_{1.5}$F$_6$PSClRu) is triclinic, space group $P\bar{1}$ where $M = 791.18$, $a = 9.987(4)$ $b = 12.883(7)$, $c = 14.287(7)$ Å, $\alpha = 72.11(4)$, $\beta = 78.65(3)$, $\gamma = 88.39(4)°$, $U = 1714(1)$ Å^3, $T = 20°$C, $Z = 2$ and $D_c = 1.533$ g cm^{-3}.

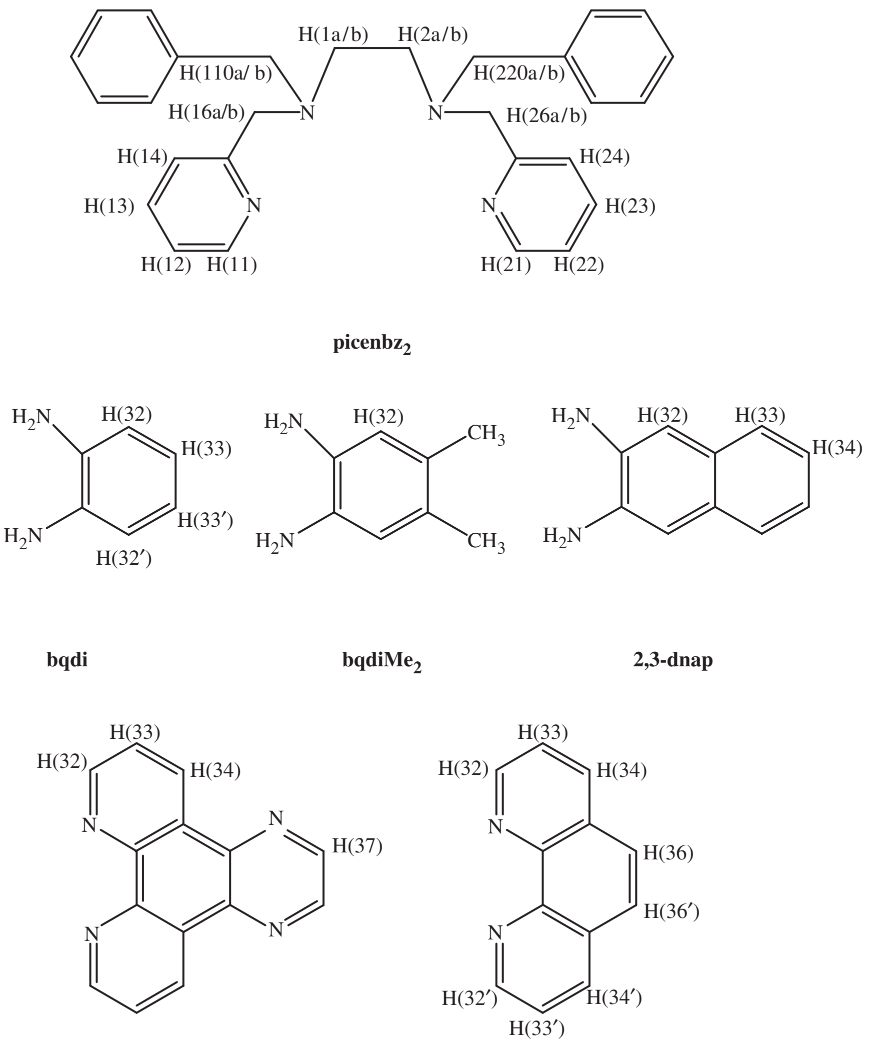
Pale yellow-green prismatic crystals were grown by slow evaporation from a concentrated 3 : 3 : 1 (v/v) methanol/acetone/water solution. A well-formed pinacoidal prism with dimensions 0.22 × 0.40 × 0.22 mm^3 and readily indexable faces was used for the data collection, with the preliminary unit cell parameters and space group being determined from single-crystal precession photographs using Mo-Kα radiation. Accurate cell parameters were obtained from a least-squares fit to the diffractometer data. Intensities were collected on a Siemens Nicolet R3m diffractometer in the range $8° < 2\theta < 50°$ using Mo-Kα radiation. Some 5990 independent reflections were obtained at 293 K and of these 5083 had $I > 2\sigma(I)$, and were subsequently used for the structure determination. The intensity data were corrected for absorption using the Gaussian face-indexed procedure via the program XPREP [20].

The structure was solved by Patterson and difference Fourier techniques using SHELXS-86 [21] and SHELXL-97 [22] and refined by full-matrix least-squares using neutral atom scattering factors. Successive difference Fourier maps, phased by an increasing number of atoms, revealed the positions of all non-hydrogen atoms in the complex cation and the PF$_6^-$ anion, and also the presence of two water molecule oxygen

Table 3. Chemical shifts[a] (δ), multiplicities, integration and coupling constants (Hz) for β-[Ru(picenbz$_2$)(X)(Y)]$^{n+}$ in dmso-d$_6$.

Proton	β-[Ru(picenbz$_2$)(dmso)(Cl)]$^+$ (**6**)	β-[Ru(picenbz$_2$)(bqdi)]$^{2+}$ (**8**)	β-[Ru(picenbz$_2$)(bqdiMe$_2$)]$^{2+}$ (**9**)	β-[Ru(picenbz$_2$)(2,3-dnap)]$^{2+}$ (**10**)	β-[Ru(picenbz$_2$)(phen)]$^{2+}$ (**11**)
CH_3 dmso	2.92, s, 3H				
CH_3 dmso	3.55, s, 3H				
CH_3			2.17, s, 3H		
CH_3			2.25, s, 3H		
H(1a)	4.26, obscured	4.45, dd, 1H, 13.3, 13.3, 5.0 Hz	4.41, t, 1H, 12.6, 12.4, 2.8 Hz	4.38, t, 1H, 12.6, 12.4, 2.8 Hz	4.77, t, 1H, 12.6, 12.4, 2.8 Hz
H(1b)	2.93, m, 1H	3.03 dd, 1H, 13.5, 4.2, 5.0 Hz	3.22, dd, 1H, 11.1, 5.1 Hz	3.06, dd, 1H, 12.3, 6.1 Hz	3.59, d, 1H, 12.6, 4.9, 5.9 Hz
H(2a)	3.04, m 1 H	3.25, dd, 1H, 13.3, 4.2, 5.0 Hz	3.02, dd, 1H, 11.1, 5.1 Hz	3.06, dd, 1H, 12.3, 6.1 Hz	3.33, d, 1H, 12.6, 4.9, 5.9 Hz
H(2b	2.25, m, 1H	2.42, t, 1H, 13.3, 13.3, 5.0 Hz		2.22, t, 1H, 12.6, 12.4, 2.8 Hz	2.39, t, 1H, 12.6, 12.4, 2.8 Hz
H(16a)	5.01, d, 1H, 16.8 Hz	4.64, d, 1H, 16.8 Hz	3.64, d, 1H, 16.1 Hz	5.07, d, 1H, 15.9 Hz	4.60, d, 1H, 17.3 Hz
H(16b)	3.79, d, 1H, 16.8 Hz	4.09, d, 1H, 16.8 Hz	4.06, d, 1H, 16.1 Hz	3.94, d, 1H, 15.9 Hz	4.24, d, 1H, 17.3 Hz
H(26a)	4.85, d, 1H, 14.7 Hz	4.64, d, 1H, 16.6 Hz	4.59, d, 1H, 17.0 Hz	4.32, d, 1H, 17.3 Hz	4.78, d, 1H, 16.7 Hz
H(26b)	3.45, d, 1H, 14.7 Hz	3.67, d, 1H, 16.6 Hz	4.57, d, 1H, 17.0 Hz	3.39, d, 1H, 17.3 Hz	4.01, d, 1H, 16.7 Hz
H(110b)	3.57, d, 1H, 16.2 Hz	2.19, d, 1H, 14.1 Hz		3.64, d, 1H, 13.0 Hz	4.52, d, 1H, 12.5, 1.8 Hz
H(110a)	4.26, d, 1H, 16.2 Hz	3.45, d, 1H, 14.1 Hz	3.53, d, 1H, 13.0 Hz	4.52, d, 1H, 13.0 Hz	5.55, d, 1H, 12.5, 1.8 Hz
H(220b)	4.52, d, 1H, 13.8 Hz	4.49, d, 1H, 13.8 Hz	4.41, d, 1H, 14.1 Hz	3.68, d, 1H, 14.2 Hz	2.95, d, 1H, 13.3 Hz
H(220a)	4.94, d, 1H, 13.8 Hz	5.80, d, 1H, 13.8 Hz	5.65, d, 1H, 14.1 Hz	4.58, d, 1H, 14.2 Hz	3.72, d, 1H, 13.3 Hz
H(114)/H(224)	7.26 m, 2H	7.10, m, 2H			
ArH	7.46–7.65, m, 8H	7.35–7.52, m, 10H	7.40–7.46, m, 10H	7.40–7.6, m, 10H	7.32–7.48, m, 8H
H(11)	8.59, d, 1H, 5.4 Hz	6.44, d, 1H, 5.5 Hz	6.53, d, 1H, 4.8 Hz	7.67, d, 1H, 5.6 Hz	6.72, d, 1H, 5.5 Hz
H(12)	7.52, m, 1H	7.35–7.52, m, 1H	7.56, m, 2H	7.95, t, 1H, 7.7, 7.7, 1.3 Hz	7.04, t, 1H, 6.2, 6.2, 1.7 Hz
H(13)	8.06, t, 1H, 7.8, 7.8, 1.3 Hz	7.59, m, 1H	8.04, t, 2H, 7.6, 7.7.1.7 Hz	7.75, t, 1H, 8.0, 7.6.1.4 Hz	8.09, t, 1H, 8.0, 8.0, 1.1 Hz
H(14)	7.82, d, 1H, 8.1 Hz	7.59, m, 1H	7.74, d, 1H, 8.2 Hz	7.31, d, 1H, 7.5 Hz	7.78, d, 1H, 8.0 Hz
H(21)	7.26, m, 1H	7.96, d, 1H, 5.5 Hz		8.02, d, 1H, 5.8 Hz	7.54–7.60, m, 2H
H(22)	7.77 obscured	8.07, dd, 1H, 7.8, 7.8 Hz	7.56, m, 2H	7.95, t, 1H, 7.7, 7.7, 1.3 Hz	7.90, t, 1H, 6.2, 6.2, 1.7 Hz
H(23)	7.87, t, 1H, 7.8, 7.8, 1.3 Hz	8.07, dd, 1H, 7.8, 7.8 Hz	8.04, t, 2H, 7.6, 7.7.1.7 Hz	7.75, t, 1H, 8.0, 7.6.1.4 Hz	8.09, t, 1H, 7.9, 7.9, 1.2 Hz
H(24)	7.74, d, 5.4 Hz	7.77, d, 1H, 7.6 Hz	7.93, d, 1H, 8.2 Hz	7.78, d, 1H, 7.5 Hz	7.84, d, 1H, 8.0 Hz
NH (31)/(32)		13.9/12.7, s, 2H	13.4/11.7, s, 1H	8.07–8.07, s, 1H	
Diimine H(32)				7.40–7.6, m, 1H	7.54–7.60, m, 1H
Diimine H(32')					9.85, d, 1H, 4.3 Hz
Diimine H(33)		7.35, m, 1H	7.40–7.46, m, 1H	7.40–7.6, m, 1H	7.87, dd, 2H, 7.9, 8.1 Hz
Diimine H(34)		7.26–7.64, m, 1H		7.40–7.6, m, 1H	8.75, d, 1H, 8.0 Hz
Diimine H(34')					8.83, d, 1H, 8.0 Hz
Diimine H(35)		7.26–7.64, m, 1H		7.40–7.6, m, 1H	
Diimine H(35')				7.40–7.6, m, 1H	
Diimine H(36)		7.35, m, 1H	7.40–7.46, m, 1H	7.40–7.6, m, 1H	8.42, s, 2H

[a] Chemical shifts in ppm (±0.01); [b] relative to TMS as an internal standard and coupling constants in Hz (±0.1); s: singlet d: doublet; dd: doublet of doublets; m: multiple.



picenbz$_2$

bqdi **bqdiMe$_2$** **2,3-dnap**

dpq **phen**

Figure 2. Proton numbering convention for picenbz$_2$ and the bidentate ligands; bqdi, bqdiMe$_2$, 2,3-dnap, dpq and phen, referred to in tables 2 and 3.

atoms in fractionally occupied lattice sites. Anisotropic refinement of this structure proceeded smoothly and all hydrogen atoms in the cation were then positioned using the appropriate geometry and relevant C–H and N–H bond lengths; the accuracy of these positions was confirmed by a subsequent difference synthesis. However, the hydrogen atoms associated with the two water molecules in the partially occupied sites could not be located. Refinement was continued with hydrogen atoms riding on the atoms to which they were bonded, with fixed isotropic thermal parameters, and with anisotropic temperature factors for all other atoms. Refinement was terminated when the minimisation factor changed by $<0.1\%$ and a final difference map showed no significant residual electron density. The final value for R, based on 5083 reflections, was 0.0443 and for $R_{\mathrm{w}}^2 = \{[\sum w(F_{\mathrm{o}}^2 - F_{\mathrm{c}}^2)^2 / \sum w(F_{\mathrm{o}}^2)^2]^{1/2}\}$ was 0.1183. Lists of crystal structure data, atomic coordinates, bond lengths and angles and anisotropic displacement parameters are presented in tables S1 to S6 in the Supplementary Material.

2.3.2. β-[(Ru(picenbz$_2$)(bqdi)](PF$_6$)$_2$ (8). β-[(Ru(picenbz$_2$)(bqdi)](PF$_6$)$_2$ ($C_{34}H_{38}N_6F_{12}P_2Ru$) is triclinic, space group $P\bar{1}$, $a = 10.129(3)$, $b = 10.338(2)$, $c = 19.587(4)$ Å, $\alpha = 104.42(2)$, $\beta = 93.36(2)$, $\gamma = 92.00(2)°$, $U = 1980.4(1)$ Å^3, $T = 25°$C, $Z = 2$, $D_{\mathrm{c}} = 1.545\ \mathrm{g\,cm^{-3}}$, μ(Mo-Kα) $= 5.66\ \mathrm{cm^{-1}}$.

Deep orange trapezoidal needles were grown by slow evaporation of a concentrated 1 : 1 (v/v) methanol/water solution in the dark. A crystal of dimensions $0.22 \times 0.40 \times 0.22\ \mathrm{mm}^3$ was used for the data collection, with the preliminary unit cell parameters and space group being determined from single-crystal precession photographs using Mo-Kα radiation. Accurate cell parameters were obtained from a least-squares fit to the diffractometer data. Intensities were collected on a Nicolet XRD-P3 four-circle diffractometer in the range $4° < 2\theta < 45°$ using Mo-Kα radiation. Some 4996 independent reflections were obtained, of which 3057 had $I > 3\sigma(I)$, and these were used for the structure determination.

The structure was solved by the heavy atom method and refined by Fourier and least-squares techniques. Neutral atom scattering factors were taken from standard sources [23, 24]. Hydrogen atoms were included with $B = 5.00$ Å^2 in positions calculated assuming C–H and N–H distances to be 1.0 Å and with the appropriate geometry of the atom to which each was attached. These positions were optimised during later least-squares refinement, but were not included as variables in the refinement. Successive Fourier maps, phased by an increasing number of atoms, revealed the complete structure of the cation and the position of the P atoms. It was evident from these maps, however, that both PF_6^- groups were subjected to disorder. For alternative sites, estimates of occupancies were derived from difference maps assuming individual occupancy to be directly proportional to peak height. The total occupancies for the fluorine atoms were stoichiometrically correct for each PF_6^- group.

Block-matrix least-squares refinement was undertaken using anisotropic temperature factors for all non-hydrogen atoms of the cations and the two P atoms. In view of the disorder associated with the anions, only isotropic temperature factors (with fixed occupancies) were used for the fluorine atoms. The refinement converged smoothly, and the resulting uniform set of fluorine atom temperature factors, in combination with stoichiometrically consistent overall site occupancy for the atoms, was seen as strong support for the proposed disordered nature of the anions.

The refinement was terminated when the change in the minimisation function was <1%, at which stage only the atom F(1i) showed positional oscillation and the maximum shift in the parameters for the other atoms was $<0.1\sigma$. A final difference map showed no unusual features, with a maximum positive electron density of $|1.0|$ eÅ^{-3}. The final value for R, based on 3057 reflections, was 0.071 and for $R'_{\mathrm{w}} = [(\sum w\Delta^2 / \sum w|F_{\mathrm{o}}|^2)^{1/2}]$ was 0.077. Lists of crystal structure data, atomic coordinates, bond lengths and angles and anisotropic displacement parameters are presented in tables S7 to S14 in Supplementary material.

3. Results and discussion

3.1. *Metal complex synthesis, isolation and characterisation*

Picenbz$_2$ **3** readily coordinated to *cis*-[Ru(dmso)$_4$Cl$_2$] [19] with excellent yields. The product recovered from the reaction was a mixture of α- and β-isomers that appeared, by NMR, to be present in approximately equal amounts. Recrystallisation was straightforward with the β-isomer being first to be recovered as large yellow-green crystals. A second crop recovered from the same solution approximately one day later, contained small dark green-crystals of the α-isomer. The last crop of product was similar in composition to the crude product. Proton NMR and the corresponding chemical shifts of each isomer permitted isomeric identification and determination of the isomeric ratio in crop 3. Total yields of α and β are 45 and 46%, respectively. Crystals of the β-isomer proved to be suitable for X-ray crystallography but the crystals of the α-isomer were not.

The geometry of tetradentate ligands coordinated in a cis arrangement around an octahedral metal can be defined as follows. The α-isomer has C$_2$ symmetry for the metal-tetradentate fragment, and which is conserved when two equivalent monodentate ligands or a symmetrical bidentate ligand is coordinated in the remaining two positions. This can best be characterised by the observation that in the α-isomer three different chelate rings planes, are present whereas in the β-isomer two of these rings lie in the same plane (figure 1). Two different forms of the β-isomer are possible, β_1 and β_2, corresponding to the two alternative ways in which the dmso and chloride ligands coordinate. Only the β_1 isomer was isolated in this work, as confirmed, by X-ray crystallography. A *trans* isomer is theoretically possible, but the steric interaction which would occur between H(11) and H(21) protons suggests that it would be the least energetically favourable. No *trans*-isomers were detected.

NMR assignment of the proton resonances of the two isomers was achieved using a combination of proton 1D and 2D NMR and decoupling experiments. The α- and β-configurations are easily distinguished in these spectra. Unfortunately, the α-[Ru(picenbz$_2$)(dmso)Cl]$^+$ (**5**) form has only pseudo C$_2$ symmetry, producing a more complicated spectrum than its symmetrical α-[Co(picenbz$_2$)Cl$_2$]$^+$ (**4**) analogue. Chemical shifts, highlighted in figure 3 and detailed in table 2, are distinctive and characteristic of the structural configuration. The H(11) and H(21) proton resonances of α-[Ru(picenbz$_2$)(dmso)Cl]$^+$ (**5**) are almost coincidental and produce a triplet signal. This is very unlike the individual doublets of the β-structure, which are observed as unique signals at higher fields, consistent with their individual environments. Even the aliphatic protons observed between 5.3 and 2.2 ppm have characteristic resonances, attributable to individual isomers. In particular, the chemical shifts of the protons from the ethylene bridge, where the H(1a) and H(2b) resonances occur at 4.26 and 2.25 ppm, respectively, for the β-complex, contrast with the α-isomer, for which these resonances occur as a common complex signal at 2.55 ppm.

The proton spectrum of the symmetrical isomers α-[Ru(picenbz$_2$)(dpq)]$^{2+}$ (**7**), synthesised and isolated from α-[Ru(picenbz$_2$)(dmso)Cl]$^+$ (**5**), is very similar to that of the α-precursor. The number of proton resonances is halved, due to its C$_2$ symmetry (table 2). The aromatic protons H(21) and H(22) of the tetradentate ligand are shielded by the dpq ligand, resulting in the signals being observed at lower field than that of H(21)and H(22) in α-[Ru(picenbz$_2$)(dmso)Cl]$^+$ (**5**). Furthermore, resonances

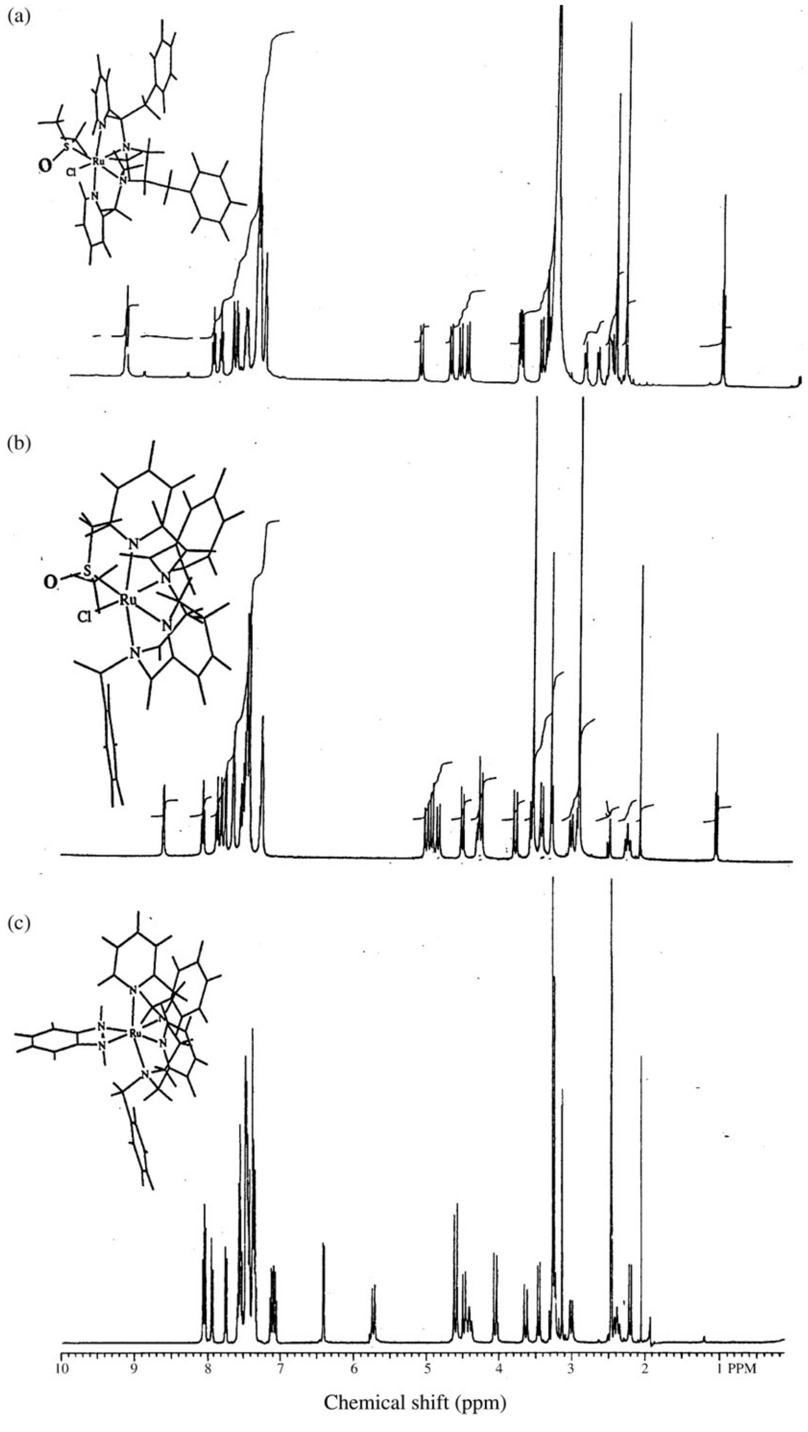


Figure 3. Proton NMR spectra of (a) α-[Ru(picenbz$_2$)(dmso)Cl]$^+$ (**5**), (b) β-[Ru(picenbz$_2$)(dmso)Cl]$^+$ (**6**) and (c) β-[Ru(picenbz$_2$)(bqdi)]$^{2+}$ (**8**), showing the splitting pattern of the methylene protons and the ethylene bridge of the tetradentate ligand.

attributable to H(32), H(33), H(34) and H(37) of dpq (**1**) could be assigned with relative ease as they are each observed as two doublets, a singlet and a doublet of doublets at δ 10.06, 9.60, 9.34 and 8.37 ppm, respectively. H(32) is deshielded by the aromatic rings of picenbz$_2$ (**3**) and is shifted to higher field than for complexes of the type $[Ru(phen)_2(dpq)]^{2+}$ where the equivalent protons occur at 8.33 ppm [6].

Products recovered when using β_1-$[Ru(picenbz_2)(dmso)Cl]^+$ (**6**) were invariably β but when benzene-1,2-diamine was used the diimine, 1,2-benzoquinone diimine (bqdi) formed to produce β-$[Ru(picenbz_2)(bqdi)]^{2+}$ (**8**). This is evident in the crystal structure as well as the characteristic chemical shifts. The chemical shifts of the iimine protons at 13.7 and 12.7 ppm are consistent with those reported for the highly symmetrical species $[Os(bqdi)_3]^{2+}$ [27] (13.7 ppm). The topology of β-$[Ru(picenbz_2)(bqdi)]^{2+}$ (**8**) was also revealed by proton 1D (figure 5) and 2D NMR analysis (Supplementary material). The asymmetries of β_1-$[Ru(picenbz_2)(dmso)Cl]^+$ (**6**) and β-$[Ru(picenbz_2)(bqdi)]^{2+}$ (**8**) are exemplified by the complexity of their spectra in comparison with that of the corresponding α-precursor. The large number of resonances observed for these β species serves to both aid and hinder certain aspects of the structural interpretation. The spectrum of β_1-$[Ru(picenbz_2)(dmso)Cl]^+$ (**6**) (figure 5) can be interpreted on the basis of symmetry considerations, where the H(21) resonance occurs at a higher field than that of H(11) as a result of shielding of the former by an adjacent pyridyl ring [28]. H(11) is *cis* to both the Cl and dmso ligand groups, each of which has a deshielding effect, resulting in its signal being at lower field than that of H(21). A striking feature of the β-$[Ru(picenbz_2)(bqdi)]^{2+}$ (**8**) spectrum is the upfield shift of the H(11) doublet found at 8.66 ppm in the dmso/Cl precursor. This resonance now is observed at 6.44 ppm, an upfield shift of 2.22 ppm, and as confirmed by the 2D NMR analysis, it is coupled to the aromatic multiplet at 7.35 ppm. H(11) of β-$[Ru(picenbz_2)(bqdi)]^{2+}$ (**8**) would experience a considerable electronic shielding effect from the aromatic ring of the coordinated bqdi ligand which it sits over, as illustrated in figure 4. This results in the observed shift to significantly higher field than that of H(21) in this complex.

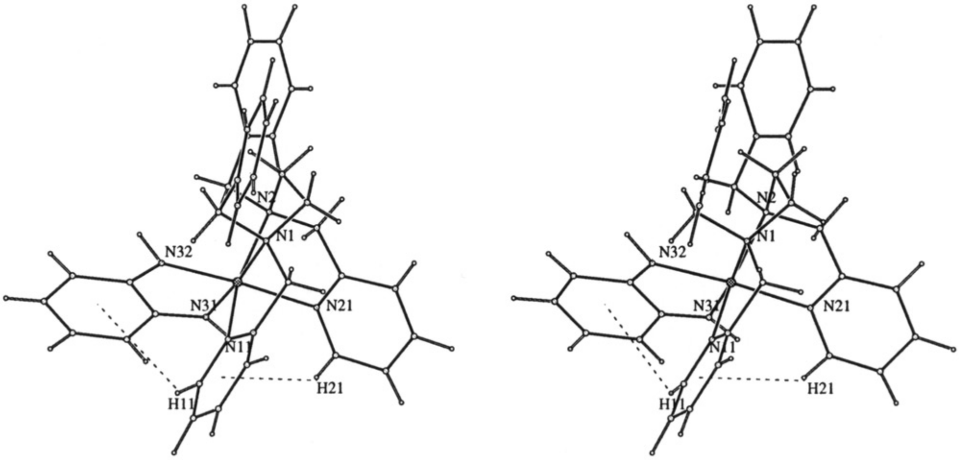


Figure 4. A stereoview of β-$[Ru(picenbz_2)(bqdi)]^{2+}$ (**8**) with the shielding interactions experienced by H(21) and H(11) protons represented by dashed lines.

The assignment of aliphatic resonances for the complex was assisted by decoupling experiments and confirmed by the 2D NMR analysis, with these signals being relatively unaffected by coordination of the bqdi. The mutual coupling of resonances for H(110a), H(110b), H(220a) and H(220b), occurring at 5.77 and 4.52 and 3.50 and 2.20 ppm, respectively, was confirmed by cross verification in the 2D NMR spectrum.

The rigid conformation of the tetradentate ligand leads to the *anti* and *gauche* dispositions observed for the vicinal hydrogen atoms of the central ethyl bridge, similar to those previously reported [26] for Δ-β-[Co(R-picpn)$(NO_2)_2$]$^+$. The mutually coupled signals which are attributed to the two pairs of geminal methylene protons, H(1a), H(1b), and H(2a), H(2b), produce an AA′BB′ splitting pattern that may be distinguished in the NMR analysis. They have substantially different chemical shifts from those of the pseudo-C_2 α-[Ru(picenbz$_2$)(dmso)Cl]$^+$ (**5**) complex, for which all ethylene-bridge signals fall between 2.7 and 3.0 ppm. For the unsymmetrical β topology, H(1a) and H(1b) resonances shift to lower field due to deshielding by a benzyl ring, differently positioned in this isomer. Theoretical coupling constants were calculated [29] using the crystallographic information for the vicinal protons. The coupling constants which give rise to resonance structures observed in the NMR spectrum are due to the four protons in the ethyl bridge being in *geminal*, *anti* and *gauche* relative dispositions. For example, the experimental value obtained for the coupling constants between H(1a), H(2b), H(1b) and H(2a) are in good agreement with those derived from the Bothner-By [30] formulation (table 4). This confirms that the structure observed in the crystalline state is maintained in solution. The observed geminal coupling constant for both (J2a, 2b) and (J1a, 1b) of 13.4 Hz is consistent with reported values [30, 31].

The complexes that formed upon coordination of 4,5-dimethylbenzene-1,2-diamine or naphthalene-2,3-diamine were similar to β-[Ru(picenbz$_2$)(bqdi)]$^{2+}$ (**8**) and were straightforward to assign using ^{1}H NMR (see table 3). β-[Ru(picenbz$_2$)(bqdiMe$_2$)]$^{2+}$ (**9**) formed a complex of the diimine, 4,5-dimethyl-1,2-benzoquinone diamine, with two signal from the N–H protons of the diimine at 13.7 and 11.7 ppm in addition to the two methyl singlets at 2.55 and 2.17 ppm. The β-[Ru(picenbz$_2$)(2,3-dnap)]$^{2+}$ (**10**) produced an amine when coordinated to ruthenium(II). This conclusion is supported by microanalysis (table 2) and NMR. Resonances for NH_2 are broad, integrate for 4 protons and are upfield at 8.07–8.03 ppm compared to the N–H protons of β-[Ru(picenbz$_2$)(bqdi)]$^{2+}$ (**8**) at 13.9 and 12.7 ppm.

H(11) proton of β-[Ru(picenbz$_2$)(phen)]$^{2+}$ (**11**) is observed to experience significant electronic shielding effects from the adjacent aromatic rings of the coordinated diimines, as reported in table 3. Even symmetrical bidentate ligands, such as phen,

Table 4. Calculated and observed vicinal proton coupling constants [13]. Derived from H–C–C–H torsion angles for β-[Ru(picenbz$_2$)(bqdi)]$^{2+}$ (**8**).

Vicinal group		Coupling constant (Hz)		
H1–X1–X2–H2	Angle (°)	[a]	[b]	Observed
H(1a)–C(1)–C(2)–H(2a)	57.5	5.25	4.35	5.0
H(1a)–C(1)–C(2)–H(2b)	177.5	9.21	12.98	13.3
H(1b)–C(1)–C(2)–H(2a)	63.4	4.90	3.55	2.4
H(1b)–C(1)–C(2)–H(2b)	56.5	5.31	4.49	4.2

[a] Karplus formulation: $JHH = 4.22 - 0.5\cos Ø + 4.5\cos^2 Ø$.
[b] Bothner-By modification: $JHH = 7 - \cos Ø + 5\cos^2 Ø$.

reflect the dissymmetry of the β configuration, such that the protons H(36) and H(36′) of phen, for example, have separate resonances which may be distinguished as split singlets at 8.44 and 8.41 ppm.

3.2. *X-ray crystallography*

3.2.1. β_1-[(Ru(picenbz$_2$)(dmso)Cl]PF$_6$ · 0.5H$_2$O. The molecular structure of the β_1-[Ru(picenbz$_2$)(dmso)Cl]$^+$ (**6**), together with the atom labelling scheme, is shown in figure 5. The β_1 topology is clearly confirmed and there are no unusual dimensional parameters, where the Ru–N(en) bond dimensions of 2.178(3) and 2.167(4) Å, and the Ru–N(11) and Ru–N(21) bond lengths of 2.086(4) and 2.072(3) Å (see table 5) are similar to those for the related compound β-[(Ru(picenbz$_2$)(bqdi)](PF$_6$)$_2$ (**8**), also reported here (see table 6) and discussion below.

In β_1-[(Ru(picenbz$_2$)(dmso)Cl]PF$_6$ · 0.5H$_2$O (**6**) the anions occupy distinct positions within the cell, where any free movement of the PF$_6^-$ group is apparently inhibited by

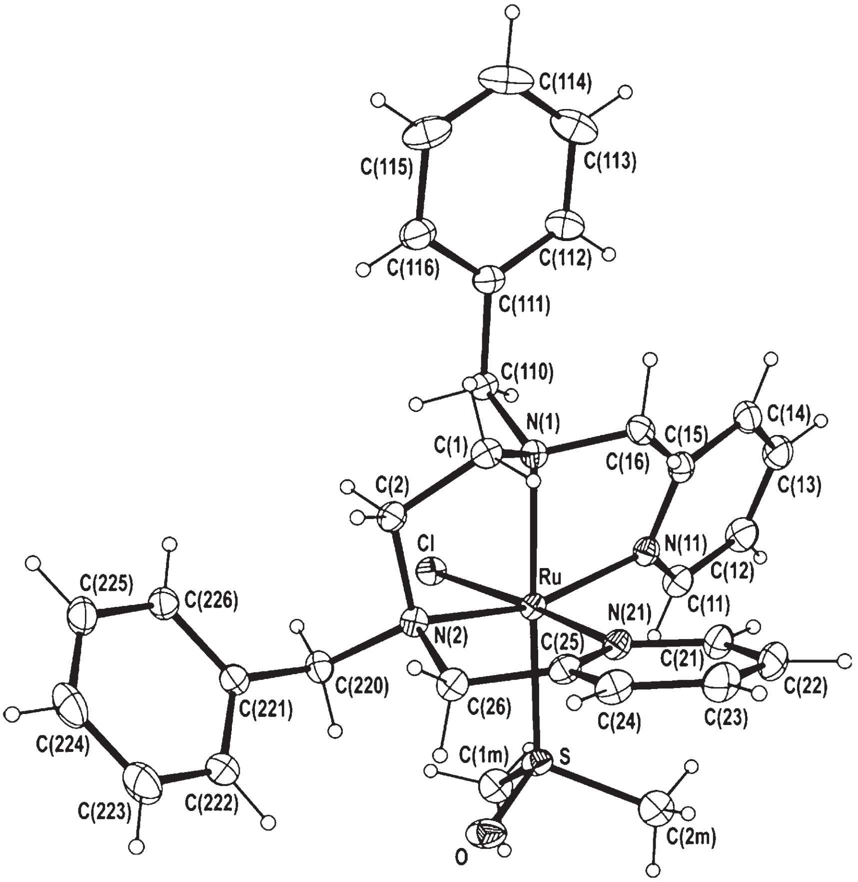


Figure 5. A drawing of the cation β-[Ru(picenbz$_2$)(dmso)(Cl)]$^+$ (**6**) showing thermal parameters (25% probability for non-H atoms) at ambient temperature. For reasons of clarity H atoms are shown with $B = 1.0\,\text{Å}^2$.

Table 5. Selected bond distances (Å) and angles (°) in the *cis*-β_1-[Ru(picenbz$_2$)(dmso)Cl]$^+$ cation at 25°C.

Bond dimensions at Ru					
Bond lengths (Å) to					
N(1)	N(11)	N(2)	N(21)	S	Cl
2.178(3)	2.167(4)	2.086(4)	2.072(3)	2.248(2)	2.419(2)
Bond angles (°)					
N(1)	78.5(14)	83.7(13)	89.2(13)	176.7(9)	92.1(9)
N(11)		161.8(13)	95.9(14)	101.9(11)	88.6(10)
N(2)			80.2(13)	95.8(10)	95.7(10)
N(21)				87.5(11)	175.5(10)
S					91.2(5)

Table 6. Selected bond distances (Å) and angles (°) in the *cis*-β-[Ru(picenbz$_2$)(bqdi)]$^{2+}$ cation at 25 and −80°C.

25°C					
Bond dimensions at Ru					
Bond lengths (Å) to					
N(1)	N(11)	N(2)	N(21)	N(31)	N(32)
2.140(9)	2.064(10)	2.140(10)	2.094(9)	1.994(9)	2.013(8)
Bond angles (°)					
N(1)	78.9(4)	84.5(3)	91.6(4)	174.8(4)	97.8(3)
N(11)		160.9(4)	90.9(4)	99.4(5)	91.4(4)
N(2)			80.0(4)	97.9(4)	100.3(4)
N(21)				93.3(4)	170.6(4)
N(31)					77.3(4)
−80°C					
Bond dimensions at Ru					
Bond lengths (Å) to					
N(1)	N(11)	N(2)	N(21)	N(31)	N(32)
2.181	2.125	2.022	2.147	1.973	2.017
Bond angles (°)					
N(1)	76.1	86.2	96.2	171.8	95.1
N(11)		161.6	99.7	104.7	88.5
N(2)			76.6	93.6	98.5
N(21)				91.7	167.4
N(31)					76.9

the relatively close contact with the cation. The stabilising influence of the cation is also promoted by the presence of lattice water molecules which, although statistically distributed over two relatively close (~1.3–1.4 Å) crystallographic sites (with quite low population parameters), occupy interstitial positions where hydrogen bonding is almost certainly significant. As a result, the hexafluorophosphate anion shows no evidence of disorder, unlike the significant disorder exhibited by the hexafluorophosphate F atoms in the two crystallographically independent anions in the structure of the related β-[(Ru(picenbz$_2$)(bqdi)](PF$_6$)$_2$ (**8**), as described below.

3.2.2. β-[(Ru(picenbz$_2$)(bqdi)](PF$_6$)$_2$. The molecular structure of β-[Ru(picenbz$_2$)(bqdi)]$^{2+}$ (**8**), together with the atom labelling scheme, is shown in figure 6. We observed a temperature-dependent change in unit cell parameters that was unexpected, and a significant loss of crystalline nature was obvious from the very

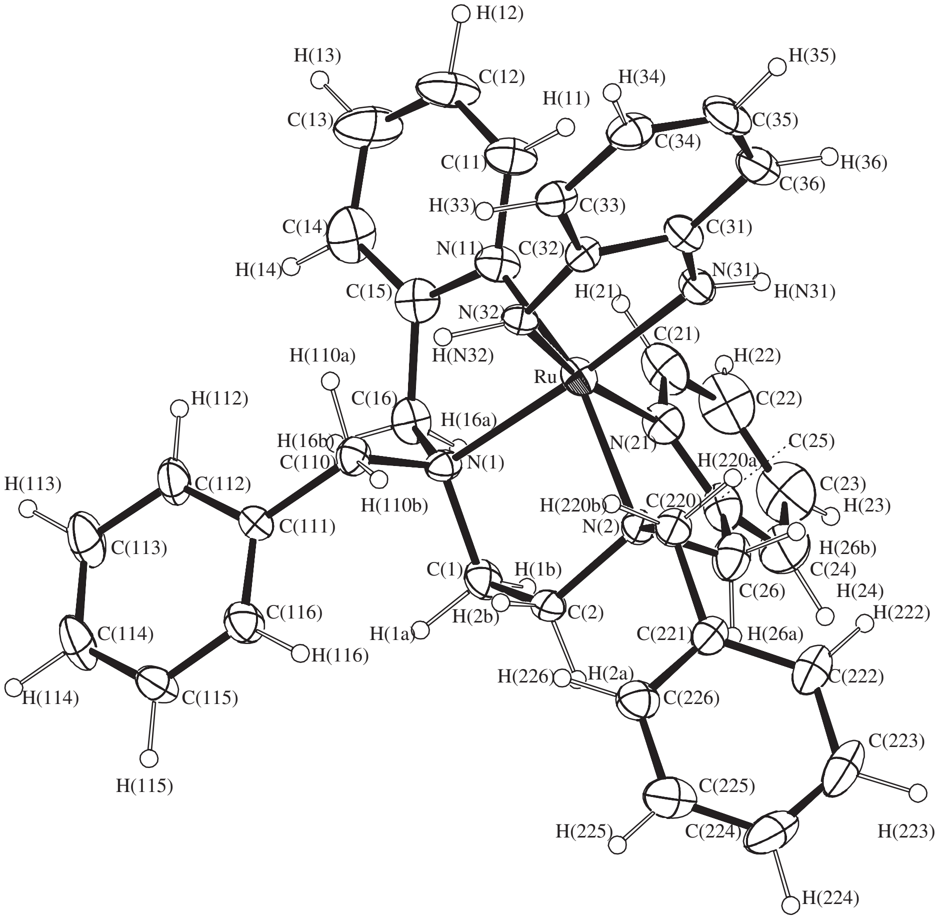


Figure 6. A drawing of the cation β-[Ru(picenbz$_2$)(bqdi)]$^{2+}$ (**8**) showing thermal parameters (25% probability for non-H atoms) at ambient temperature. For reasons of clarity H atoms are shown with $B = 1.0\,\text{Å}^2$.

limited amount of intensity data that was collected at low temperature. The temperature effect was found to be irreversible. Two sets of data were collected from the same crystal at 25°C and then −105°C, after which the crystal was allowed to return to room temperature. This did not result in a return of crystalline properties corresponding to the 25°C structure. Biner *et al.* [34] had investigated the crystal structures of [Ru(bpy)$_3$](PF$_6$)$_2$ at ambient and low temperatures, and found that this compound undergoes changes in cell parameters and crystal symmetry as a consequence of changes in temperature. Positional change involving the hexafluorophosphate anions were shown to be the reason for this temperature effect.

The bond dimensions Ru–N(bqdi) 1.994(9), 2.013(8) and Ru–N(en) 2.140(9) and 2.140(10) Å, compare favourably with reported Ru–N(amine) values of 2.06 Å [28, 34–38] and Os–N(bqdi) values of 1.990(4), 1.994(3) and 1.980(3) Å [27]. Reported bond lengths for RuN(bqdi) and RuN(bqdi) are 1.99 and 2.07 Å, respectively, demonstrating the imine bond to be shorter by some 0.05 Å [33]. The Ru–N(11) and Ru–N(21) bond lengths of 2.064(10) and 2.094(9), are approximately 0.1 Å larger than those observed with Co(III) cis-β complexes [13–16] and compare favourably with dimensions observed for $[Ru(bpy)_2(phi)]^{2+}$ and Ru(II)-picchxn complexes [36, 37].

The disorder exhibited by the hexafluorophosphate F atoms warrants some comment. An interpretation involving partial occupancies is problematic, although the sense of the final model is verified by the P–F bond lengths, which are all within the expected range of 1.5 to 1.6 Å. Further evidence for the integrity of the fluorine atom positions is provided by their distribution around each of the phosphorus centres. Each anion can be interpreted as being derived from a pair of unique octahedra, four distinct species, with two PF_6 units deriving from P(1) and two PF_6 units from P(2).

The anions occupy distinct positions within the cell some distance away from the cations, thereby limiting the cation's stabilising influence; in particular, the P(2) anions have very limited contact. Hence, some free movement of the PF_6^- groups might be expected. This is likely to be a contributing factor both to the disordered nature of the anions, and also the dependence on temperature of the crystallinity of the compound.

4. Conclusions

Several ruthenium complexes have been synthesised using the N_4-tetradentate ligand 1,6-di(2′-pyridyl)-2,5-dibenzyl-2,5-diazahexane ($picenbz_2$). Metal complexes containnig $picenbz_2$, produce only two isomers which can be separated by recrystallisation into α- and β-$[Ru(picenbz_2)(dmso)Cl]PF_6$. Isomeric structure of the precursor, α or β, is conserved upon the coordination of a bidentate ligand, such as benzene-1,2-diamine, 4,5-dimethyl-benzene-1,2-diamine, naphthalene-2,3-diamine, 2,2′-bipyridine, 1,10-phenanthroline or dipyrido[3,2-d:2′3′-*f*]quinoxaline, to produce complexes of the type α- or β-$[Ru(picenbz_2)(bidentate)](PF_6)_2$. All the metal complexes were fully characterised by 1D and 2D ^1H NMR. The crystal structures for β-$[Ru(picenbz_2)(dmso)Cl]PF_6 \cdot 0.5H_2O$ and β-$[Ru(picenbz_2)(bqdi)](PF_6)_2$, have also been determined.

Supplementary material

^1H and ^1H COSY NMR spectra of β-$[Ru(picenbz_2)(dmso)Cl](PF_6)$ and β-$Ru(picenbz_2)(bqdi)](PF_6)_2$ in deuterated dmso are available. Lists of crystal structure data, atomic coordinates, bond lengths and angles and anisotropic displacement parameters are presented in the Supplementary material.

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