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Structural and photophysical characterisation of coordination and optical isomers of mononuclear ruthenium(II) polypyridyl 1,2,4-triazole complexes †

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The X-ray crystal structure of the N^2 isomers of the $Ru(bipy)_2$ complexes of Hphpztr (**1**) and Hpztr (**2**), (bipy = 2,2′-bipyridine, Hphpztr = 2-(5′-phenyl-4′*H*-[1,2,4]triazol-3′-yl)pyrazine and Hpztr = 2-(4′*H*-[1,2,4]triazol-3′-yl)pyrazine) are reported. The molecular structure obtained for **2** demonstrates an interesting structural aspect in the sharing of a single proton between two molecular units. The isolation of the Δ and Λ stereoisomers of **1** and $[Ru(phen)_2(pztr)]^+$ (phen = 1,10-phenanthroline) (**3**) by semipreparative HPLC is also reported. The compounds obtained are characterised by electronic spectroscopy and particular attention is paid to the photophysical properties of Δ and Λ isomers of **1** and **3**, in chiral enantiopure and racemic solvents.

Introduction

There is continuing interest in the photochemical and photophysical properties of ruthenium polypyridyl complexes[1] due to their well-recognised role in photomolecular devices.[2] The issue of isomerism in terms of both stereochemistry[3] and coordination mode[4] is of particular relevance to the large and often complex systems employed in these studies.[5,6] The importance of stereochemistry and, in particular, chirality is well illustrated in the studies carried out on the stereoselective interaction of transition metal complexes with DNA[7] and proteins.[8] The isolation of the stereoisomers of mono- and polynuclear ruthenium(II) and osmium(II) diimine complexes has been reviewed recently.[3]

One class of compounds, which has been investigated in great detail, are Ru(II) polypyridyl complexes of ligands such as 2-(4′*H*-[1,2,4]triazol-3′-yl)pyrazine) and its analogues (see Fig. 1). These compounds show very unusual photophysical behaviour and detailed investigations have shown that the emitting ^{3}MLCT state can be localised on either the pyrazine or 2,2′-bipyridyl ligands depending on the protonation state of the triazole ring. In addition dual emission is observed for these complexes over a wide temperature range.[9] One complication in the study of these compounds is the formation of coordination isomers due to the presence of two inequivalent nitrogen atoms in the triazole ring, (*i.e.* N^2 and N^4, see Fig. 1). NMR studies were used to tentatively assign the coordination mode of the triazole rings, however, so far no X-ray data have been reported for Ru(II) polypyridyl complexes of this type to confirm this assignment. Another intriguing observation is that under certain conditions ruthenium complexes containing 'pyrazine-triazole' ligands are obtained with 1½ PF_6^- counter ions, rather than one or two as expected from the two possible protonation states of the triazole ring. Finally, no efforts have been made to isolate and investigate the optical isomers in compounds of this type.

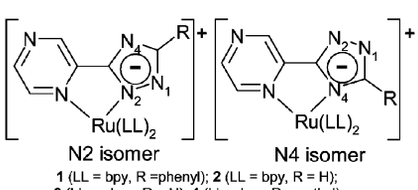

Fig. 1 Structures of compounds **1**–**4**.

In the present contribution these structural issues are addressed. The X-ray crystal structures of the compounds $[Ru(bipy)_2(phpztr)]PF_6{\cdot}CH_3OH$ (**1**) and $H([Ru(bipy)_2(pztr)])_2(PF_6)_3{\cdot}H_2O$ (**2**) (bipy = 2,2′-bipyridine, Hphpztr = 2-(5′-phenyl-4′*H*-[1,2,4]triazol-3′-yl)pyrazine and Hpztr = 2-(4′*H*-[1,2,4]-triazol-3′-yl)pyrazine) are reported. The resolution of the Δ and Λ stereoisomers of **1** and $[Ru(phen)_2(pztr)]^+$ **3** (phen = 1,10-phenathroline), by semipreparative HPLC is described also. The electronic properties of the compounds obtained are discussed and particular attention is given to the photophysical properties of the enantiomers of **1** and **3**.

Results and discussion

Synthetic considerations

The preparation of compounds **1**–**3** was carried out using standard procedures.[4,6] As expected from steric considerations, the presence of a phenyl group in the 5 position of the 1,2,4-

† Electronic supplementary information (ESI) available: analytical and semipreparative HPLC chromatograms, CD and UV/vis spectra. See http://www.rsc.org/suppdata/dt/b3/b301961f/

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triazole ring results in one main fraction being obtained for **1**. This was further purified by column chromatography and recrystallisation.[4] The molecular structure (*vide infra*) obtained for the compound indicates that, as expected, in the isomer obtained the triazole ring is coordinated *via* the N^2 atom (Fig. 1). For compounds **2** and **3**, in which the 5 position of the 1,2,4-triazole ring is an –H, the absence of steric constraints results in equimolar amounts of both N^2 and N^4 isomers. After separation on neutral alumina the pure isomers were obtained upon crystallisation of the appropriate fraction. The compounds obtained are pure as evidenced from NMR and HPLC analysis, however, elemental analysis indicates the presence of 1½ PF_6^- counter ions for every ruthenium centre. To investigate this rather surprising observation crystals of **2** (N^2 isomer) were grown and its molecular structure was determined.

X-Ray crystallography

The molecular structures of **1** and **2** are shown in Figs. 2 and 3, respectively. Complex **1** co-crystallised with disordered ethanol/water molecules, and a hexafluorophosphate counter anion (not shown). Complex **2** co-crystallised with disordered water molecules, and hexafluorophosphate counter anions (not shown). (see Experimerntal section). From the crystal structure it is clear that for both **1** (*via* N(1) and N(2) in Fig. 2) and **2** (*via* N(1) and N(4) in Fig. 3), the ligand is bound through the pyrazine-N and N^2 of the triazole ring (Fig. 1), as predicted by ^{1}H NMR spectroscopy.

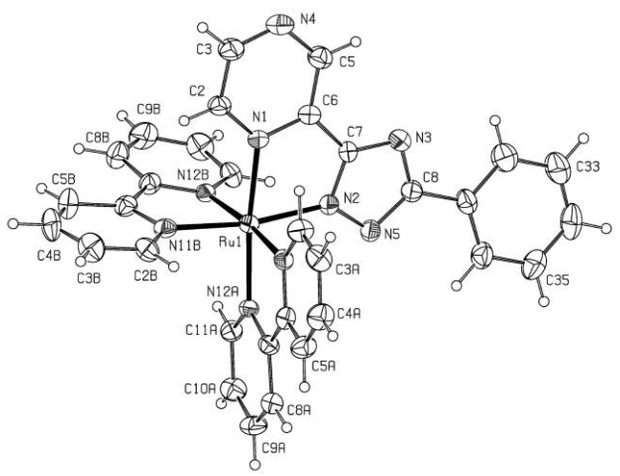

Fig. 2 Molecular structure and labelling scheme for **1**.

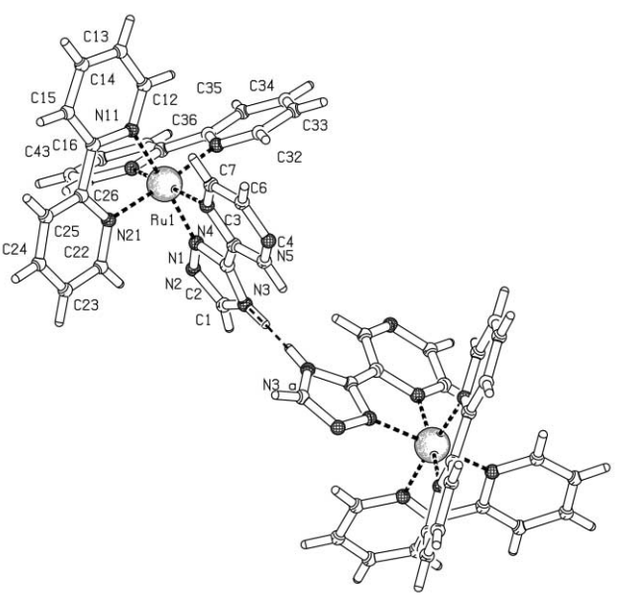

Fig. 3 Diagram of the hydrogen bridged dimer for **2**.

For both **1** [N(1)–Ru(1)–N(2) 78.2(4)°] and **2** [N(1)–Ru(1)–N(4) 78.18(18)°] the bite angle corresponds well with the bite angle obtained for $[Ru(bipy)_2$(3,5-bis(pyridin-2-yl)-1,2,4-triazole)$]PF_6\cdot\frac{1}{2}H_2O$ of 78(1)°, 77.98(6)° for $[Ru(bipy)_2$(3-(pyrazin-2′-yl)-5-(pyridin-2″-yl)-1,2,4-triazole)$]PF_6\cdot$MeOH,[10] and 77.9(1)° for $[Ru(bipy)_2$(3-(2-hydroxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole)$]PF_6\cdot CH_3COCH_3$.[11] Bite angles of 78.4(4) and 78.6(4)° {**1**} and 79.0(2) and 79.01(19)° {**2**} for bipyridyl ligands are typical for this class of complex. Ruthenium–nitrogen distances of 2.036(10)–2.069(9) Å {**1**} and 2.023(4)–2.071(4) Å {**2**} are also comparable to those found in other complexes.[12] For both **1** (Ru(1)–N(1) 2.069(9) Å) and **2** (Ru(1)–N(4) 2.071(4) Å), the ruthenium–pyrazine bond is the longest Ru–N bond in the complex.

An interesting crystallographic feature observed for **2** is the presence of a shared hydrogen atom between the N^3 of two molecular units (Fig. 3). That both nitrogens are bonded to the same proton is evident from the intermolecular nitrogen to nitrogen separation (see Fig. 3). The intermolecular N ··· N distance for the N–H ··· N hydrogen bond is 2.672(7) Å. This observation is important and is in agreement with CHN analysis (see Experimental section). A common feature of pyrazine-triazole based Ru(II) complexes is their tendency to crystallise from aqueous solutions to give CHN analysis suggesting a mixed protonation state. The X-ray structural data presented here provides considerable support to the validity of this assumption.

Separation of the stereoisomers

The Δ and Λ stereoisomers of **1** were separated using HPLC employing a chiral carbamate stationary phase. The separation achieved using this column is excellent with retention times of 12.5 min (Λ) and 25.2 min (Δ) (see ESI, † Fig. S1). Similar results were observed on an analytical column for the related complex, $[Ru(bipy)_2(mepztr)]^+$ (**4**) (Hmepztr = 2-(5′-methyl-4′*H*-[1,2,4]-triazol-3′-yl)pyrazine) (Fig. 1), however it is very noticeable that the retention times (7.61 and 10.28 min) for the enantiomers of this complex were much shorter than for **1**. This is not unexpected considering the reversed phase nature of the column would favour the retention of the more lipophillic phenyl containing complex **1**.

The analytical separation of the stereoisomers of **2** has been reported earlier by Gasparrini *et al.*[13,14] The analytical and semi-preparative separation of **3** was carried out using a non-commercial teicoplanin based column (see ESI, † Fig. S2 and S3).[13]

Circular dichroism spectroscopy

The CD spectra for the Δ and Λ stereoisomers **3** are shown in Fig. 4. As expected both stereoisomers exhibit very strong opposite (but equal) Cotton effects. Identification of each of the stereoisomers as either Λ or Δ is made by comparison with CD spectra of $[Ru(bipy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ of known

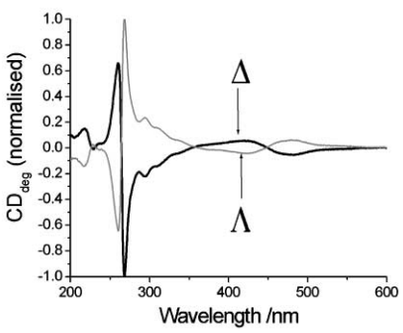

Fig. 4 CD spectra for the Δ and Λ stereoisomers of **3** in CH_3CN.

configuration.[3,15] The CD spectra of the stereoisomers of **1** (see ESI,† Fig. S4) and **3** are, to a first approximation, very similar and show only very minor differences in the position of maxima and minima. The first enantiomer of **1** to elute on the carbamate based chiral HPLC column has a CD spectrum featuring two bisignate couplets in the LCT (ligand centred tansitions, π–π*) (250–300 nm) and MLCT (350–520 nm) regions, with negative signs for the lower wavelength bands within each couplet. These spectral features are characteristic of complexes having Λ configuration (see ESI,† Fig. S4). The elution order on the carbamate column is thus Λ before Δ for **1**. The same elution order was obtained for the enantiomers of **3** on the teicoplanin column.

Electronic properties

The absorption and emission properties of all complexes are reported in Table 1. The lowest energy absorption feature for the ruthenium complexes is assigned to a singlet metal-to-ligand charge-transfer (^{1}MLCT) transition ($\log\varepsilon \sim 4$) by comparison with similar Ru(II) polypyridyl complexes.[2–6] All compounds show strong absorptions ($\log\varepsilon \sim 5$) at about 280 nm which are π–π* in nature. Overall the electronic properties of all complexes are typical for pyrazyl-1,2,4-triazole complexes.[6] All complexes examined are luminescent in acetonitrile at room temperature and at 77 K. The ruthenium complexes examined all emit in the 650–700 nm region and a large blue shift is observed between 300 and 77 K, typical for ^{3}MLCT emission (Table 1).[4]

The photophysical properties of the stereoisomers of **1** and **3** have been examined in racemic 1-phenylethanol, in (*S*)-(−)-1-phenylethanol (Table 2) and in acetonitrile (Table 1). 1-Phenylethanol was chosen as a solvent for two reasons. First the solvent is inherently chiral and can be obtained in enantiomerically pure form. Secondly the presence of a phenyl group and a hydroxyl moiety allows for the possibility of a π-stacking interaction and hydrogen bonding interaction between the pyridyl/phenyl/pyrazyl-rings of the complex and the solvent phenyl group and hydroxyl group, respectively. Such interactions have been reported by Patterson and Keene[16] and by Hesek *et al.*.[17]

For both **1** and **3** no differences in the electronic or photophysical properties between the enantiomeric pairs and a racemic mixture were observed as is apparent from Table 2. The slight increase in lifetime observed in (*S*)-(−)-1-phenylethanol compared with the racemic solvent is probably due to different H_2O contents in the solvents employed. In each case measurements were recorded under identical conditions of solvent and temperature.

The excited ^{3}MLCT state of $[Ru(bipy)_3]^{2+}$ is known to possess a considerable amount of charge transfer to solvent character (CTTS)[18] and this is expected to be the case for other ruthenium(II) polypyridyl complexes. Hence for the systems under examination, excited state interaction with the solvent would be expected to be substantial. The use of chiral solvents amenable to intermolecular interactions such as π-stacking and hydrogen bonding could in principle, affect the electronic structure of stereoisomers of transition metal complexes.

However, for such intermolecular interactions to produce measurable differences in the photophysical properties of such complexes, they must be sufficiently strong/non-random to affect the complex over the timescale of the lifetime of the excited states of such molecules. In fluid solutions, and indeed in glassy matrices, the randomness of the solvent orientation around the complex is almost complete. Hence, if solvent–solute interactions significantly effect the excited state lifetime then multi-exponential behaviour would be anticipated. Only if such intermolecular interactions are significant will differences in the photophysical properties of the stereoisomers be observed. For each of the enantiomeric pairs of **1**, or **3** both intramolecular and intermolecular interactions (in achiral solvents) are identical and hence no differences in their photophysical properties are expected. However, the use of enantiopure hosts could, in principle, result in differential stabilisation of the enantiomers. No differences are observed in the photophysical properties of the stereoisomers of **1** or **3** in both achiral and chiral solvents.

Table 1 Electronic properties

	λ_{max}(abs.)/nm ($\log\varepsilon$)[a]	λ_{max}(em.)/nm (τ/ns)[a]	λ_{max}/nm (τ/μs)[b]
1	453 (4.02)	670 (220)	645 (6.7)
2	456 (3.81)	668 (250)	640 (6.0)
3	430 (3.68)	654 (860)	595 (9.2)

N² isomers only. [a] All measurements in deaerated acetonitrile at 298 K. [b] In EtOH–MeOH (1 : 1) at 77 K.

Conclusions

The confirmation of the coordination mode in two Ru(II) polypyridyl complexes containing pyrazine-triazole based ligands as being *via* the N² position justifies previous assignments. In addition, the X-ray structure of **2** in a mixed protonation state confirms the interpretation of CHN results for this class of complex. The photophysical results reported here are in agreement with those obtained for $[(Ru(bipy)_2)_2(bpt)]^{3+}$ (Hbpt = 2,5-bis(pyrid-2′-yl)-4*H*-1,2,4-triazole), and indicate that the presence of stereoisomers does not affect the general photophysical properties in both mononuclear and binuclear complexes. That no differences in the photophysical properties of the stereoisomers are observable either at 77 K or at room temperature in both racemic and enantiomerically pure solvents, suggests strongly that the differences between the stereoisomers in either ground or excited state structure are not significant.

Experimental

Materials

All solvents employed were of HPLC grade. For emission measurements UVASOL grade solvents were employed. Racemic and enantiopure (*S*)-(−)-1-phenylethanol (Aldrich) were used as received. All reagents employed in synthetic procedures were of reagent grade or better. Hpztr[6] and

Table 2 Spectroscopic data

	rac-1-Phenylethanol	(*S*)-(−)-1-Phenylethanol	
	τ/ns (λ_{max}/nm) 298 K[a]	τ/ns (λ_{max}/nm) 298 K[a]	τ/μs (λ_{max}/nm) 77 K
1a	160 (680)	165 (680)	5.0 (610)
1b	161 (680)	168 (680)	5.2 (610)
3a	230 (657)	223 (657)	7.6 (590)
3b	229 (656)	219 (657)	7.6 (590)

N² isomers only. [a] Samples deaerated by argon purge, λ ±5 nm (τ ±5%).

Table 3 X-Ray experimental crystal data for **1** and **2**

	1	**2**
Empirical formula	$RuC_{32}H_{24}N_9 \cdot PF_6 \cdot 0.7C_2H_5OH \cdot 0.5H_2O$	$RuC_{26}H_{20.5}N_9 \cdot 1.5PF_6 \cdot 0.75H_2O$
Formula weight/g mol^{-1}	821.90	791.52
Temperature/K	293(2)	293(2)
Wavelength/Å	0.71073	0.71073
Symmetry, space group	Triclinic, $P\bar{1}$	Orthorhombic, *B*2*cb*
Unit cell dimensions:		
a/Å	12.232(17)	17.4944(15)
b/Å	12.301(2)	17.5143(16)
c/Å	13.296(2)	19.5605(19)
α/°	78.996(12)	
β/°	64.996(10)	
γ/°	77.151(10)	
V/Å^3, *Z*	1757.0(5), 2	5993.4(10), 8
D_c/Mg m^{-3}	1.554	1.738
Crystal dimensions/mm	0.15 × 0.15 × 0.1	0.25 × 0.15 × 0.1
μ/mm^{-1}	0.566	0.697
F(000)	830	3126
θ range for data collection/°	1.9–25.3	2.1–27.1
Limiting indices	$-14 \le h \le 1$; $-14 \le k \le 14$; $-15 \le l \le 14$	$0 \le h \le 22$; $0 \le k \le 22$; $0 \le l \le 25$
No. reflections collected	7145	3430
Independent reflections (R_{int})	4344 (0.0433)	2184 (0.052)
$\Delta\rho/\sigma$ (mean)	0.063 (0.005)	0.027 (0.004)
Data/restraints/parameters	6202/162/596	3430/88/533
GOF F^2	1.023	0.977
Final *R*1 [$I > 2\sigma(I)$]	0.0653	0.0351
Final *R*1 (all data)	0.1540	0.0568
Largest difference peak and hole/e Å^{-3}	1.31/−0.76	0.303/−0.368

cis-$[Ru(LL)_2Cl_2] \cdot 2H_2O$[19] (LL = 2,2′-bipyridine or 1,10-phenanthroline) were prepared by literature methods. $[Ru(bipy)_2(mepztr)](PF_6)$ **4** was available from earlier studies.[6]

Syntheses

2-(5′-Phenyl-4′*H*-[1,2,4]triazol-3′-yl)pyrazine (Hphpztr). Sodium metal (0.8 g) were added (carefully) to 35 cm^3 of methanol followed by the addition of 2-pyrazine carbonitrile (10.9 g, 104 mmol). The solution was heated at reflux for 3 h after which, it was allowed to cool and phenyl hydrazide (17 g, 104 mmol) was added and the solution refluxed for a further 15 min yielding a dark yellow solution. Yellow crystals formed on cooling to room temperature overnight and were filtered under vacuum and air dried for one hour. The crystals were dissolved in 40 cm^3 of ethylene glycol and refluxed for 3 h. On cooling overnight the white target ligand precipitated and was collected by vacuum filtration, followed by washing with 50 cm^3 methanol. The product was recrystallised from hot ethanol. Yield of Hphpztr (15 g, 64%); *m*/*z* 224 (HM^+); ^{1}H NMR (400 MHz, D_6-DMSO): δ 9.35 (d, 1H, pz-H^3), 8.795 (dd, 1H, pz-H^5), 8.765 (d, 1H, pz-H^6), 8.11 (d, 2H, Ph-H^2/H^6), 7.54 (dd, 2H, Ph-H^3/H^5), 7.49 (t, 1H, Ph-H^4)

$[Ru(bipy)_2(phpztr)](PF_6) \cdot 2H_2O$ (1). Hphpztr (0.63 g, 2.8 mmol) and *cis*-$[Ru(bipy)_2Cl_2] \cdot 2H_2O$ (1 g, 2.1 mmol) in 80 cm^3 were heated at reflux in ethanol–water (2 : 1) for 4 h. The ethanol was subsequently removed and the product precipitated with concentrated $NH_4PF_{6(aq)}$ solution. The precipitate was collected under vacuum and recrystallised from 30 cm^3 acetone–water (5 : 1) with two drops of conc. ammonia solution. The N^2 isomer was isolated by column chromatography on neutral alumina with acetonitrile as eluent (0.55 g, 25%). Crystals for X-ray studies were grown from ethanol solution (Found: C, 46.92; H, 3.02; N, 15.54; P, 3.47. $RuPF_6N_9C_{32}H_{24} \cdot 2H_2O$ requires C, 47.06; H, 3.19; N, 15.44; P, 3.80%); *m*/*z* 635 (M^+).

$H([Ru(bipy)_2(pztr)])_2(PF_6)_3 \cdot H_2O$ (2). *cis*-$[Ru(bipy)_2Cl_2] \cdot 2H_2O$ (0.5 g, 1 mmol) and Hpztr (0.3 g, 2 mmol) were heated at reflux in 50 cm^3 of ethanol for 8 h, after which the ethanol was removed by evaporation and the product redissolved in 10 cm^3 of water and precipitated with saturated aqueous NH_4PF_6. The complex was collected by vacuum filtration and recrystallised from acetone–water (5 : 1). The N^2 isomer was isolated by column chromatography as for **1** (720 mg, 90% {both N^2 and N^4 isomer combined}) (Found: C, 39.3; H, 2.70; N, 15.48. $RuP_{1.5}F_9N_9C_{30}H_{21} \cdot H_2O$ requires C, 39.25; H, 2.64; N, 15.85 %).

$H([Ru(phen)_2(pztr)])_2(PF_6)_3 \cdot H_2O$ (3). *cis*-$[Ru(phen)_2Cl_2] \cdot 2H_2O$ (0.53 g, 1 mmol) and Hpztr (0.3 g, 2 mmol) were heated at reflux in 50 cm^3 of ethanol for 8 h, after which the ethanol was removed by evaporation and the product redissolved in water a precipitated with saturated aqueous NH_4PF_6. The complex was collected by vacuum filtration and recrystallised from acetone–water (5 : 1). The N^2 isomer was isolated by column chromatography as for **1** (600 mg, 72% combined yield of N^4 and N^2 isomers) (Found: C, 42.86; H, 2.65; N, 14.55. $RuP_{1.5}F_9N_9C_{30}H_{20} \cdot H_2O$ requires C, 42.70; H, 2.49; N, 14.95%).

X-Ray crystallography

Data for **1** was collected on a Bruker P4 diffractometer using the XSCANS[20] software with graphite monochromated Mo-Kα radiation (Table 3). Data for **2** was collected on a Enraf Nonus CAD4 diffractometer with graphite monochromated Mo-Kα radiation (Table 3)[21] using the NRCVAX system of programs. Relevant experimental data are presented in Table 3. The structures were solved using direct methods and refined with the SHELXL-97 program[22] and the non-hydrogen atoms were refined with anisotropic thermal parameters. There is considerable disorder in the molecular structures of **1** and **2**. In **1** the hexafluorophosphate anion $[PF_6]^-$ anion is present as two half molecules residing on inversion centres both of which are disordered over two sites and which refine to site occupancy factors of 0.81(5)/0.19(5) and 0.58(13)/0.42(13) in the final refinement cycles. A partial occupancy molecule of ethanol was discerned and modelled in the penultimate stages of refinement with occupancies of 0.35 : 0.35 site occupancy together with a water molecule with occupancies of 0.25 : 0.25. Loose restraints using DFIX controls were used for the P–F/*cis*-F ⋯ F distances in the hexafluorophosphate anion, the C–O and O–H bond lengths, as well as DELU/ISOR controls for the components of the displacement ellipsoids in all three disordered moieties (anion/ethanol/water). In **2**, disorder is present in the hexafluorophosphate anions with the $[PF_6]^-$ anion which resides on a general position disordered over two sites with

occupancies of 0.522(16) and 0.478(16), respectively, and 0.33 : 0.17 for the half occupancy anion (per unit cell anion). Partial occupancy water is present which refines to a site occupancy factor of 0.75: the H atoms on water were located from difference maps and were treated as riding atoms with loose O–H bond length DFIX restraints.

CCDC reference numbers 204725 and 204726.

See http://www.rsc.org/suppdata/dt/b3/b301961f/ for crystallographic data in CIF or other electronic format.

Chromatography

Separation of the Δ and Λ stereoisomers of **1** was carried out using a JASCO Gulliver system equipped with a single-wavelength UV-visible detector set to 290 nm, Rheodyne injection valve and a Daicel Chiralcel OD–RH stainless steel (15 cm × 4.6 mm i.d.) carbamate based semi-preparative column. The column temperature was set at 28 °C and column pressure 40 kg cm^{-2}. Elution was with 0.1 M $NaPF_6$ water–acetonitrile (60 : 40 v/v). Separation of the Δ and Λ stereoisomers of **3** was carried out with semi-preparative HPLC using a chiral stationary phase (CSP 1) containing Teicoplanin bonded to silica gel microparticles, packed in a 250 × 10 mm i.d. column.[13,14] A Waters Delta Prep 3000 preparative HPLC apparatus, equipped with Knauer UV and RI detectors and a 7010 Rheodyne injector, was employed for the separation. Analytical control of the collected fractions was carried out on a Waters 2690 Separation Module equipped with a UV 481 detector set at 288 nm. Samples of **3** were dissolved in the eluent (40 mg mL^{-1}) and filtered through a 0.45-micron filter prior to injection. Typical column loadings were 10–15 mg per run, using CH_3CN–C_2H_5-OH–0.1 M $AcONH_4$ (40 : 40 : 20) mobile phase.

Elemental analysis

Performed for C, H, N and P at the Microanalytical Laboratory at University College Dublin.

^{1}H NMR spectra

Recorded on a Bruker Avance AC400 (400 MHz) NMR spectrometer. Peak positions are relative to residual solvent peaks.

Mass spectra

Mass spectra were obtained using a Bruker-EsquireLC_00050 electrospray ionization mass spectrometer at positive polarity with a cap-exit voltage of 167 V. Spectra were recorded in the scan range of *m*/*z* 50–2200 with an acquisition time of between 300 and 900 μs and a potential of between 30 and 70 V. Each spectrum was recorded by a summation of 20 scans.

Photophysical measurements

UV/Vis absorption spectra (accuracy ±2 nm) were recorded on a Shimadzu UV/Vis-NIR 3100 spectrophotometer interfaced with an Elonex PC466 using a UV/Vis data manager. Emission spectra (accuracy ±5 nm) were recorded at 298 and 77 K using a Perkin-Elmer LS50B luminescence spectrophotometer, equipped with a red-sensitive Hamamatsu R928 PMT detector, interfaced with an Elonex PC466 employing Perkin-Elmer Fl WinLab custom built software. Emission and excitation slit widths were 5 nm at 77 K and 10 nm at 298 K. Emission spectra are uncorrected for photomultiplier response. 10 or 2 mm pathlength quartz cells were used for recording spectra. Emission measurements at 77 K were carried out in a liquid-nitrogen filled glass cryostat, with the sample held in a borosilicate NMR tube. Circular dichroism (CD) spectra were recorded on a JASCO J-710 spectropolarimeter in CH_3CN at 25 °C. Time correlated single photon counting luminescence lifetime measurements were obtained using an Edinburgh Analytical Instruments (EAI) *T*ime-*C*orrelated *S*ingle-*P*hoton *C*ounting apparatus (TCSPC) comprising of two model J-yA monochromators (emission and excitation), a single photon photomultiplier detection system model 5300, and a F900 nanosecond flashlamp (N_2 filled at 1.1 atm pressure, 40 kHz), interfaced with a personal computer *via* a Norland MCA card. A 500 nm cut-off filter was used in emission to attenuate scatter of the excitation light (337 nm) luminescence was monitored at 650 nm. Data correlation and manipulation was carried out using EAI F900 software version 5.1.3. Samples were deaerated for 20 min using Ar gas before measurements were carried out, followed by repeated deaeration to ensure total oxygen exclusion. Emission lifetimes were calculated using a single exponential fitting function; Levenberg–Marquardt algorithm with iterative reconvolution (Edinburgh instruments F900 software). The reduced χ^2 and residual plots were used to judge the quality of the fits. Lifetimes are ±5%.

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