DALTON
FULL PAPER

The stereospecific synthesis of Λ-α-{dipyrido[3,2-*a*:2′3′-*c*]-(6,7,8,9-tetrahydro)phenazine[*N*,*N*′-di(2-picolyl)-2,5-dimethyl-2*S*,5*S*-diaminocyclohexane]ruthenium(II)} and related β-isomers †

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The conglomerate Δ,Λ-α-[Ru(picchxnMe$_2$)(dpqC)](ClO$_4$)$_2$·0.5H$_2$O and Λ-α-[Ru(*S*,*S*-picchxnMe$_2$)(dpqC)](ClO$_4$)$_2$·0.5H$_2$O (where picchxnMe$_2$ = *N*,*N*′-dimethyl-1,2-di(2′-picolyl)-*S*,*S*-diaminocyclohexane and dpqC = dipyrido[3,2-a:2′3′-c](6,7,8,9-tetrahydro)phenazine) have been isolated. Single crystal X-ray structures have been determined, although it was discovered only after initial data had been collected that the Δ,Λ-α-[Ru(picchxnMe$_2$)(dpqC)](ClO$_4$)$_2$·0.5H$_2$O species was in fact a conglomerate. Λ-α-[Ru(*S*,*S*-picchxnMe$_2$)(dpqC)](ClO$_4$)$_2$·0.5H$_2$O crystallises in the orthorhombic space group $C222_1$ with a = 15.127(2), b = 22.976(4), c = 25.561(7) Å, (alternatively a = 15.187(3), b = 23.003(6), c = 25. 685(7) Å, for the separate determination of a crystal of the conglomerate), Z = 8, and the Λ-α structure was refined to an R value of 0.059. This structure enables, for the first time, the correlation of the absolute configurations for Ru(II) complexes of the N_4 tetradentate with their CD spectra. We also report here a procedure to synthesise and isolate enantiomerically pure isomers of tetradentate metal complexes of the types α- and β-[Ru(*R**,*R**-picchxnMe$_2$)(dpqC)]$^{2+}$.

Introduction

The non-intercalating or ancillary ligands of octahedral metal complexes that interact with DNA are not restricted to bidentate ligands such as 1,10-phenantroline or 2,2′-bipyridine because tetradentate ligands can also be used. Well-designed tetradentate ligand-based complexes may interact with the base-pairs at the face of the intercalation site with sequence selectivity.[1–6] *Cis*-α-isomers are of particular interest as they can produce *enantiomers* having C_2 symmetry. The complex Δ-α-[Rh(*R*,*R*-Me$_2$trien)(phi)]$^{3+}$ (*R*,*R*-Me$_2$trien = 2*R*,9*R*-2,9-diamino-4,7-diazadecane and phi = 9,10-phenanthrenenequinone diimine) was shown to bind to DNA with sequence specificity by taking advantage of hydrogen-bonding interactions between the tetradentate ligand and the DNA helix.[4] The *R**,*R**-Me$_2$trien ligand coordinated to form several isomers including the Δ-α-isomer and its C_2 symmetry is ideally suited for sequence selective binding to DNA.

The structural versatility of tetradentates can, however, lead to different geometric configurations, when coordinated to octahedral metals. If a *cis*-β configuration is adopted C_2 symmetry is lost. Limited control over coordination geometry with Ru(II) complexes has impeded the development of tetradentate metal complexes for use as structural probes for DNA. Tetradentate ligand design and synthetic procedures that predispose chirality or stereoisomerism upon metal complex coordination are critical for further progress in this area.

The tetradentate ligand picen was first synthesised by Goodwin and Lions,[7] and has been subtly altered to produce an array of tetradentate chelates.[8] Among these are the N_4 tetradentates, *N*,*N*′-dimethyl-1,2-di(2′-picolyl)-*S*,*S*-diaminocyclohexane (picchxnMe$_2$)[9] as shown in Fig. 1. Stereochemistries adopted by these tetradentate ligands upon coordination are due in part to intraligand torsional effects and steric constraints,[8] but kinetic effects are also sometimes manifested. Substitution that introduces chirality can produce highly

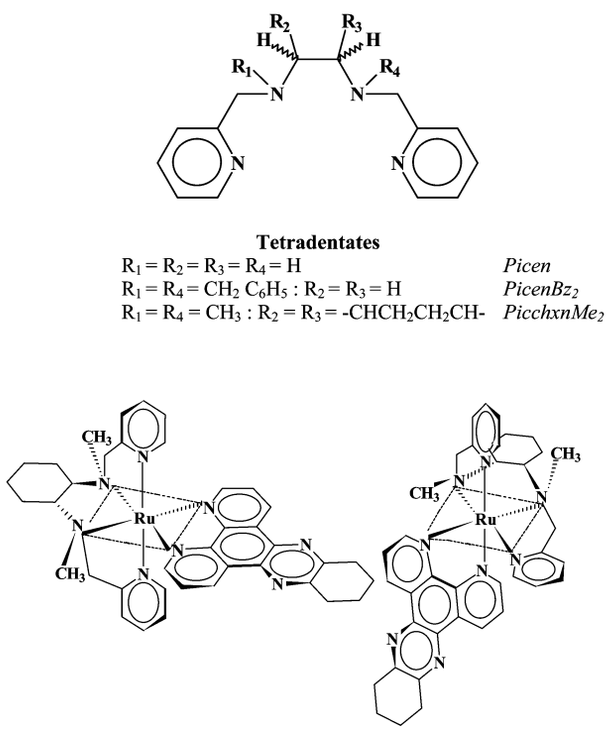

Fig. 1 The tetradentate ligands: picen, picenBz$_2$ and picchxnMe$_2$; and the structures of (α) Λ-α- and (β) Λ-β-[Ru(picchxnMe$_2$)(dpqC)]$^{2+}$.

† Electronic supplementary information (ESI) available: coordinates, lengths and angles; 2D NMR spectra. See http://www.rsc.org/suppdata/dt/b2/b208369h/

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Table 1 Chemical shifts[a] (δ), multiplicities, integration and coupling constants (Hz) for concentrated solutions of *rac*-α- and β-[Ru(picchxnMe_2)-(dpqC)]$^{2+}$ in acetone-d_6

Proton	α-[Ru(picchxMe_2)(dpqC)]$^{2+}$	β-[Ru(picchxMe_2)(dpqC)]$^{2+}$
CH_3	2.83,[b] s, 6H	3.44, s, 3H
CH_3'		2.25, s, 3H
H4a,b;H5a,b	1.22, m, 4H	1.80, m, 4H
H3a,b;H6a,b	1.78 m, 4H	2.89, m, 2H
H1a	2.54, d, 1H, *J* 13.2Hz	3.82, m, 1H
H1b	2.54, d, 1H, *J* 13.2Hz	
H2a & 2b		1.73, m, 1H
H16a	5.30, d, 2H, *J* 9 Hz	4.89, d, 1H, *J* 16.9 Hz
H16b	5.07, d, 2H, *J* 9 Hz	3.93, d, 1H, *J* 17.3 Hz
H26a; H26b		4.77, s, 2H
H11	7.98, d, 2H, *J* 5.1 Hz	7.09, d, 1H, *J* 5.4 Hz
H12	7.11, t, 2H, *J* 7.3 Hz	6.97, t, 1H, *J* 6.6 Hz
H13	7.77, t, 2H, *J* 7.5 Hz	7.85, m, 1H
H14	7.69, d, 2H, *J* 7.8 Hz	7.77, d, 1H, *J* 7.1 Hz
H21		7.93, d, 1H, *J* 5.7, Hz
H22		7.70, t, 1H, *J* 6.4 Hz
H23		8.23, m, 1H
H24		8.06, d, 1H, *J* 8.1 Hz
H2	10.15, d, 2H, *J* 5.4 Hz	10.00, d, 1H, *J* 5.4 Hz
H2′		7.95, d, 1H, *J* 5.7 Hz
H3	8.27, dd, 2H, *J* 8.1, 5.2 Hz	8.23, m, 1H
H3′		7.85, m, 1H
H4		9.72, d, 1H, *J* 8.1 Hz
H4′	9.54, d, 2H, *J* 8.4 Hz	9.54, d, 1H, *J* 8.1 Hz
H8a,b	3.28, m, 4H	3.35, m, 4H
H9a,b	2.11, m, 4H	2.15, m, 4H

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

stereo- and enantioselective coordination behaviour. For example, the chirality of picchxnMe_2 and a resulting metal complex can be predetermined by resolution of the diamine precursor diaminocyclohexane.[8] Stereoselective coordination behaviour can be enhanced by further substitution at nitrogen, which is a primary stereochemical determinant.[8] Cobalt(III) complexes of *N*,*N*′-dimethyl-substituted isomers of 1,4,7,10-tetraazadecane (trien) and picchxnMe_2 have been shown to adopt a largely *cis*-α configuration.[8–12] However, this degree of stereochemical control has not been demonstrated with ruthenium. This is thought to be due to the greater kinetic inertness of Ru(II) in that, once formed, α- and β-isomers (Fig. 1) remain intact. We report here a procedure to synthesise and isolate enantiomerically pure tetradentate metal complexes of the type α- and β-[Ru(picchxn)(bidentate)]$^{2+}$.

Experimental

Instrumentation

Absorbance spectra were recorded on a Shimadzu UV-2100 recording spectrophotometer and CD spectra on a Jasco 500C spectropolarimeter. ^{1}H NMR spectra were recorded at 25 °C on a Varian XL 300 MHz Spectrometer.

Materials

SP-Sephadex C-25, aluminum oxide (activated neutral Brockmann 1) and amberlite IRA-400(Cl) ion exchange resin were obtained from Aldrich. Aqueous sodium (−)-*O*,*O*′-dibenzoyl-*L*-tartrate solutions were prepared by the addition of aqueous sodium hydroxide solution to the acid (Fluka), until a pH of 8–9 was obtained. Laboratory grade reagents, metal salts and solvents were used for synthetic work as supplied, unless otherwise specified.

Synthesis

Λ-α-[Ru(*S*,*S*-picchxnMe_2)(dpqC)]$(PF_6)_2$ 1. Syntheses of *N*,*N*′-dimethyl-1,2-di(2′-picolyl)-*S*,*S*-diamino cyclohexane (*S*,*S*-picchxnMe_2) and dipyrido[3,2-a:2′3′-c](6,7,8,9-tetrahydro)phenazine (dpqC) have been described previously.[12,13] The new complex was prepared as follows: a mixture of *S*,*S*-picchxnMe_2 (2.00 g, 6.17 mmol) and $RuCl_3 \cdot 3H_2O$ (1.30 g, 4.97 mmol) in 1,2-propanediol (30 mL) was heated until the $RuCl_3$ had dissolved. The solution was refluxed for 2 h, cooled, then water (30 mL) and excess potassium iodide (10.0 g) were added. The resulting mixture was heated until all the potassium iodide had dissolved and left to cool overnight. The precipitated solid was filtered and washed with water (20 mL) and diethyl ether (50 mL) to yield a brown solid. The resulting solid and dpqC (1.5 g, 5.2 mmol) in ethanol/water (400/50 mL) were refluxed for 6 h until the solution assumed an orange colour. The cooled solution was filtered, reduced in volume and filtered a second time to remove excess dpqC. A saturated aqueous solution of potassium hexafluorophosphate was added (1 mL) to precipitate an orange solid, which was filtered, washed with water (100 mL) and then diethyl ether (50 mL). This orange product was purified by chromatography on a column (2 × 10 cm) of aluminium oxide (activated, neutral Brockmann 1) by eluting with acetone. An orange band was collected (200 mL), water was added (20 mL) and the solution was left to evaporate at room temperature. Crystals of **1** that formed were filtered off, washed with diethyl ether (50 mL) and air-dried. Yield: 3.01 g, 60.5%. Anal. – calc. for $C_{38}H_{42}N_8P_2F_{12}Ru$ (%): C 45.56; N 11.19, H 4.23; found C 45.73, N 10.37, H 4.66. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), acetone/water): 263 (57900), 340 (57900), 445 (5670), 480 (5665). CD spectrum (λ_{max}/nm ($\Delta\varepsilon$/dm^2 mol^{-1}), 10% acetone in water) = 361 (−23.1), 394 (+16.0), shoulder 437 (+8.4). ^{1}H NMR data are given in Table 1.

Δ,Λ-α-[Ru(picchxnMe_2)(dpqC)]$(PF_6)_2$ 2. The synthesis of the conglomerate followed the same procedure as for the Λ-α-[Ru(*S*,*S*-picchxnMe_2)(dpqC)]$(PF_6)_2$, with *rac*-picchxnMe_2 being substituted for *S*,*S*-picchxnMe_2. Yield: 0.17 g, 59.5%. MS (ESMS, CH_2CN, MW = 1003.2) *m*/*z* = 858.2 (M–PF_6^-).

Δ,Λ-β-[Ru(picchxnMe_2)(dpqC)]$(PF_6)_2 \cdot 3H_2O$ 3. A mixture of *rac*-picchxnMe_2 (2.20 g, 6.78 mmol) and [Ru(DMSO)$_4$(Cl)$_2$][14] (3.00 g, 6.19 mmol) in ethanol (300 mL) and water (150 mL)

Table 2 Crystal data for Λ-α-[Ru(*S*,*S*-picchxnMe$_2$)(dpqC)](ClO$_4$)$_2$·0.5H$_2$O

Empirical formula	$C_{38}H_{42}Cl_2N_8O_{8.5}Ru$
Formula weight	918.78
Crystal system	orthorhombic
a/Å	15.127(2)
b/Å	22.976(4)
c/Å	25.561(4)
V/Å^3	8884(2)
Space group	$C222_1$
Z	8
Absorption coeff./μm^{-1}	0.72
Reflections total	4279
Reflections observed	3313
$R(F_o)$ [a]	0.060
R_w [b]	0.059

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$.

was refluxed for 6 h. The solution was then reduced in volume to about 100 mL. When the solution had cooled, excess potassium hexafluorophosphate (1 mL) was added and a dark green compound precipitated. The solid was filtered off, washed with diethyl ether (50 mL) and recrystallised from acetone/water. The recrystallised product and dpqC (2.00 g, 6.99 mmol) were dissolved in ethanol/water (250/100 mL) and refluxed for 6 h until the solution became orange. The solution was cooled, filtered and reduced under vacuum to 80 mL. Excess potassium hexafluorophosphate (1 mL) was added to precipitate an orange product, which was filtered, washed with water (100 mL) and diethyl ether (50 mL). The orange solid was recrystallised from acetone/water (150/50) to give **2** that contained a small amount of the α-isomer. Yield 3.91 g, 63%.

The mixtures of stereoisomers as noted above were separated by the following method. The counterion was exchanged for chloride by stirring crude **2** (0.1 g) with Amberlite IRA-400(CI) ion exchange resin (5.0 g) and water (100 mL). The mixture was filtered and washed with water (10 mL). The filtrate was reduced in volume (10 mL) and was applied to an SP-Sephadex C-25 cation exchange column (100 × 1.6 cm) and eluted with aqueous 0.1 M disodium (−)-*O*,*O*′-dibenzoyl-*R*,*R*-tartrate. The α- and β-isomers separated cleanly, with the β-complex eluting first. Addition of excess potassium hexafluorophosphate (1 mL) afforded orange precipitates. Typical yields; α-isomer 0.009 g, 9%; β-isomer 0.086 g, 86%. Anal. – calc. for $C_{36}H_{48}N_8F_{12}O_3P_2Ru$ (%): C 43.23, H 4.58, N 10.61; found C 43.20, H 4.16, N 10.09. Electronic spectrum (λ_{max}/nm (ε/dm^2 mol^{-1}), 10% acetone in water): 264 (57900), 340 (57900), 445 (6220), 481 (6200). ^{1}H NMR data are given in Table 1 along with the proton numbering scheme.

X-Ray crystallography

Crystals of Λ-α-[Ru(*S*,*S*-picchxnMe$_2$)(dpqC)](ClO$_4$)$_2$. ½H$_2$O and the conglomerate were obtained by mixing Amberlite IRA-400(Cl) ion exchange resin and either α-[Ru(*S*,*S*-picchxnMe$_2$)(dpqC)](PF$_6$)$_2$ or *rac*-α-[Ru(*N*,*N*-picchxnMe$_2$)(dpqC)](PF$_6$)$_2$ (1.0 g) with water until the solid dissolved. Excess sodium perchlorate was added to the filtrate to precipitate product, which was filtered off, washed with water (20 mL) and diethyl ether (20 mL) and recrystallised from 1 : 1 (v/v) ethanol/acetone.

Caution: Perchlorate salts may be explosive.

Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured and refined on an Enraf Nonius CAD4 diffractometer. Crystallographic data are summarized in Table 2. Data reduction and application of Lorentz, polarisation and analytical absorption corrections were carried out using the teXsan package.[15] The structure was solved by direct methods using SHELXS-86[16] and refined using full-matrix least-squares methods with teXsan.[15] Hydrogen atoms were included at calculated sites with thermal parameters derived from the parent atoms. Non-hydrogen atoms were refined anisotropically. Scattering factors were taken from *International Tables*.[17] Anomalous dispersion effects were included in F_c;[18] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[19] Values for mass attenuation coefficients were those of Creagh and Hubbell.[20] All other calculations were performed using the teXsan[15] crystallographic software package of the Molecular Structure Corporation. Selected bond lengths and angles are listed in Table 3. Atomic nomenclature is defined in Fig. 2.[21] Lists of the positional atomic coordinates, bond lengths and angles are presented in Tables S1 to S3. †

Table 3 Selected bond lengths and angles at Ru for the coordination sphere of Λ-α-[Ru(*S*,*S*-picchxnMe$_2$)(dpqC)](ClO$_4$)$_2$·0.5H$_2$O

Bond lengths/Å

N(1)	N(2)	N(5)	N(6)	N(7)	N(8)
2.110(8)	2.095(9)	2.147(8)	2.154(8)	2.08(1)	2.072(9)

Bond angles/°

	N(2)	N(5)	N(6)	N(7)	N(8)
N(1)	78.7(4)	98.9(4)	175.5(3)	87.1(4)	95.6(4)
N(2)		173.7(4)	101.5(4)	94.2(3)	88.0(3)
N(5)			81.4(4)	79.9(3)	98.1(4)
N(6)				97.4(3)	79.8(3)
N(7)					176.9(4)

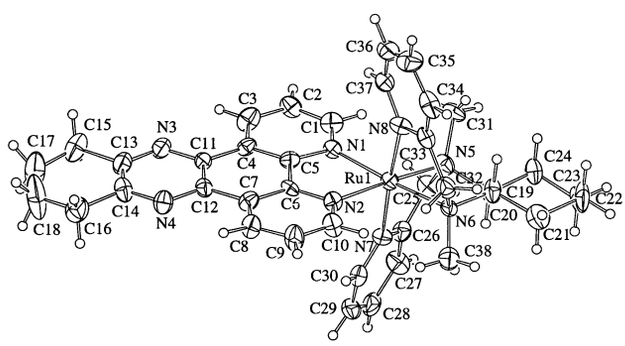


Fig. 2 An ORTEP plot (30% thermal ellipsoids) with the atom numbering scheme of the cation.

CCDC reference number 192811.

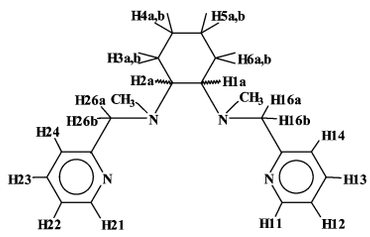
See http://www.rsc.org/suppdata/dt/b2/b208369h/ for crystallographic data in CIF or other electronic format.

Results and discussion

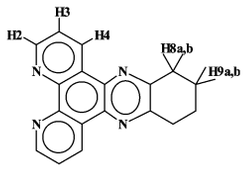
Metal complex synthesis, isolation and characterisation

The synthesis of picchxnMe$_2$ is well-established.[10] Purification of the starting materials pyridine-2-carboxaldehyde[22] and *rac*-, *R*,*R*- or *S*,*S*-diaminocyclohexane by distillation is required to give high yields. *N*-methylation of picchxn[8] can often result in the formation of the mono-*N*-methyl species, but elevation of the reaction temperature to 60 °C, addition of sodium cyanoborohydride in portions and adjustment of pH after each addition consistently results in *N*,*N*′-dimethylated product.

Metal complex synthesis as described by Searle[11] and Fenton[12] affords a mixture of both α- and β-stereoisomers, which can be separated by chromatography. The complex β-[Ru(picchxnMe$_2$)(dpqC)]$^{2+}$ was formed in greater amounts, often more than 90%, irrespective of tetradentate chirality. Yields of the α-isomer were relatively low, and at times, virtually undetectable in the reaction mixtures. A method for the synthesis of α-[Ru(picchxnMe$_2$)(dpqC)]$^{2+}$ in significant quantities was necessary as the α configuration, with its C_2 symmetry, is of particular interest for investigating metal complex interactions with DNA.



picchxnMe$_2$



dpqc

Two methods are reported which yield each structural isomer (α or β) with high purity. The formation of α-[Ru(picchxnMe$_2$)(dpqC)]$^{2+}$ was achieved *via* the intermediate α-[Ru(picchxnMe$_2$)I$_2$], which was subsequently refluxed with the planar ligand, dpqC, to obtain the product. Recrystallisation from ethanol/acetone and chromatography gave the pure complex, reproducibly. The previously described method[11,13] using [Ru(DMSO)$_4$Cl$_2$] afforded 90% β-[Ru(picchxme$_2$)(dpqC)](PF$_6$)$_2$ and by reducing the reaction temperature, a yield of some 98% could be attained. Clearly, the β-isomer is the kinetic product. Isolation of pure α- or β-isomers is achieved by elution using 0.1 M disodium (−)-*O*,*O*′-dibenzoyl-*R*,*R*-tartrate of the complex on an SP-Sephadex column. The isomers elute as two distinct bands with the β-isomer being eluted first in our case. Since our aim was to synthesise metal complexes with predetermined chirality we did not attempt to resolve the compounds by column chromatography we only used this thechique to purify the isomers.

^{1}H NMR spectra obtained for α- and β-[Ru(picchxme$_2$)(dpqC)](PF$_6$)$_2$ are typical of other published ^{1}H NMR spectra of analogous Ru(II) complexes.[10,12,23] NMR assignments were based on 1D NMR and 2D NOESY and COSY experiments. Proton numbering is illustrated in Table 2. Fig. 3 shows the

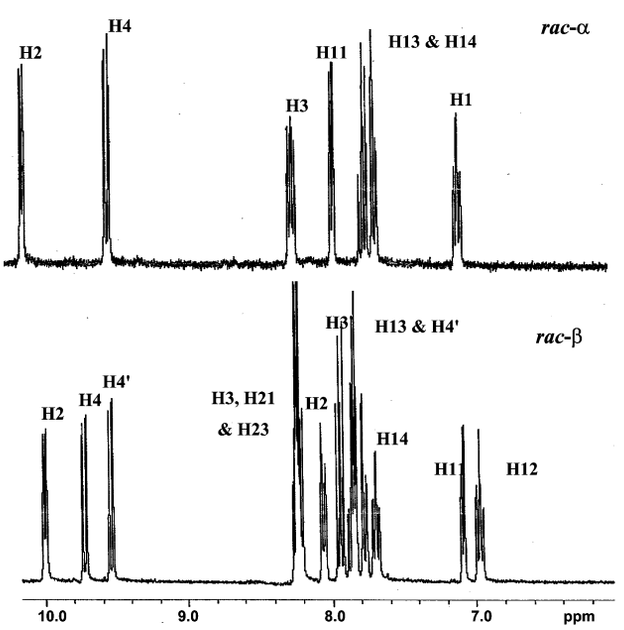


Fig. 3 Aromatic regions of the 300 MHz ^{1}H NMR spectra of *rac*-α- and *rac*-β-isomers of [Ru(picchxnMe$_2$)(dpqC)]$^{2+}$ in acetone-d_6.

NMR spectrum (aromatic region) of α-[Ru(picchxnMe$_2$)(dpqC)](PF$_6$)$_2$. The relatively simple proton spectrum of the α-complex is attributable to its symmetry. In the NMR spectrum of *rac*-α-[Ru(picchxnMe$_2$)(dpqC)](PF$_6$)$_2$, resonances from the dpqC protons are easily distinguished from the picchxnMe$_2$ protons by integration and COSY correlation. In the latter, two proton spin systems were observed for dpqC, the first belonging to the aromatic protons is found most downfield between 10.2 and 9.5 ppm (H2, H3, H4); see the Supplementary Material.† The second dpqC spin system resides in the upfield region, and is associated with the aliphatic cyclohexane protons (H8a,b, H9a,b).

Both NOESY and COSY spectra were used to assign the picchxnMe$_2$ tetradentate resonances. The aromatic pyridyl spin system (H11, H12, H13, H14) was found in the downfield region. H11 and H14 were assigned on the basis of weak NOE correlations to the aromatic protons of dpqC. Aliphatic proton signals observed between 1.2 and 5.3 ppm have characteristic resonances, the *N*-methyl groups being distinguished by a singlet with appropriate integration. Cyclohexane protons were found as single spin systems (H4a,b–H5a,b; H3a,b–H4a,b; H1a,b) in the COSY spectra. H16a and H16b signals were found in the 5.3–5.0 ppm region, characterised by individual doublet resonances.

The loss of formal C_2 symmetry when the β topology is adopted is clearly illustrated by the NMR spectra. As a result of the β-geometry, one of the pyridyl rings is more "face to face" with the dpqC. This causes protons on this pyridyl unit to become deshielded and the affected protons are shifted to a small extent further downfield than the other corresponding protons, H4 (9.54 ppm) – α-complex, H4′ (9.54 ppm) and H4 (9.72 ppm) β-complex (Fig. 3).

Assignment of the β-complex was made by the same method as the α-complex. The dpqC resonances were split into three spin systems. Two are aromatic resonances (H2, H3, H4 and H2′, H3′, H4′) and the other the aliphatic cyclohexane ring resonances (H8a,b, H9a,b). The pyridyl picchxnMe$_2$ aromatic resonances were assigned to two spin systems (H11, H12, H13, H14 and H21, H22, H23, H24). NOESY spectra assigned the protons (H11 and H14, H21 and H24) by use of relative NOE intensities between the dpqC protons and molecular modeling measurements. The H11 and H21 resonances (7.98 ppm) were assigned through observation of a weak NOE between the resonance at 10.15 ppm and the H2/H2′ (dpqC) protons, as the H11–H2 and H21–H2′ distances are shorter than the H2–H14 and H2′–H24 distances.

Assignment of the aliphatic picchxnMe$_2$ region also showed resonance splitting due to loss of symmetry. The *N*-methyl resonances appear as two singlets, while the cyclohexane resonances were split into two separate spin systems in the COSY spectra (H4a,b–H5a,b; H3a,b–H4a,b; H1a and H4a,b–H5a,b; H3a,b–H4a,b; H2a). Methylene (H16a,b and H26a,b) resonances were assigned to a singlet peak belonging to the H26a,b protons, and into two doublets, H16a and H16b; each methylene resonance was assigned by NOESY correlations.

Analysis of NMR spectra of *rac*-α-[Ru(pichxnMe$_2$)(dpqC)](PF$_6$)$_2$ and Λ-α-[Ru(pichxnMe$_2$) (dpqC)](PF$_6$)$_2$ in acetone-d_6 indicated apparent inconsistencies concerning the chemical shifts of the dpqC protons. Fig. 4 shows three NMR spectra, that of concentrated *rac*-α: dilute Λ-α (approximately 1 to 4); and concentrated Λ-α-[Ru(pichxnMe$_2$)(dpqC)](PF$_6$)$_2$ complexes. The concentrated solutions gave a signal for H4 at 9.54 ppm for the *rac*-α complex and 9.01 ppm for the Λ-α-complex. This upfield shift of H4, and to a lesser extent of H3, is thought to result from interaction with another complex molecule in solution as found for other aromatic systems.[24] To test this hypothesis the Λ-α-complex solution was diluted, whereupon the signals of the H4 and H3 protons of dpqC migrated downfield. This shift supports the idea that self-association in concentrated solution affects the chemical shift of the dpqC protons of the Λ-α-isomer, and it is noted that such interactions are different for optically active and racemic systems though differentiation of Δ and Λ have been achieved by NMR spectroscopy.[23] Assignments were confirmed by COSY spectra (see the Supplementary Material†); Kidd[25] observed similar π stacking interactions for related picen-based compounds. When metal complexes associate in solution, by 'stacking' with an adjacent metal complex, the interaction is influenced by the chirality of each metal complex. For Λ-α, only Λ–Λ inter-

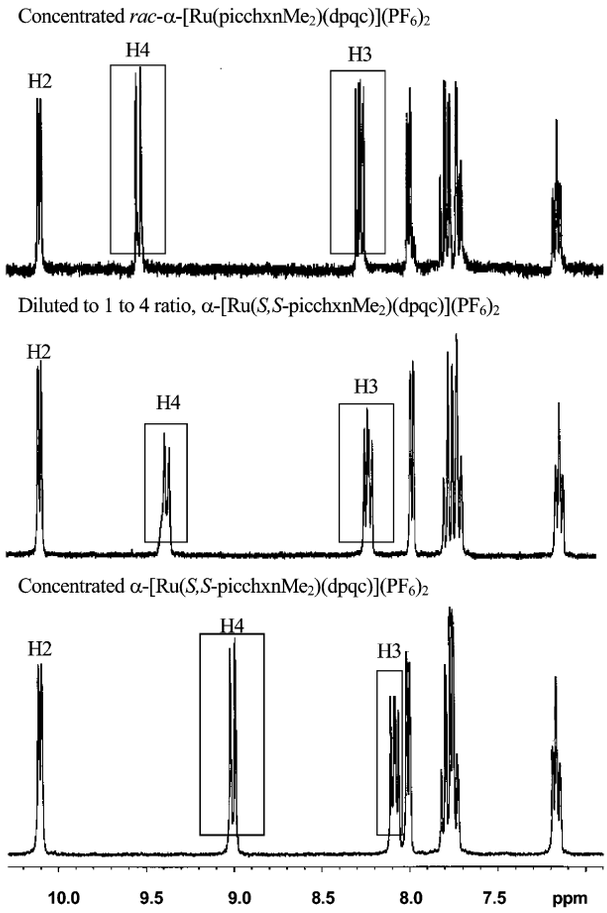


Fig. 4 The ^{1}H NMR spectra of *rac*-α- and Λ-α-[Ru(*S*,*S*-picchxnMe$_2$)(dpqC)]$^{2+}$. The spectra illustrate the different NMR shifts observed for the H3 and H4 dpqC protons at different concentrations.

actions are available, but for *rac*, these plus Δ–Λ interactions are possible. Indeed, the spectroscopic differences must arise because of diastereisomer interaction. Furthermore, π stacking is evident in the crystal structure of Λ-α-[Ru(*S*,*S*-picchxnMe$_2$)-(dpqC)](ClO$_4$)$_2$·0.5H$_2$O (Fig. 5), between the dpqC rings. This interaction may well reflect that evident in concentrated solutions.

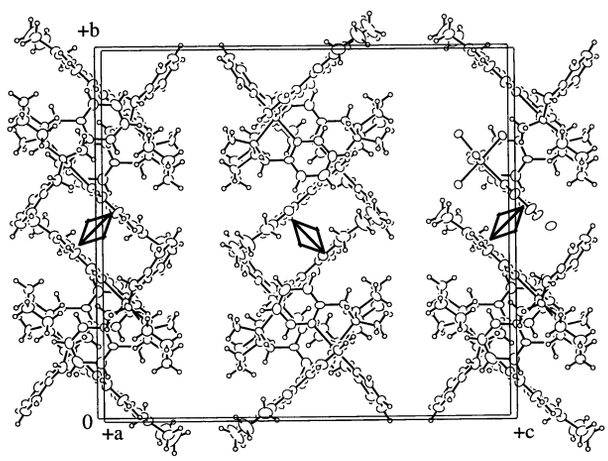


Fig. 5 Projection of the cell contents of Λ-α-[Ru(*S*,*S*-picchxnMe$_2$)-(dpqC)](ClO$_4$)$_2$·0.5H$_2$O, showing the stacking of the dpqC ligand (arrows).

Circular dichroism

Although ^{1}H NMR experiments can confidently be used in these systems to assign a particular geometric configuration,[24] X-ray crystallography is usually unequivocal for determining detailed molecular structure. Circular dichroism spectroscopy can only distinguish between Ru(II)-based enantiomers and absolute configurations can at this stage only be confidently assigned after X-ray analysis due to the lack of data for these d^6 systems. Here for the first time for this class of complexes, it has been possible to relate the absolute configuration of the complex to its CD spectrum. In these species considerable charge transfer involving the metal-based transitions is manifested in the electronic spectrum. However, we note that the bimodal distribution of the visible CD spectrum of the Λ-α-isomer positional transitional longer wavelengths, parallels that of related Ru(II) complexes of diimines such as 1,10-phenanthroline.[26] At this stage it is only possible to argue configuration by analogy, but further work along these lines with related Ru(II) complexes with tetradentates and planar diimines is in progress. It is anticipated that this wider study will cast further light on the chiroptical properties of these kinds of species.

X-Ray crystallography

Crystals of *rac*-α-[Ru(picchxnMe$_2$)(dpqC)](ClO$_4$)$_2$·0.5H$_2$O and Λ-α-[Ru(*S*,*S*-picchxnMe$_2$)(dpqC)](ClO$_4$)$_2$·0.5H$_2$O, grown from an ethanol/acetone mixture, were suitable for X-ray analysis. An ORTEP[14] diagram is shown in Fig. 2 of both structures, although it was discovered only after data had been collected that Δ,Λ-α-[Ru(picchxnMe$_2$)(dpqC)](ClO$_4$)$_2$·0.5H$_2$O was a conglomerate that is a mixture of Δ and Λ-α-[Ru(picchxnMe$_2$)-(dpqC)](ClO$_4$)$_2$ crystals. Assignment of the absolute configuration of Λ-α-[Ru(*S*,*S*-picchxnMe$_2$)(dpqC)](ClO$_4$)$_2$·0.5H$_2$O is important because it proves for the first time that the tetradentate *S*,*S*-picchxnMe$_2$ exclusively forms the Λ-enantiomer of the α-isomer. The CD spectrum of Λ-α-[Ru(*S*,*S*-picchxnMe$_2$)(dpqC)]$^{2+}$ is shown in Fig. 6, and may be used to assign the absolute configuration of the related systems by analogy.

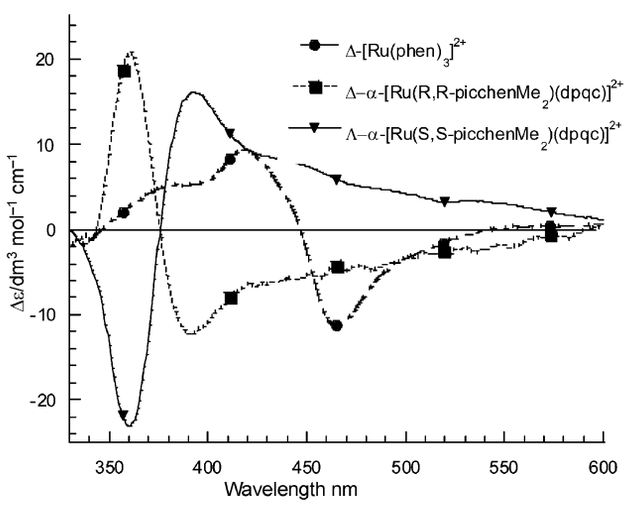


Fig. 6 The CD spectrum of Δ-α-[Ru(*R*,*R*-picchxnMe$_2$)(dpqC)]$^{2+}$, Λ-α-[Ru(*S*,*S*-picchxnMe$_2$)(dpqC)]$^{2+}$ and Λ-[Ru(phen)$_3$]$^{2+}$ as solutions. The blank spectrum (acetone/water) has been subtracted.

Λ-α-[Ru(*S*,*S*-picchxnMe$_2$)(dpqC)]$^{2+}$ has a coordination geometry that is distorted from octahedral as a consequence of the small bites of the dpqC and picchxnMe$_2$ ligands (Table 3). Ruthenium–dpqC and ruthenium–picchxnMe$_2$ bonds are within the ranges 2.110(8)–2.095(9) Å and 2.072(9)–2.154(1) Å, respectively, and all other distances and angles are quite normal.

Conclusion

Tetradentate metal complexes of the type of α- and β-[Ru(picchxnMe$_2$)(dpqC)]$^{2+}$ have been prepared. The enantio-

and stereoselective preparations of α- and β-[Ru(picchxnMe_2)(dpqC)]$^{2+}$ indicate that synthetic control can be achieved for complexes of the tetradentate ligand. The crystal structure of Λ-α-[Ru(*S*,*S*-picchxnMe_2)(dpqC)](ClO_4)$_2$·0.5H_2O confirms its absolute configuration and for the first time CD assignment can be made with confidence. ^{1}H NMR spectra of Λ-α-[Ru (*S*,*S*-picchxnMe_2)(dpqC)]$^{2+}$ and *rac*-α-[Ru(picchxnMe_2)(dpqC)]$^{2+}$ indicate that each is involved with π–π stacking interactions in solution.

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