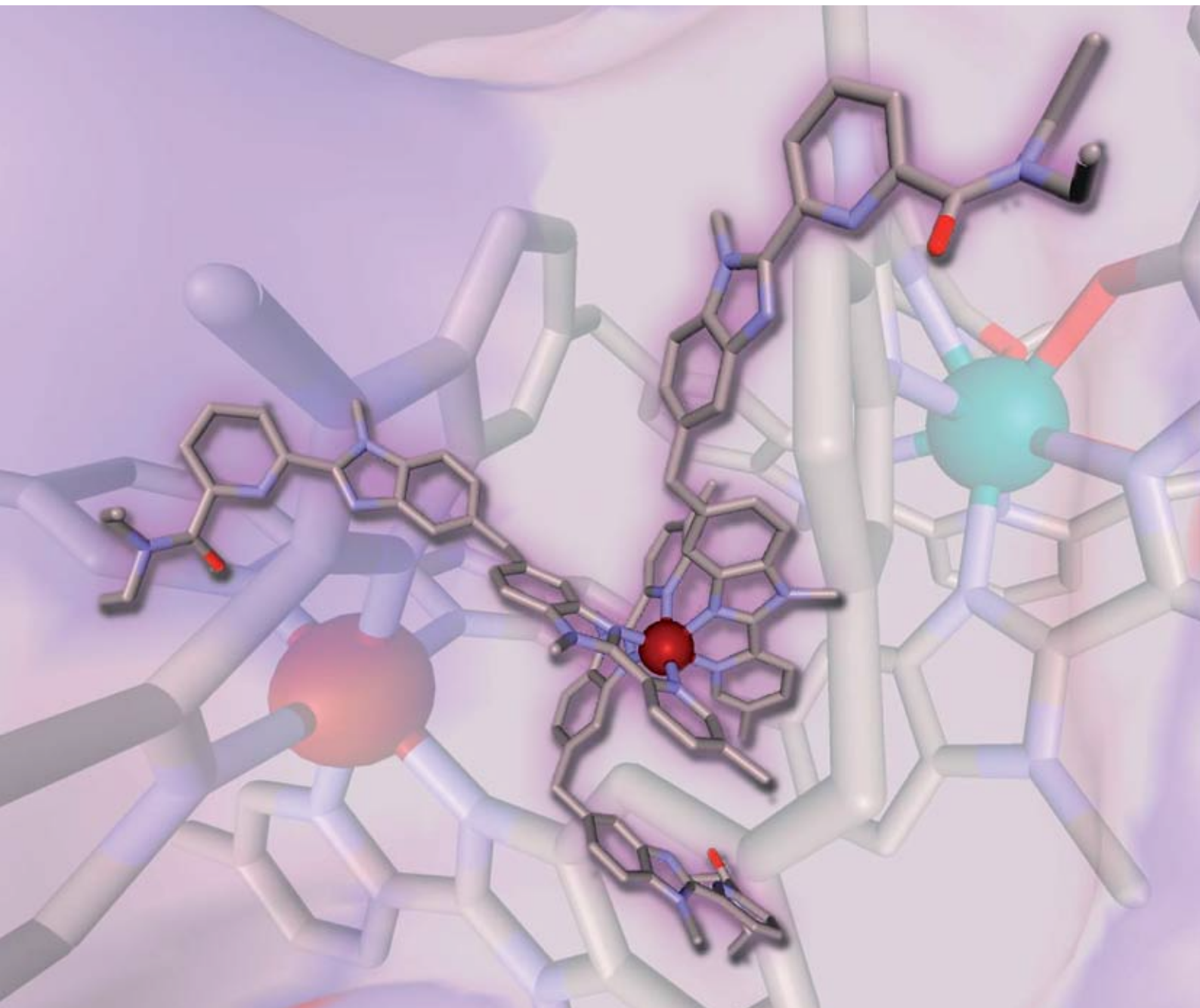


Dalton Transactions

An international journal of inorganic chemistry

www.rsc.org/dalton

Number 28 | 28 July 2008 | Pages 3621–3760



ISSN 1477-9226

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1477-9226(2008)28;1-#

Towards inert and preorganized d-block-containing receptors for trivalent lanthanides: The synthesis and characterization of triple-helical monometallic Os^{II} and bimetallic Os^{II}–Ln^{III} complexes†

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Received 6th December 2007, Accepted 26th March 2008

First published as an Advance Article on the web 9th May 2008

DOI: 10.1039/b718885d

The mononuclear Os^{II} complex [Os(L1)₃](PF₆)₂ (L1 = 5-methyl(1-methylbenzimidazol-2-yl)pyridine) is an obvious candidate for the design of an inert d-block-based tripodal receptor capable of binding and photosensitizing trivalent lanthanides (Ln^{III}). It has thus been prepared and its two enantiomeric meridional (Δ -*mer* and Λ -*mer*) and facial (*rac-fac*) isomers have been separated by ion-exchange chromatography. The optical isomers have been characterized by CD spectroscopy and assignments of absolute configuration confirmed by an X-ray crystallographic study of Λ -*mer*-[Os(L1)₃](PF₆)₂·1.5MeCN (monoclinic, *P*2₁, *Z* = 4). Comparison of the latter structure with that of racemic *fac*-[Os(L1)₃](PF₆)₂ (monoclinic, *C*2/*c*, *Z* = 8) and [Os(bipy)₃](PF₆)₂ (where bipy = 2,2'-bipyridine) shows minimal structural variations, but differences are observed in the photophysical and electrochemical properties of the respective compounds. Luminescence emissions from Os^{II} complexes of L1 are typically lower in energy, with shorter lifetimes and lower quantum yields than their bipy analogues, whilst metal-centred oxidation processes are more facile due to the enhanced π -donor ability of L1. The key relationships between these parameters are discussed. Finally, though challenged by (i) the low reactivity of many osmium precursors and (ii) the irreversible formation of competing side products, the synthesis and purification of the heterobimetallic triple-stranded helicate *HHH*-[OsLu(L2)₃](CF₃SO₃)₅ has been realised, in which L2 is a segmental ligand containing the same bidentate unit as that found in L1 further connected to a tridentate binding site adapted for complexing Ln^{III}. Its solid-state structure has been established by X-ray crystallography (triclinic, *P* $\bar{1}$, *Z* = 2).

Introduction

The last five years have seen a steady surge of interest in the use of d-block chromophores for the sensitisation of near infra-red (NIR) emitting trivalent lanthanides (Ln^{III}) such as Pr^{III}, Nd^{III}, Er^{III} and Yb^{III}.¹ Many of these chromophores, those containing Ru^{II} and Os^{II} in particular, possess long-lived (triplet) metal-to-ligand charge transfer (³MLCT) excited states which can be

efficiently populated from a range of excitation energies in the Vis/NIR region.^{1,2} A close match between donor/acceptor energy levels of the respective chromophore and Ln^{III} (Ln = Pr, Nd, Er, Yb) components can then facilitate rapid and efficient energy transfer, either through conjugated bridging ligands (double electron exchange mechanism) or through space (multipolar interaction).³ They thus hold great promise in (i) overcoming problems associated with the transparency of biological tissue, which only certain, typically lower energy, radiations are capable of penetrating and (ii) sensitising Ln^{III} emissions for luminescence imaging and immunoassays.¹ Furthermore, when both the d-block donor and the Ln^{III} acceptor have long-lived excited states, energy transfer can be monitored *via* the attenuation and growth of the respective donor and acceptor excited state lifetimes (or emission intensities) and valuable insight into the fundamental mechanism of energy transfer can be gained. NIR sensitisation is usually achieved by coordination of Ln(β -diketonate)₃ emitters to kinetically inert d-block chromophores such as polypyridyl Ru^{II} fragments (*e.g.* [Ru(bipy)₃]²⁺⁴ and [Ru(bipy)(CN)₄]^{2–1c,5}) (bipy = 2,2'-bipyridyl), Pt^{II} acetylides⁶ and 2,2':6',2''-terpyridyl⁷ fragments, ferrocenyl,^{4a} Pd^{II} porphyrino⁸ and [Re(bipy)(CO)₃Cl]^{4b,6c,d,9} fragments. In particular, a notable contribution from Faulkner and coworkers saw, for the first time, the use of a functionalised [Os(bipy)₃]²⁺ unit as sensitizer (Fig. 1a).^{4b,c} An alternative approach exploits thermodynamic self-assembly processes to generate

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† Electronic supplementary information (ESI) available: ¹H NMR spectra showing solvent dependence of *mer*-/ *fac*-[Os(L1)₃]³⁺ ratio (Fig. S1) and complex decomposition operating during reaction of L1 with [Os(DMSO)₄Cl₂] (Fig. S2); Born–Haber cycles (Fig. S3) and plot of luminescence lifetime τ vs temperature for [Os(L1)₃]³⁺ (Fig. S4); an optimized superimposition of helicates *HHH*-[OsLu(L2)₃]³⁺ and *HHH*-[RuLu(L2)₃]³⁺ (Fig. S5); selected structural parameters for the metallic coordination spheres in 1–3 (Tables S1–S3), with accompanying definitions (Schemes S1–S3); CIF file for the unrestrained model of 3(CF₃SO₃)₅·MeOH·2MeCN. CCDC reference numbers 664400–664402. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b718885d

discrete heterobimetallic triple-stranded d–f helicates based on the pyridyl-benzimidazole ligand **L2** (Fig. 1b and c).¹⁰ A helical *head–head–head* (*HHH*) arrangement of three such ligands generates two C_3 -symmetric binding sites, one N_6 and one N_6O_3 , each suitable for selectively complexing transition metal and lanthanide cations respectively. When $M = Ru^{II}$, or the more inert $M = Cr^{III}$ ion, resides in the six-coordinate sites of C_3 -symmetric helicates $HHH-[MLn(L2)_3]^{z+}$ ($M = Ru^{II}$, $Ln = Nd^{III}$, Er^{III} , Yb^{III} and $z = 5$; $M = Cr^{III}$, $Ln = Nd^{III}$, Yb^{III} and $z = 6$), irradiation of the d-block chromophore results in slow directional energy transfer to the Ln^{III} ion situated *ca.* 9 Å away.¹¹ Consequently, the Ln^{III} emission lifetime mirrors that of the d-block chromophore and, in the case of Cr^{III} (which provides energy from its long-lived 2E state), emissive decay from Nd^{III} and Yb^{III} can be prolonged well into the millisecond time domain.¹¹ There are however, several practical disadvantages associated with working with Cr^{III} - and Ru^{II} -based chromophores as sensitizers. Firstly, the synthetic stages required to obtain the pure $HHH-[Cr^{III}Ln^{III}(L2)_3]^{6+}$ helicate are heavily burdened by the slow electronic relaxation of the singly degenerate $^4A_{2g}$ ground state of the Cr^{III} ion, which completely precludes 1H NMR characterization.^{10a} Using the diamagnetic Ru^{II} ion overcomes this issue, but then low-lying d–d states in the $[Ru(L1)_3]^{2+}$ chromophore limit its kinetic integrity in polar solvents.^{10b} Eventual goals of obtaining the enantiomerically pure Δ - and Λ -isomers of $HHH-[RuLn(L2)_3]^{5+}$ for circularly-polarised luminescence (CPL) studies are thus clearly unrealistic since this requires prolonged exposure to aqueous media on chiral ion-exchange supports.¹² The photolability likewise encumbers the successive extraction and re-introduction of different Ln^{III} ions into the *fac*- $[Ru(L2)_3]^{2+}$ tripodal receptor, thereby limiting its reusability.

Like their Ru^{II} analogues, $[Os(\alpha,\alpha'$ -diimine) $_3]^{2+}$ fragments, *e.g.* $[Os(bipy)_3]^{2+}$, often display long-lived emission from their readily accessible 3MLCT state,^{2,13} the energy and lifetime of which can be tuned according to the π -acceptor/donor abilities of the ligands.¹⁴ The 3MLCT state for $[Os(bipy)_3]^{2+}$ is typically lower in energy ($\tilde{\nu} \approx 13\,000\text{ cm}^{-1}$) and shorter lived, by *ca.* one order of magnitude, than that of $[Ru(bipy)_3]^{2+}$ ($\tilde{\nu} \approx 16\,000\text{ cm}^{-1}$).^{2a,c,13} However, this can make $[Os(\alpha,\alpha'$ -diimine) $_3]^{2+}$ fragments more suitable for sensitising the NIR emitters, in particular Er^{III} and Yb^{III} , since a closer donor/acceptor energy match will facilitate more efficient energy transfer to the Ln^{III} ion. Furthermore, as Faulkner *et al.* recently pointed out, the short(er)-lived luminescence of Os^{II} -based chromophores should be easier to separate from that of the Ln^{III} , offering possibilities for improving detection limits for the emission of the latter.^{4b} From a synthetic viewpoint, the 30% increase in ligand-field strength on going from Ru^{II} to Os^{II} means that the d–d states in $[Os(Li)_3]^{2+}$ ($i = 1, 2$) are expected to lie significantly higher in energy.^{2a,13c,14a,15} The restricted accessibility of these states, which effectively comprise metal–ligand anti-bonding orbitals, will in principle make for a correspondingly more photo-resistant complex. We have therefore directed our attention towards developing chromophores based on the more inert $5d^6$ Os^{II} ion, with the ultimate goals of (i) achieving sensitised NIR emission from Ln^{III} ions in heterobimetallic helicates of the type $HHH-[OsLn(L2)_3]^{5+}$ ($Ln = Nd, Er, Yb$) and (ii) resolving the two optical (Δ/Λ) isomers of the tripodal receptor *fac*- $[Os(L2)_3]^{2+}$ for subsequent recomplexation with luminescent lanthanides and generation of the chiral helicates Δ - and Λ - $HHH-[OsLn(L2)_3]^{5+}$ ($Ln = Nd, Er, Yb$). In the following report, we first describe the synthetic strategy, separation, photophysical properties and electrochemical behaviours of the *mer* and *fac* isomers of the model

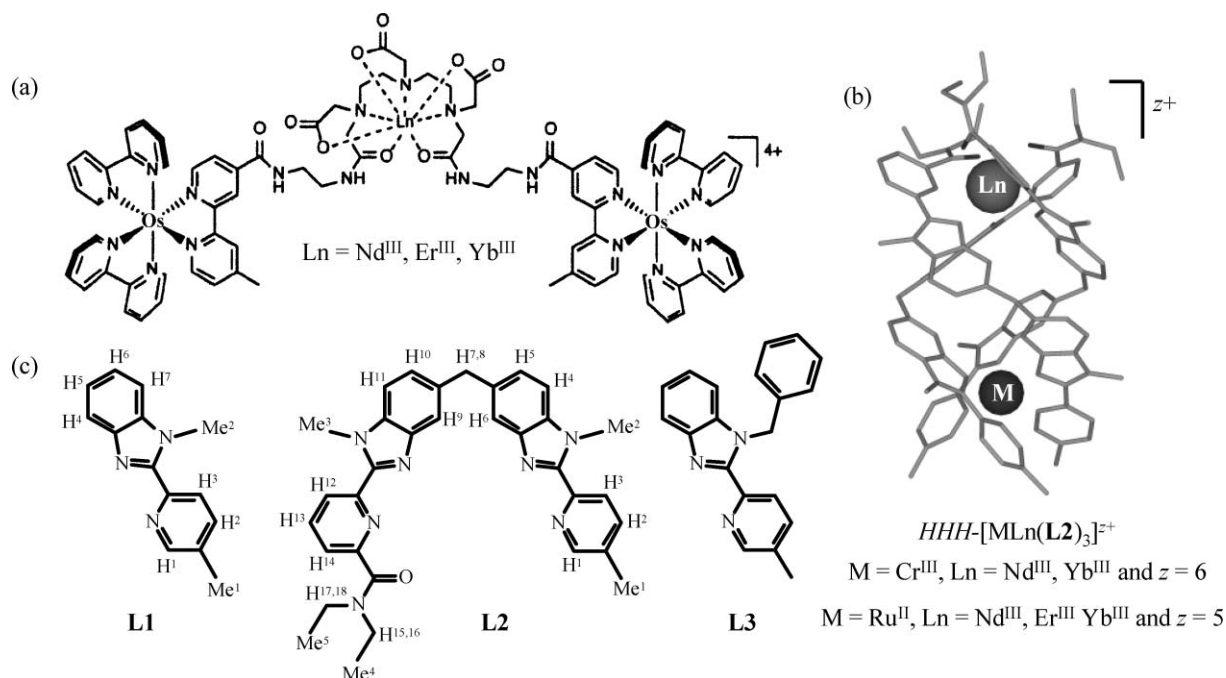


Fig. 1 (a) Recent osmium-containing d–f complex reported by Faulkner *et al.*^{4b,c} (b) Structure of the heterobimetallic triple-stranded helicates $HHH-[MLn(L2)_3]^{z+}$. (c) Structures and 1H NMR numbering scheme for ligands **L1**–**L3**.

complex $[\text{Os}(\text{L1})_3]^{2+}$, whereby **L1** corresponds to the bidentate part of the segmental ligand **L2** (Fig. 1c). We then focus on the challenging task of directing an Os^{II} ion into the same bidentate pyridyl-benzimidazole site in **L2** to form the heterobimetallic helicate $\text{HHH-}[\text{OsLn}(\text{L2})_3]^{5+}$.

Results and discussion

Synthesis, separation and characterization of *mer*- $[\text{Os}(\text{L1})_3](\text{PF}_6)_2$, **1**(PF_6)₂, and *fac*- $[\text{Os}(\text{L1})_3](\text{PF}_6)_2$, **2**(PF_6)₂

The synthesis of $[\text{Os}(\text{L1})_3]^{2+}$ was attempted using a variety of different solvents (alcohols, glycols, glymes, *N*-methylpyrrolidone, propylene carbonate, dimethylformamide), osmium reagents ($\text{K}_2[\text{Os}^{\text{IV}}\text{Cl}_6]$, $(\text{NH}_4)_2[\text{Os}^{\text{IV}}\text{Cl}_6]$, $\text{Os}^{\text{III}}\text{Cl}_3$ and *trans*- $[\text{Os}^{\text{II}}\text{Cl}_2(\text{DMSO})_4]$) and reaction conditions (temperature 80–180 °C and pressure 1–20 bar). In solvents with boiling points of less than 170 °C (at ambient pressure) such as ethanol (80 °C), diglyme (160 °C) and DMF (150 °C) heating at reflux for up to 60 h yielded little other than free ligand. The more esoteric solvents, *e.g.* *N*-methylpyrrolidone and propylene carbonate proved equally unfruitful. The most encouraging results were obtained using either ethylene glycol, propan-1,3-diol or butan-1,4-diol at *ca.* 180 °C, with reaction times of up to 90 h depending on the osmium salt used. Fig. 2a shows the ^1H NMR spectrum (CD_3CN ,

10^{-2} M) of the crude solid isolated from a solution containing a 3 : 1 molar ratio of **L1** : $\text{Os}^{\text{III}}\text{Cl}_3$ in ethylene glycol ($[\text{L1}]_{\text{tot}} = 20$ mM) after stirring at reflux for several days. On cooling, addition of aqueous NH_4PF_6 precipitates the hexafluorophosphate salt, allowing complete recovery of the crude solid by filtration. The crowded aromatic region (δ 7.00–8.50 ppm)—where a large number of overlapping proton resonances appear—is somewhat difficult to interpret, but for the methyl groups Me^1 (2.1–2.4 ppm) and Me^2 (4.2–4.6 ppm, Fig. 2a), four singlets of approximately equal intensity are easily discernable. Combined with the fact that no peaks for the free ligand remain, the spectrum is thus consistent with the quantitative formation of an *ca.* 3 : 1 ratio of the C_1 -symmetric meridional (*mer*) and C_3 -symmetric facial (*fac*) isomers of $[\text{Os}(\text{L1})_3]^{2+}$; an expected outcome if the distribution of isomers is to be governed by simple statistics. As previously reported for $[\text{Ru}(\text{L}i)_3]^{2+}$ ($i = 1, 3$),^{10b} the H^4 proton of each ligand in $[\text{Os}(\text{L1})_3]^{2+}$ is held above the plane of the benzimidazolylpyridine rings of one of the adjacent ligand strands. The ring current anisotropies experienced by these protons cause a marked decrease in their resonance frequencies and three doublets are indeed observed in the range δ 5.60–6.00 ppm with relative intensities of 2 : 1 : 1 (Fig. 2a). Two of these resonances (one of which corresponds to two superimposed signals) are due to the benzylic protons H^4 of the *mer* isomer (Fig. 2b), leaving assignment of the central doublet to H^4 in the *fac* isomer (Fig. 2c). Scalar spin–spin coupling data (from

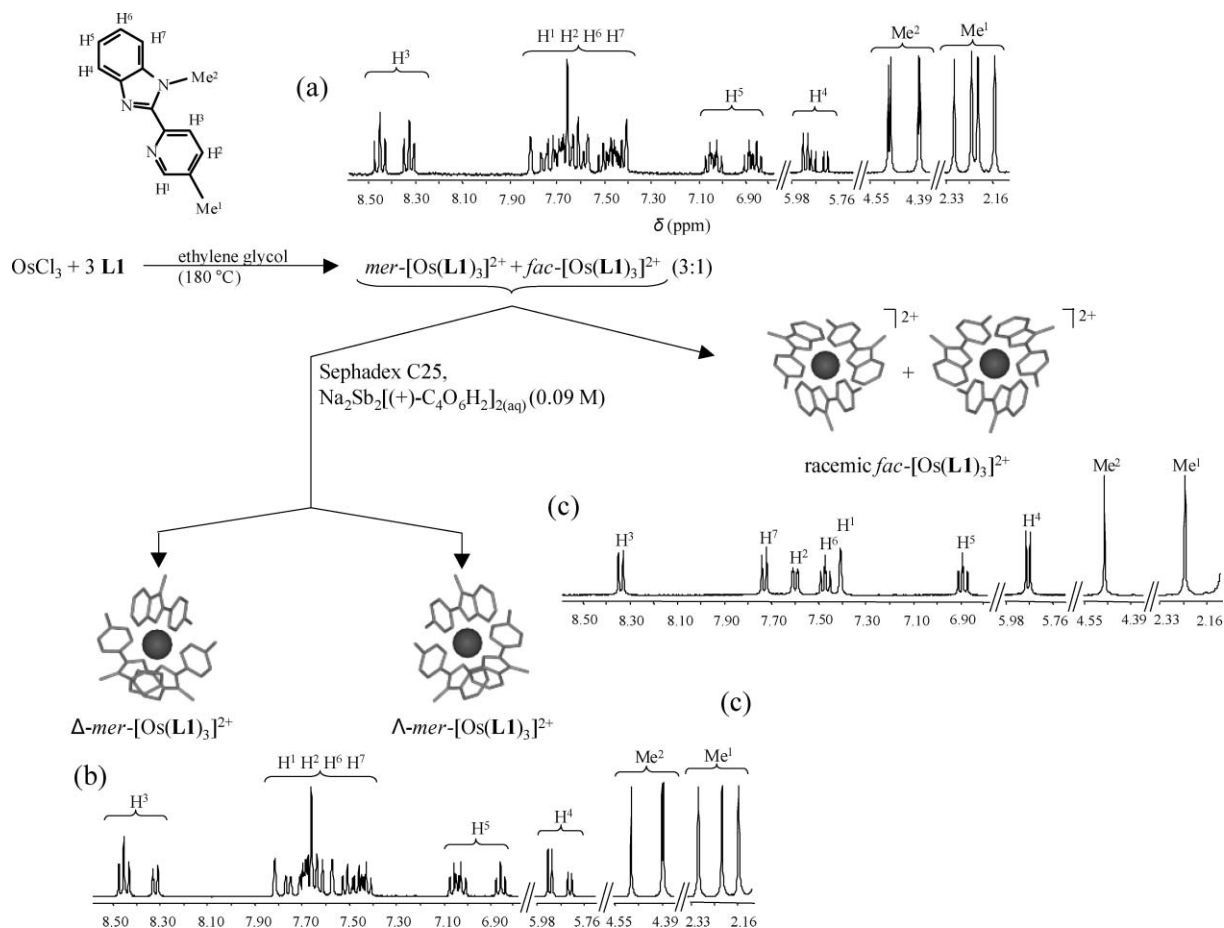


Fig. 2 Schematic synthesis and separation, and ^1H NMR characterization of (a) crude 3 : 1 mixture of *mer*-/*fac*- $[\text{Os}(\text{L1})_3]^{2+}$ isomers, (b) *mer*- $[\text{Os}(\text{L1})_3]^{2+}$ (**1**) isomers and (c) *fac*- $[\text{Os}(\text{L1})_3]^{2+}$ (**2**) (CD_3CN , 298 K).

Table 1 ^1H NMR assignments (ppm) for complexes $\text{mer-}[\text{Os}(\text{L1})_3]^{2+}$ **1** and $\text{fac-}[\text{Os}(\text{L1})_3]^{2+}$ **2** in CD_3CN (298 K)

	H^1	H^2	H^3	H^4	H^5	H^6	H^7	Me^1	Me^2
$\text{mer-}[\text{Os}(\text{L1})_3]^{2+}$	7.83	7.78	8.48	5.93	7.07	7.52	7.70	2.33	4.49
	7.70	7.72	8.46	5.93	7.04	7.48	7.69	2.27	4.40
	7.59	7.67	8.34	5.83	6.88	7.45	7.64	2.22	4.39
$\text{fac-}[\text{Os}(\text{L1})_3]^{2+}$	7.40	7.60	8.33	5.87	6.89	7.47	7.73	2.26	4.46

^1H - ^1H COSY) and comparisons with the spectra obtained for isolated *mer* and *fac* isomers (see below) provide final confirmation for these assignments (Table 1).

Of the osmium reagents explored, $\text{trans-}[\text{Os}^{\text{II}}\text{Cl}_2(\text{DMSO})_4]^{16}$ proved the most promising in terms of reactivity. Quantitative formation of the tris-substituted complex $[\text{Os}(\text{L1})_3]^{2+}$ was achieved within 5–10 h at reflux in ethylene glycol, whilst for other salts ($\text{K}_2[\text{Os}^{\text{IV}}\text{Cl}_6]$, $(\text{NH}_4)_2[\text{Os}^{\text{IV}}\text{Cl}_6]$, $\text{Os}^{\text{III}}\text{Cl}_3$) reaction times of up to several days were required before ligand complexation and/or metal reduction were complete. Of particular note, for the reaction between $\text{trans-}[\text{Os}^{\text{II}}\text{Cl}_2(\text{DMSO})_4]$ and **L1**, glycol chain length was observed to have a significant impact on the distribution of *mer/fac* isomers. Stirring at 180°C in butan-1,4-diol, propan-1,3-diol and ethylene glycol yielded *mer/fac* ratios of *ca.* 3 : 2.5, 3 : 2.5 and 3 : 1.5 respectively after 16 h (Fig. S1, ESI†). Subsequent periodic analysis showed that the *mer/fac* ratio very gradually tends towards the statistical value of 3 : 1, together with partial complex degradation evidenced by the appearance of peaks corresponding to free ligand in the ^1H NMR spectrum (Fig. S2, ESI†) and the deposition of insoluble black material. We thus conclude that (i) once formed the product distribution is still largely under kinetic control¹⁷ and (ii) the selected hydroxylic solvent clearly plays a non-innocent role in the ligand complexation mechanism. These results are further corroborated by the opposite isomer *mer/fac* ratio of 2 : 3 obtained when conducting the same reaction (1 : 3 *trans-}[\text{Os}^{\text{II}}\text{Cl}_2(\text{DMSO})_4] and **L1**) in ethanol at high pressure, either in a sealed pressure tube (at 160°C and 8–10 bar), or in a microwave reactor (at 180°C and 17–20 bar; Fig. S1, ESI†). However, the limited conversion rates (10–50%) observed under these conditions after 90 h severely limit this approach for increasing the quantity of the desired *fac-}[\text{Os}(\text{L1})_3]^{2+} isomer.**

As previously demonstrated for the Ru^{II} analogues,^{10b} separation and purification of a crude mixture of the *mer* and *fac* isomers could be achieved using ion-exchange chromatography.¹⁸ To improve solubility in water, the mixture of *mer-/fac-}[\text{Os}(\text{L1})_3](\text{PF}_6)_2 was first (re)converted to its chloride salt (LiCl in acetone), before being sorbed as an aqueous solution onto a SP Sephadex C25 ion exchange resin. Elution with $\text{Na}_2\text{Sb}_2[(+)\text{-C}_4\text{O}_6\text{H}_2]_2$ (aq) (0.09 M) then resulted in the appearance of three well-resolved dark red/brown bands, which were collected separately. A final anion metathesis with aqueous NH_4PF_6 converts back to dark red/brown hexafluorophosphate salts which were recrystallised by slow diffusion of diethyl ether vapour into a concentrated solution of each fraction in acetonitrile. Elemental analysis and electrospray ionisation mass spectra (ESI-MS) of the microcrystalline solids obtained were consistent with the original formulation $[\text{Os}(\text{L1})_3](\text{PF}_6)_2$, whilst the ^1H NMR spectra further revealed the structural identities of each complex. The spectra recorded for the first two fractions (I and II by order of elution) are identical (Fig. 2b) and show a total of 27 unique proton resonances (of which several are overlapping), as expected for the three non-*

equivalent ligand strands of the C_1 -symmetric *mer-}[\text{Os}(\text{L1})_3](\text{PF}_6)_2 isomer (Table 1). The spectrum of the last fraction (III) (Fig. 2c) is contrastingly simple with only 9 resonances, allowing unambiguous assignment to the C_3 -symmetric *fac* isomer, in which all three ligand strands are equivalent. The kinetic inertness of these complexes towards isomerisation is evidenced by the fact that no changes are observed in the spectrum of *fac-}[\text{Os}(\text{L1})_3]^{2+}, even after standing in polar solvents (*e.g.* CD_3CN , CD_3OD) for months. This behaviour distinguishes $[\text{Os}(\text{L1})_3]^{2+}$ from the more labile complex $[\text{Ru}(\text{L1})_3]^{2+}$, for which an initial 3 : 1 mixture of *mer/fac* isomers equilibrates to pure *mer-}[\text{Ru}(\text{L1})_3]^{2+} on standing in MeCN for only 4 d.^{10b}***

The observation of two well defined bands for the *mer* isomer immediately invokes further separation of the latter into resolved Δ - and Λ -enantiomers, a phenomenon which was not observed for the Ru^{II} analogues.^{10b} Circular dichroism (CD) spectra verify that this is indeed the case, fractions I and II showing equal and opposite Cotton effects (Fig. 3). Exciton coupling observed for the long-axis polarized π - π^* transitions in the range 36 600–28 000 cm^{-1} allow a tentative assignment of the absolute configuration of the enantiomer present in each fraction. As now well established, certain combinations of ligand-centred π - π^* transitions in tris-chelate complexes can produce co-linear electric and magnetic transition dipole moments.¹⁹ Depending on screw sense (with respect to 3- and 2-fold molecular axes), these helical charge displacements result in differential absorption of left- or right-handed circularly polarised light, a property which can then be correlated with the absolute configuration (*e.g.* Δ/Λ -chirality) of the enantiomerically pure compound.¹⁹ Detailed studies carried out by Mason *et al.* have verified applicability of the so called exciton model for the family of resolved tris-chelate complexes Δ - and Λ - $[\text{M}(\text{L})_3]^{z+}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$; $\text{L} = 2,2$ -bipy, phenanthroline; $z = 2, 3$).²⁰ In keeping with predictions, the

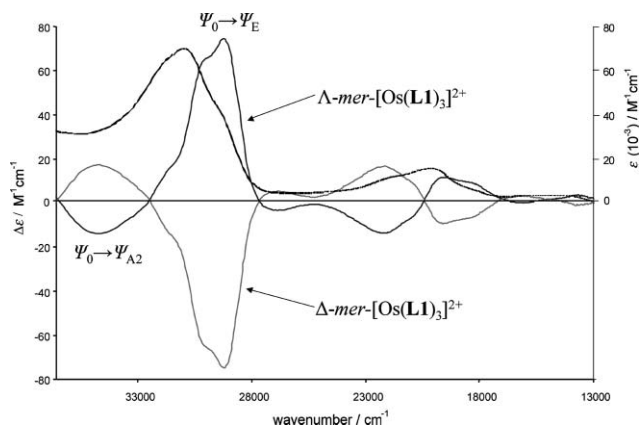


Fig. 3 CD spectra of fractions I (Λ -*mer-}[\text{Os}(\text{L1})_3]^{2+}) and II (Δ -*mer-}[\text{Os}(\text{L1})_3]^{2+}) in MeCN (10^{-5} M) and the electronic absorption spectrum of *mer-}[\text{Os}(\text{L1})_3]^{2+}.***

ligand-based transitions in *e.g.* Λ -[Os(bipy)₃]²⁺ were split into a low energy component displaying positive dichroism ($\Psi_0 \rightarrow \Psi_E$; 33 900 cm⁻¹, +4.1 × 10⁻³⁸ cgs) and a high energy component displaying negative dichroism ($\Psi_0 \rightarrow \Psi_{A_2}$; 35 500 cm⁻¹, -2.7 × 10⁻³⁸ cgs). Later studies carried out by Noble and Peacock on the opposite enantiomer Δ -[Os(bipy)₃]²⁺ showed the expected sign-inversion for all bands in the CD spectra,²¹ and even more recently, the assignments have been further corroborated by modern TD-DFT calculations.²² Based on these trends, the first and second fractions of *mer*-[Os(L1)₃]²⁺ may thus be assigned Λ - and Δ -configurations respectively. The broad ligand-centred π - π^* transition centred at $\tilde{\nu}_{\max} \approx 31\,050$ cm⁻¹ is in each case split into two main components displaying Cotton effects of opposite sign and with an energy separation of *ca.* 5000 cm⁻¹ (Fig. 3). The more intense low energy components at $\tilde{\nu}_{\max} \approx 29\,000$ cm⁻¹ are attributed to doubly degenerate $\Psi_0 \rightarrow \Psi_E$ type transitions (fraction I: $\Delta\epsilon = +72$ M⁻¹ cm⁻¹; fraction II: $\Delta\epsilon = -72$ M⁻¹ cm⁻¹), with the singly degenerate $\Psi_0 \rightarrow \Psi_{A_2}$ type transitions appearing at $\tilde{\nu}_{\max} \approx 34\,500$ cm⁻¹ (fraction I: $\Delta\epsilon = -15$ M⁻¹ cm⁻¹; fraction II: $\Delta\epsilon = +15$ M⁻¹ cm⁻¹). It is worth noting that the prediction of the exciton model obtained for the *D*₃-symmetric [Os(bipy)₃]²⁺ model complex may be affected by the lower symmetry (*C*₁) of the *mer*-[Os(L1)₃]²⁺ complex and confirmation has therefore been obtained by X-ray diffraction studies on a single crystal grown from fraction I (see below). The solid-state structure of the *mer*-[Os(L1)₃](PF₆)₂ complex was solved in the chiral space group *P*2₁ and refinement of the absolute structure (Flack) parameter to a value of -0.001(6) unambiguously confirms its configuration as Λ -*mer*-[Os(L1)₃](PF₆)₂. The CD spectrum of the single crystal is superimposable on that of the bulk sample and a definitive assignment of fraction I to Λ -*mer*-[Os(L1)₃](PF₆)₂ and fraction II to Δ -*mer*-[Os(L1)₃](PF₆)₂ can be safely made.

Solid-state and molecular structures of Λ -*mer*-[Os(L1)₃](PF₆)₂, Λ -1(PF₆)₂, and *fac*-[Os(L1)₃](PF₆)₂, 2(PF₆)₂

Slow diffusion of diethyl ether vapour into concentrated acetonitrile solutions of fractions I and III resulted in the formation of X-ray quality crystals of Λ -*mer*-[Os(L1)₃](PF₆)₂·1.5MeCN (Λ -1(PF₆)₂·1.5MeCN, *P*2₁, *Z'* = 2) and *fac*-[Os(L1)₃](PF₆)₂ (2(PF₆)₂, *C*2/*c*, *Z'* = 1) respectively. The structures, shown in Fig. 4 and 5, each display pseudo-octahedral coordination of the three

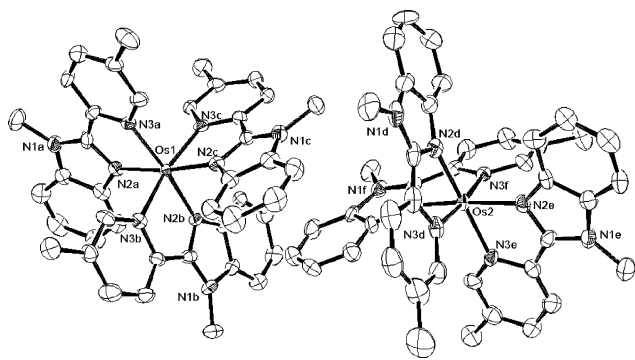


Fig. 4 Crystal structure of Λ -*mer*-[Os(L1)₃]²⁺ (Λ -1) showing the two independent complex cations. Hydrogens, anions and solvate molecules have been omitted for clarity. Thermal ellipsoids are shown at a 50% probability level.

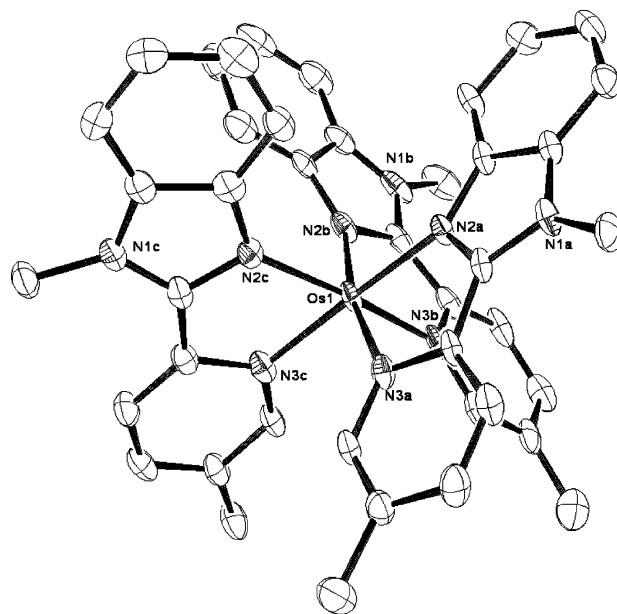


Fig. 5 Solid-state structure of the complex cation *fac*-[Os(L1)₃]²⁺ **2**. Hydrogens and anions have been omitted for clarity. Thermal ellipsoids are shown at a 50% probability level.

bidentate ligands to the central Os^{II} centres. In keeping with the ¹H NMR assignments, anti-parallel alignment of one of the ligands (with respect to the other two) in Λ -1(PF₆)₂ distinguishes the *C*₁-symmetric *mer* isomer from the *fac* isomer (**2**(PF₆)₂).

Selected metric parameters for both structures are given in Table 2. The overall coordination environments around the Os^{II} centres in **1** and **2** are by and large the same; collective metal–ligand separations are distributed over the fairly narrow range Os–N = 2.043(7)–2.079(7) Å (average 2.06(1) Å), the standard deviation of which ($\sigma = 0.01$) suggests that the minor discrepancies observed between isomers/crystal sites are due to little other than packing effects.²³ The ionic radii, as calculated according to Shannon's definition (and with $r(N) = 1.46$ Å), are $R_{Os}^{CN=6} = 0.60$ Å and 0.61 Å for **1** and **2** respectively, in keeping with the tabulated value of 0.63 Å.²⁴ The metal–ligand bond lengths are comparable to those observed in the Ru^{II} complex of related ligand **L3** (Ru–N = 2.054(3)–2.079(3) Å, average 2.069(8) Å; $R_{Ru}^{CN=6} = 0.60$ Å), and marginally longer than those reported for the low-spin Fe^{II} centre in [FeLa(**L2**)₃]⁵⁺ (Fe–N = 1.93(2)–2.04(2) Å, average 1.98(4) Å).²⁵

Both complex cations **1** and **2** exhibit the typical structural distortions expected for pseudo-octahedral tris-chelate complexes of bidentate benzimidazole-pyridyl ligands.¹⁰ A detailed analysis of the geometric parameters pertaining to the bending (ϕ), flattening (θ_i) and twist (ω_{ij}) of the octahedral coordination spheres (Table S1 and Scheme S1, ESI†)²⁵ shows no significant bending ($\phi = 178^\circ$ vs $\phi = 180^\circ$ for a perfect octahedron), but standard compression along the pseudo-threefold axis ($57(1)^\circ < \theta_i < 63(1)^\circ$ for **1** and **2** vs $\theta_i = 54.7^\circ$ for a perfect octahedron) combined with a minor twist of the two facial tripods ($49(1)^\circ < \omega_{ij} < 53(1)^\circ$; average = $51(1)^\circ$ for **1** and **2**) from octahedral ($\omega_{ij} = 60^\circ$) towards trigonal prismatic geometry ($\omega_{ij} = 0^\circ$), as found in [Os(bipy)₃]²⁺ (Os–N = 2.062(4) Å; $\theta_i = 59.6^\circ$; $\omega_{ij} = 51.2^\circ$).²⁶ We conclude that the structural impact on the Os^{II} coordination sphere of both *mer*/*fac* isomerisation when replacing **L1** with the more symmetric bipy

Table 2 Selected bond lengths (Å) and angles (°) for Λ -*mer*-[Os(L1)₃](PF₆)₂·1.5MeCN (**1**-1(PF₆)₂·1.5MeCN) and *fac*-[Os(L1)₃](PF₆)₂ (**2**(PF₆)₂)

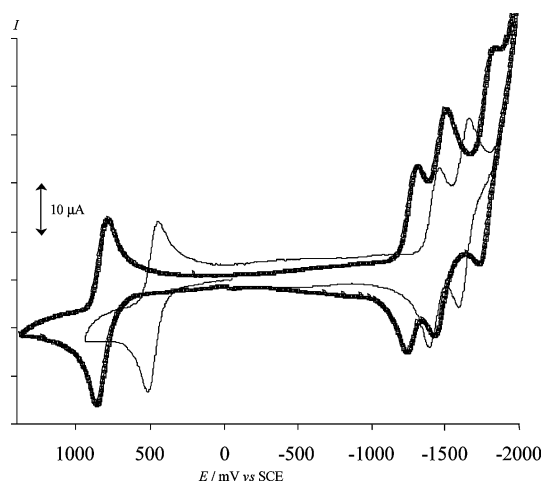
	Λ - <i>mer</i> -[Os(L1) ₃](PF ₆) ₂ ·1.5MeCN						<i>fac</i> -[Os(L1) ₃](PF ₆) ₂		
	Os1			Os2			Ligand a	Ligand b	Ligand c
	Ligand a	Ligand b	Ligand c	Ligand d	Ligand e	Ligand f			
Os–N2	2.060(7)	2.043(7)	2.079(7)	2.062(8)	2.058(8)	2.043(7)	2.072(5)	2.066(5)	2.061(5)
Os–N3	2.077(7)	2.067(5)	2.075(6)	2.066(7)	2.064(7)	2.047(6)	2.072(5)	2.073(6)	2.053(5)
N2–Os–N3	76.9(3)	76.9(3)	76.9(2)	76.4(3)	77.3(3)	76.7(3)	77.2(2)	77.3(2)	77.4(2)
N2a–Os–N2b	99.0(3)			100.1(3)			95.6(2)		
N2a–Os–N3b	89.0(3)			174.8(3)			88.0(2)		
N2a–Os–N2c	172.8(3)			87.5(3)			99.6(2)		
N2a–Os–N3c	99.0(3)			98.9(3)			172.9(2)		
N3a–Os–N2b	173.9(2)			86.5(3)			169.3(2)		
N3a–Os–N3b	98.3(2)			98.9(3)			94.4(2)		
N3a–Os–N2c	97.0(3)			99.6(3)			90.8(2)		
N3a–Os–N3c	89.2(2)			174.2(2)			96.3(2)		
N2b–Os–N2c	87.4(3)			171.2(3)			98.2(2)		
N2b–Os–N3c	96.0(3)			97.7(3)			91.1(2)		
N3b–Os–N2c	95.8(3)			95.4(3)			171.5(2)		
N3b–Os–N3c	170.2(3)			86.0(3)			95.5(2)		

is minimal. Indeed, even the structural changes incurred from replacing Ru^{II} by Os^{II} in the tris(benzimidazole)pyridyl complexes are beyond the resolution of the diffraction data.

Electrochemical and photophysical properties of *mer*-[Os(L1)₃](PF₆)₂, **1**(PF₆)₂, and *fac*-[Os(L1)₃](PF₆)₂, **2**(PF₆)₂

The cyclic voltammograms of **1**(PF₆)₂ and **2**(PF₆)₂ in acetonitrile (Fig. 6) are identical within experimental error and show the expected metal-centred oxidation process at $E_{1/2} = 0.48$ V *vs* SCE, corresponding to the [Os^{III}(L1)₃]³⁺/[Os^{II}(L1)₃]²⁺ couple, and two successive ligand-centred reduction processes at -1.43 and -1.63 V *vs* SCE. All peak–peak separations ΔE_p lie in the range 60–70 mV and none vary significantly with scan rates in the range 100–500 mV s^{−1}, consistent with fully reversible diffusion-controlled one-electron transfer processes. No further redox activity was observed within the solvent accessible potential window.

Electrochemical data for **1**(PF₆)₂ and **2**(PF₆)₂, their Ru^{II} analogues and the well-characterized model systems [M^{II}(bipy)₃]²⁺ (M = Ru, Os) are summarised in Table 3. The marked cathodic shift of the metal-centred oxidation process in **1**(PF₆)₂ and **2**(PF₆)₂ with respect to their bipy analogue (*ca.* 350 mV, Fig. 6) is in keeping with the enhanced π -donor ability of **L1** over bipy, whilst similar trends in the ligand reduction potentials, apparent to a

**Fig. 6** Cyclic voltammograms of *mer*- and *fac*-[Os(L1)₃]²⁺ (thin line) and [Os(bipy)₃]²⁺ (bold line) (298 K, CH₃CN + 0.1 M ⁿBu₄N)PF₆).

lesser extent in the Ru^{II} analogues, likewise evidence poorer π -acceptor ability.^{10b}

This is confirmed in the ambient temperature electronic absorption spectra of **1**(PF₆)₂ and **2**(PF₆)₂ in MeCN (10^{−5} M) (Fig. 7a, Table 4), the main features of which may be readily assigned by comparison with that of [Os(bipy)₃]²⁺.²⁷ Charge-transfer

Table 3 Electrochemical properties of *mer*- and *fac*-[Os(L1)₃](PF₆)₂ and [Os(bipy)₃](PF₆)₂ in MeCN + 0.1 M ⁿBu₄NPF₆. Values for related Ru^{II} analogues in MeCN + 0.1 M ⁿBu₄ClO₄ are also listed for comparison^a

	$E_{1/2}$ ([ML ₃] ³⁺ /[ML ₃] ²⁺)/V	$E_{1/2}$ ([ML ₃] ²⁺ /[ML ₃] ⁺)/V	$E_{1/2}$ ([ML ₃] ⁺ /[ML ₃])/V	$E_{1/2}$ ([ML ₃]/[ML ₃] [−])/V	$\Delta E_{1/2}^b$ /V	Ref.
[Os(bipy) ₃] ²⁺	0.83	−1.27	−1.46	−1.77	+2.10	10b
[Ru(bipy) ₃] ²⁺	1.27	−1.31	−1.50	−1.77	+2.58	
<i>mer</i> -[Os(L1) ₃] ²⁺	0.48	−1.43	−1.63	—	+1.91	
<i>fac</i> -[Os(L1) ₃] ²⁺	0.48	−1.43	−1.63	—	+1.91	10b
<i>mer</i> -[Ru(L1) ₃] ²⁺	0.94	−1.37	−1.56	−1.82	+2.31	
<i>fac</i> -[Ru(L1) ₃] ²⁺	0.94	−1.37	−1.56	−1.82	+2.31	
[Ru(Lu(L2) ₃)] ³⁺	0.98	−1.43	−1.58	−1.68	+2.41	30
[Ru(L2) ₃] ²⁺	0.97	−1.48	−1.68	—	+2.45	30

^a Half-wave potentials $E_{1/2}$ /V *vs* SCE at a scan rate of 100 mV s^{−1} (298 K). ^b $\Delta E_{1/2} = E_{1/2}([ML_3]^{3+}/[ML_3]^{2+}) - E_{1/2}([ML_3]^{2+}/[ML_3]^+)$ in V.

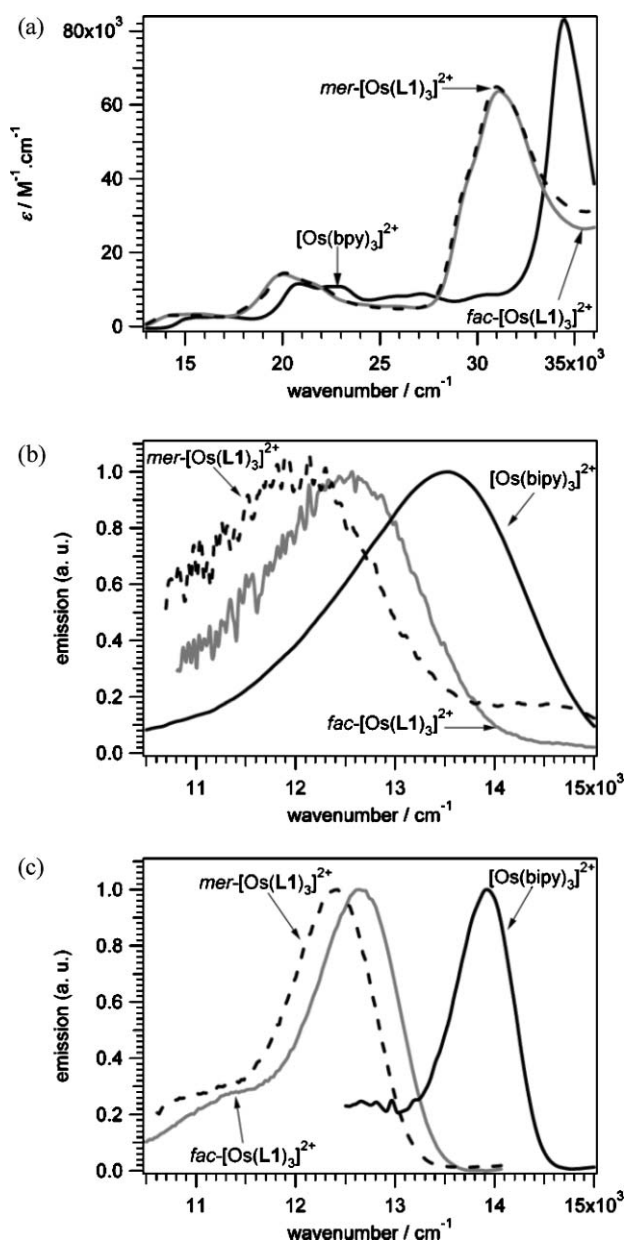


Fig. 7 (a) Room temperature absorption spectra (10^{-5} M in CH_3CN), (b) normalised room temperature emission spectra (10^{-5} M in CH_3CN) and (c) normalised 77 K emission spectra (butyronitrile-acetonitrile glass, 1:1 v/v) of *mer*- and *fac*-[Os(L1)₃]²⁺ and [Os(bipy)₃]²⁺.

ground-state (GS) to ³MLCT, GS → ¹MLCT and ligand-centred π - π^* transitions in *mer*-[Os(L1)₃]²⁺ and *fac*-[Os(L1)₃]²⁺ give rise to three broad bands which fall in the ranges $13\,000 \leq \tilde{\nu} \leq 18\,000\text{ cm}^{-1}$, $18\,000 \leq \tilde{\nu} \leq 26\,000\text{ cm}^{-1}$ and $28\,000 \leq \tilde{\nu} \leq 35\,000\text{ cm}^{-1}$ respectively, and which are all red-shifted to varying degrees with respect to those of [Os(bipy)₃]²⁺.

Broader bands for complexes of **L1**, in particular in the π - π^* region, likely arise from the lower molecular symmetries of **1**(PF₆)₂ and **2**(PF₆)₂ (*C*₁ and *C*₃ respectively) removing degeneracy from all ground and excited state configurations. Also of particular note are the presence of relatively intense GS → ³MLCT absorption bands ($2500 < \epsilon < 3500\text{ M}^{-1}\text{ cm}^{-1}$), which gain intensity due to spin-orbit coupling ($\xi_{\text{Os}} \approx 3000\text{ cm}^{-1}$).^{27e} Based on the well-established, but

approximate, relationship between the energy of the absorption maximum $\tilde{\nu}_{\text{max(abs)}}$ of the GS → ¹MLCT transition (Table 4) and the difference in half-wave potentials $\Delta E_{1/2}$ of the metal-centred oxidation and ligand reduction processes (Table 3), $h\nu_{\text{max(abs)}} = F\Delta E_{1/2} + \chi_r$ (where *F* is the Faraday constant and χ_r the reorganisational free energy),²⁸ we calculate rough reorganisational energies of $\chi_r([\text{Os}(\text{bipy})_3]^{2+}) = 3900\text{ cm}^{-1}$ and $\chi_r(\text{fac-}[\text{Os}(\text{L1})_3]^{2+}) = 4600\text{ cm}^{-1} \approx \chi_r(\text{mer-}[\text{Os}(\text{L1})_3]^{2+}) = 4700\text{ cm}^{-1}$ for relaxation from the vibrationally excited ¹MLCT states (vertical transition) to their potential energy minima at ambient temperature. The same trend was observed for the Ru^{II} analogues,^{10b} with higher χ_r values estimated for complexes of the benzimidazole-pyridyl ligands than 2,2'-bipyridine, though values obtained for the Os^{II} complexes are alarmingly two-fold greater. The presence of spin-forbidden GS → ³MLCT transitions in the electronic absorption spectra of [Os(L)₃]²⁺ (L = **L1**, bipy) also allows a direct estimate of the energy difference between the ¹MLCT and ³MLCT states: $\Delta E_{\text{ST}} \approx h\nu_{\text{abs}}(^1\text{MLCT}) - h\nu_{\text{abs}}(^3\text{MLCT}) \approx 5500 \pm 500\text{ cm}^{-1}$ for *mer*- and *fac*-[Os(L1)₃]²⁺ and *ca.* $5300 \pm 500\text{ cm}^{-1}$ for [Os(bipy)₃]²⁺. Assuming diabatic state potential energy (PE) surfaces, we can then estimate ³MLCT emission energies from $h\nu_{\text{em,calcd}}(^3\text{MLCT}) \approx h\nu_{\text{abs}}(^1\text{MLCT}) - \Delta E_{\text{ST}} - 2\chi_r$ (Fig. 8), which gives $h\nu_{\text{em,calcd}}(^3\text{MLCT}) \approx 20\,100 - 5500 - 9300 = 5300\text{ cm}^{-1}$ for [Os(L1)₃]²⁺ and $h\nu_{\text{em,calcd}} \approx 20\,833 - 5300 - 7800 = 7700\text{ cm}^{-1}$ for [Os(bipy)₃]²⁺. The emission spectra obtained upon excitation of the ¹MLCT state indeed originate from the ³MLCT level and confirm a red-shift on going from [Os(bipy)₃]²⁺ ($13\,500\text{ cm}^{-1}$) to [Os(L1)₃]²⁺ ($12\,500\text{ cm}^{-1}$, Fig. 7b, Table 4). However, the values of $h\nu_{\text{em,calcd}}(^3\text{MLCT}) = 7700\text{ cm}^{-1}$ and 5300 cm^{-1} predicted for these complexes are dramatically underestimated whilst the magnitude of observed red-shift on going from [Os(bipy)₃]²⁺ to [Os(L1)₃]²⁺ is overestimated.

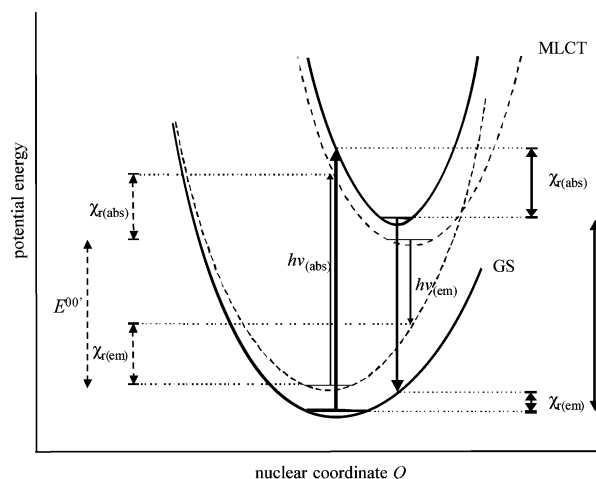


Fig. 8 Diagram showing the effect of configurational mixing on ground and excited states and $\chi_{r(\text{abs})}$ and $\chi_{r(\text{em})}$. The limiting diabatic and adiabatic cases are shown as dashed and bold curves respectively.

Correlation between electrochemical and photophysical properties in *mer*-[Os(L1)₃](PF₆)₂, **1**(PF₆)₂, and *fac*-[Os(L1)₃](PF₆)₂, **2**(PF₆)₂

A first source of error in the simple approach originally proposed by Lever and coworkers²⁸ is the assumption of similar reorganisational energies for the vertical absorption and emitting transitions

Table 4 Photophysical properties of *mer*- and *fac*-[Os(L1)₃]²⁺, [Os(bipy)₃]²⁺, [Os(L2)₃]²⁺ and [OsLu(L2)₃]⁵⁺. Corresponding values for Ru^{II} analogues are listed for comparison

	<i>T</i> /K	$\pi-\pi^*$ (abs) ^a /cm ⁻¹	¹ MLCT (abs) ^a /cm ⁻¹	³ MLCT (abs) ^a /cm ⁻¹	³ MLCT (em)/cm ⁻¹	τ^d /ns	Φ^f	Ref.
[Os(bipy) ₃] ²⁺	296 77 ^c	34 482(83 200)	20 833(11 500)	15 600(2400)	13 480 13 950	58 966	0.0049 0.081	
[Ru(bipy) ₃] ²⁺	296 77	34 843(88 800)	22 172(14 700)		16 285 17 210	643 5200	0.062 0.36	10b
<i>mer</i> -[Os(L1) ₃] ²⁺ ^b	296 77 ^e	30 959(64 900)	20 120(14 400)	14 500(3000)	12 200 12 400	16 279	0.00052 0.0094	
<i>fac</i> -[Os(L1) ₃] ²⁺ ^b	296 77 ^e	31 056(63 700)	20 000(14 100)	14 800(3300)	12 500 12 650	35 383	0.0012 0.013	
<i>mer</i> -[Ru(L1) ₃] ²⁺ ^c	296 77	30 770(41 250)	21 370(10 730)		14 325 15 150	74 1620	0.0010 0.041	10b
<i>fac</i> -[Ru(L1) ₃] ²⁺ ^c	296 77	30 960(39 850)	21 185(8440)		14 345 15 950	50 3200	0.0010 0.052	10b
<i>fac</i> -[Os(L2) ₃] ²⁺ ^{b,g}	296 77	30 120(93 350)	19 841(10 800)	14 500(3000)	12 450 12 820	53 639	0.0011 0.013	
HHH-[OsLu(L2) ₃] ⁵⁺ ^{b,g}	296 77	29 850(92 900)	19 920(10 400)	14 500(3000)	12 400 12 500	31 409	0.00073 0.0096	
HHH-[RuLu(L2) ₃] ⁵⁺ ^c	296 77	29 940(55 000)	21 100(11 100)		14 730 15 470	384 2000	0.010 0.028	10b

^a Energies are given for the maximum of the band envelope. Molar extinction coefficients $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ are given between parentheses. ^b $\tilde{\nu}_{\text{ex}} = 21\,368\text{ cm}^{-1}$. Values reported at 77 K correspond to the 0–0 phonon transitions. ^c $\tilde{\nu}_{\text{ex}} = 20\,492\text{ cm}^{-1}$ in ethanol–methanol (4 : 1 v/v, 10^{-4} M). ^d $\tilde{\nu}_{\text{ex}} = 18\,797\text{ cm}^{-1}$. Errors typically lie in the range $\pm 1\text{--}5\%$. ^e In acetonitrile–butyronitrile (1 : 1 v/v) glass. ^f Errors typically lie in the range $\pm 10\text{--}20\%$. ^g In acetonitrile–butyronitrile (1 : 4 v/v, 10^{-6} M).

(i.e. $\chi_{\text{r(abs)}} \approx \chi_{\text{r(em)}}$), which is valid only at the diabatic limit (Fig. 8, dashed PE curves). Deviation from such behaviour is expected when configurational mixing of ground and excited states occurs, since this increases the force constant of the excited state potential surface whilst decreasing that of the ground state (Fig. 8, bold PE curves).²⁹ In terms of reorganisational energies, as the adiabatic limit is approached the reorganisational energy for absorption $\chi_{\text{r(abs)}}$ increases, whilst that for emission $\chi_{\text{r(em)}}$ decreases, in principle making $\chi_{\text{r(abs)}} > \chi_{\text{r(em)}}$, but realistic configurational mixing maintains similar magnitudes for these two terms (Fig. 8). For the Os^{II} complexes under investigation, it is necessary to set $\chi_{\text{r(em)}} \approx 0$ (i.e. a non-realistic lowest limit), giving $h\nu_{\text{em,calcd}}(^3\text{MLCT}) \approx h\nu_{\text{abs}} - \Delta E_{\text{ST}} - \chi_{\text{r(abs)}} = 10\,000\text{ cm}^{-1}$ for [Os(L1)₃]²⁺ and ca. $11\,600\text{ cm}^{-1}$ for [Os(bipy)₃]²⁺, in order for $h\nu_{\text{em,calcd}}(^3\text{MLCT})$ to even faintly resemble the observed room temperature emissions occurring at $12\,500\text{ cm}^{-1}$ and $13\,333\text{ cm}^{-1}$ respectively (Fig. 7).

Though the effects of configurational mixing have previously been invoked for rationalising minor trends in the emission properties of [Ru^{II}(bipy)_n]²⁺ complexes,²⁹ it is clear that this effect cannot account for the large discrepancy between electrochemical and optical data for the Os^{II} complexes, and we suspect that the more extensive $\pi_{\text{M}}-\pi_{\text{L}}$ orbital overlap incurred on going from a 4d (Ru) to a 5d (Os) metal is likely to accentuate the correction term $\Delta G_{\text{DA}}^{\text{tot}}$ required for correlating the electrochemical parameter $\Delta E_{1/2}$ with the zero-point energy $E^{00'}$ (zpe, Fig. 8) in [Os(L)₃]²⁺ complexes (L = bipy, L1; eqn (1) and Fig. 9).²⁹

$$E^{00'} = F \times \Delta E_{1/2} + \Delta G_{\text{DA}}^{\text{tot}} \quad (1)$$

A theoretical quantum interpretation of $\Delta G_{\text{DA}}^{\text{tot}}$ is available, but it is usually of small magnitude and neglected for [Ru(α,α' -diimine)₃]²⁺.²⁹ Basic thermodynamic considerations show that $\Delta G_{\text{DA}}^{\text{tot}}$ can be partitioned into two additive contributions given in reactions (2) and (3) ($\Delta G_{\text{DA}}^{\text{tot}} = \Delta G_{\text{DA}}^1 + \Delta G_{\text{DA}}^2$), which can be

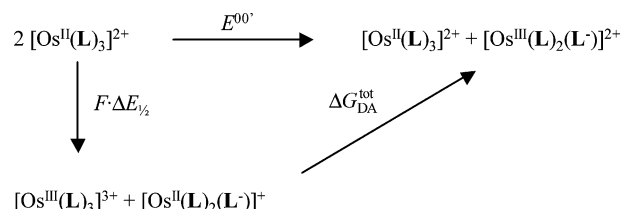
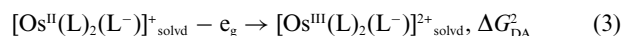
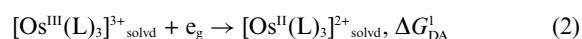


Fig. 9 Thermodynamic cycle correlating the electrochemical parameter $\Delta E_{1/2}$ with the zero-point energy (zpe) $E^{00'}$.

modelled with eqn (4) and (5) (solvd = solvated, g = gaseous; see Fig. S3 in the ESI† for the corresponding Born–Haber cycles).



$$\Delta G_{\text{DA}}^1 = \lambda_{\text{reorg}}^{\text{Os(III/II)}} + W_{\text{elec}}^{\text{gas}}([\text{Os}^{\text{III}}(\text{L})_3]^{3+}_{\text{g}}/[\text{Os}^{\text{II}}(\text{L})_3]^{2+}_{\text{g}}) + \Delta G_{\text{solv}}([\text{Os}^{\text{II}}(\text{L})_3]^{2+}) - \Delta G_{\text{solv}}([\text{Os}^{\text{III}}(\text{L})_3]^{3+}) \quad (4)$$

$$\Delta G_{\text{DA}}^2 = -\lambda_{\text{reorg}}^{\text{Os(III/II)}} - W_{\text{elec}}^{\text{gas}}([\text{Os}^{\text{III}}(\text{L})_2(\text{L}^-)]^{2+}_{\text{g}}/[\text{Os}^{\text{II}}(\text{L})_2(\text{L}^-)]^+_{\text{g}}) + \Delta G_{\text{solv}}([\text{Os}^{\text{III}}(\text{L})_2(\text{L}^-)]^{2+}) - \Delta G_{\text{solv}}([\text{Os}^{\text{II}}(\text{L})_2(\text{L}^-)]^+) \quad (5)$$

$\lambda_{\text{reorg}}^{\text{Os(III/II)}}$ corresponds to the free energy of electronic and structural reorganization accompanying the reduction of Os^{III}, which is assumed to be identical for the complexes [Os^{III}(L)₃]³⁺ and [Os^{III}(L)₂(L[−])]²⁺ in the gas phase. $W_{\text{elec}}^{\text{gas}}$ is the gas-phase point charge coulombic electrostatic work required for bringing one electron at the distance $r([\text{Os}^{\text{III}}(\text{L})_3]^{3+}_{\text{g}})$ (eqn (6)) or $r([\text{Os}^{\text{III}}(\text{L})_2(\text{L}^-)]^{2+}_{\text{g}})$ (eqn (7)) from the Os^{III} centre ($N_{\text{Av}} = 6.02 \times 10^{23}\text{ mol}^{-1}$ is Avagadro's number, $e = 1.602 \times 10^{-19}\text{ C}$ is the unit electrostatic charge, and $\epsilon_0 = 8.85 \times 10^{-12}\text{ C}^2\text{ N}^{-1}\text{ m}^{-2}$ is the vacuum permittivity; Fig. S3, ESI†).

$$W_{\text{elec}}^{\text{gas}}([\text{Os}^{\text{III}}(\text{L})_3]^{3+}_{\text{g}}/[\text{Os}^{\text{II}}(\text{L})_3]^{2+}_{\text{g}}) = -\frac{3N_{\text{Av}}e^2}{4\pi\epsilon_0 r([\text{Os}^{\text{III}}(\text{L})_3]^{3+}_{\text{g}})} \quad (6)$$

$$W_{\text{elec}}^{\text{gas}}([\text{Os}^{\text{III}}(\text{L})_2(\text{L}^-)]^{2+}_{\text{g}}/[\text{Os}^{\text{II}}(\text{L})_2(\text{L}^-)]^{+}_{\text{g}}) = -\frac{2N_{\text{Av}}e^2}{4\pi\epsilon_0 r([\text{Os}^{\text{III}}(\text{L})_2(\text{L}^-)]^{2+}_{\text{g}})} \quad (7)$$

Finally, ΔG_{solv} refer to solvation energies in acetonitrile, which can be reasonably estimated with the original Born equation (8) for large molecular ions ($\epsilon_r = 36.1$ is the relative dielectric permittivity in acetonitrile, z is the charge of the ion and ρ is the pseudo-spherical radius of the ion in the gas phase).³⁰

$$\Delta G_{\text{solv}} = -\frac{N_{\text{Av}}z^2e^2}{8\pi\epsilon_0\rho}\left(1 - \frac{1}{\epsilon_r}\right) \quad (8)$$

As previously demonstrated for $[\text{Ru}(\text{L})_3]^{2+}$,³⁰ $\rho([\text{Os}^{\text{II}}(\text{L})_3]^{2+}_{\text{g}})$ ($\text{L} = \text{bipy}$, **LI**) can be satisfyingly calculated from the diffusion coefficient $D([\text{Os}^{\text{II}}(\text{L})_3]^{2+}_{\text{g}})$ obtained by diffusion ordered NMR spectroscopy (5×10^{-4} M) in acetonitrile and using the Stokes–Einstein equation (9) ($R = 8.31$ J mol⁻¹ is the molar gas constant and $\eta = 3.60 \times 10^{-4}$ N s m⁻² is the viscosity of acetonitrile at 298 K; Table 5).

$$\rho = \frac{RT}{6\pi N_{\text{Av}}\eta D} \quad (9)$$

Since (i) the $\text{Os}^{\text{III}}/\text{Os}^{\text{II}}$ redox processes in the couples $[\text{Os}^{\text{III}}(\text{L})_3]^{3+}_{\text{g}}/[\text{Os}^{\text{II}}(\text{L})_3]^{2+}_{\text{g}}$ and $[\text{Os}^{\text{III}}(\text{L})_2(\text{L}^-)]^{2+}_{\text{g}}/[\text{Os}^{\text{II}}(\text{L})_2(\text{L}^-)]^{+}_{\text{g}}$ involve a π -bonding metal-centred orbital and (ii) the two couples only differ by the existence of a partially reduced ligand in $[\text{Os}^{\text{III}}(\text{L})_2(\text{L}^-)]^{2+}_{\text{g}}/[\text{Os}^{\text{II}}(\text{L})_2(\text{L}^-)]^{+}_{\text{g}}$ for which the additional electron occupies a weakly π -antibonding orbital, we conclude that $\rho([\text{Os}^{\text{II}}(\text{L})_3]^{2+}_{\text{g}})$ ($\text{L} = \text{bipy}$, **LI**) can be used as a reasonable approximation for the pseudo-spherical ionic radii of the four incriminated complexes, from which the solvation energies tabulated in Table 5 can be calculated with eqn (8).

Table 5 Diffusion coefficients (D), pseudo-spherical radii (ρ , eqn (9)) and solvation energies (ΔG_{solv} , eqn (8)) of *mer*- and *fac*- $[\text{Os}(\text{LI})_3](\text{PF}_6)_2$ and $[\text{Os}(\text{bipy})_3](\text{PF}_6)_2$ (acetonitrile, 298 K)

	L = bipy			L = LI (<i>fac</i> or <i>mer</i>)		
	$D \times 10^{-9}/\text{m}^2 \text{ s}^{-1}$	$\rho/\text{\AA}$	$\Delta G_{\text{solv}}/\text{kJ mol}^{-1}$	$D \times 10^{-9}/\text{m}^2 \text{ s}^{-1}$	$\rho/\text{\AA}$	$\Delta G_{\text{solv}}/\text{kJ mol}^{-1}$
$[\text{Os}^{\text{III}}(\text{L})_3]^{3+}$	—	4.43 ^a	1372	—	4.93 ^a	1233
$[\text{Os}^{\text{II}}(\text{L})_3]^{2+}$	1.37(1)	4.43(3)	610	1.23(1)	4.93(3)	548
$[\text{Os}^{\text{III}}(\text{L})_2(\text{L}^-)]^{2+}$	—	4.43 ^a	610	—	4.93 ^a	548
$[\text{Os}^{\text{II}}(\text{L})_2(\text{L}^-)]^{+}$	—	4.43 ^a	152	—	4.93 ^a	137

^a Assumed to be identical to $\rho([\text{Os}^{\text{II}}(\text{L})_3]^{2+})$, see text.

Table 6 Average reorganisational energies $\chi_r = \chi_{r(\text{abs})} \approx \chi_{r(\text{em})}$ (eqn (10)), zero-point energy $E^{00'}$ (eqn (11)), correction term $\Delta G_{\text{DA}}^{\text{tot}}$ (eqn (1)) and fitted metal–electron distances $r([\text{Os}^{\text{III}}(\text{L})_3]^{3+}_{\text{g}})$ (eqn (6)) and $r([\text{Os}^{\text{III}}(\text{L})_2(\text{L}^-)]^{2+}_{\text{g}})$ (eqn (7)) for *mer*- and *fac*- $[\text{Os}(\text{LI})_3](\text{PF}_6)_2$ and $[\text{Os}(\text{bipy})_3](\text{PF}_6)_2$ (acetonitrile, 298 K)

	χ_r/cm^{-1}	$E^{00'}/\text{cm}^{-1}$	$F\Delta E_{1/2}^a/\text{cm}^{-1}$	$\Delta G_{\text{DA}}^{\text{tot}}/\text{cm}^{-1}$	$r([\text{Os}^{\text{III}}(\text{L})_3]^{3+}_{\text{g}})/\text{\AA}$	$r([\text{Os}^{\text{III}}(\text{L})_2(\text{L}^-)]^{2+}_{\text{g}})/\text{\AA}$
$[\text{Os}(\text{bipy})_3]^{3+}$	1100	19 780	16 940	2840	2.46	1.95
<i>fac</i> - $[\text{Os}(\text{LI})_3]^{2+}$	1150	18 850	15 405	3445	2.73	2.15
<i>mer</i> - $[\text{Os}(\text{LI})_3]^{2+}$	1150	18 970	15 405	3565	2.73	2.15

^a $\Delta E_{1/2}$ is taken from Table 3.

The eventual calculation of $\Delta G_{\text{DA}}^{\text{I}}$ (eqn (4)), $\Delta G_{\text{DA}}^{\text{II}}$ (eqn (5)) and $\Delta G_{\text{DA}}^{\text{tot}} = \Delta G_{\text{DA}}^{\text{I}} + \Delta G_{\text{DA}}^{\text{II}}$ is still limited by the estimation of $W_{\text{elec}}^{\text{gas}}([\text{Os}^{\text{III}}(\text{L})_3]^{3+}_{\text{g}}/[\text{Os}^{\text{II}}(\text{L})_3]^{2+}_{\text{g}})$ (eqn (6)) and $W_{\text{elec}}^{\text{gas}}([\text{Os}^{\text{III}}(\text{L})_2(\text{L}^-)]^{2+}_{\text{g}}/[\text{Os}^{\text{II}}(\text{L})_2(\text{L}^-)]^{+}_{\text{g}})$ (eqn (7)), for which the determination of the average electron–metal distance r requires a complicated quantum approach, well beyond the scope of a contribution of this nature. We can however consider the reverse problem of estimating r with eqn (6) and (7) provided that a reasonable value of $\Delta G_{\text{DA}}^{\text{tot}}$ is available. To do this, we first assume that the configurational mixing in the Os^{II} complex, though non-negligible, remains small enough when compared with the electrostatic effects responsible for $\Delta G_{\text{DA}}^{\text{tot}}$, that similar reorganisational energies $\chi_r = \chi_{r(\text{abs})} \approx \chi_{r(\text{em})}$ exist for the MLCT absorption and emission processes (adiabatic limit, Fig. 8). The subsequent use of eqn (10) to model the Stokes shift provides an estimate for χ_r (Table 6, column 2), from which the zero-point energy $E^{00'}$ (eqn (11)) and $\Delta G_{\text{DA}}^{\text{tot}}$ (eqn (1)) can be computed (Table 6, columns 3 and 5).

$$h\nu_{\text{abs}}(^3\text{MLCT}) - h\nu_{\text{em}}(^3\text{MLCT}) = \chi_{r(\text{abs})} + \chi_{r(\text{em})} \approx 2\chi_r \quad (10)$$

$$E^{00'} = h\nu_{\text{abs}}(^1\text{MLCT}) - \chi_r \quad (11)$$

The best fits of eqn (4)–(7) to $\Delta G_{\text{DA}}^{\text{tot}}$ collected in Table 6 (column 5) give $1.95 \leq r \leq 2.73$ Å with $r([\text{Os}^{\text{III}}(\text{L})_3]^{3+}_{\text{g}}) < r([\text{Os}^{\text{III}}(\text{L})_2(\text{L}^-)]^{2+}_{\text{g}})$ (Table 6, columns 6 and 7). It is immediately apparent that these values significantly exceed the Os^{II} ionic radius observed in the solid state for $[\text{Os}(\text{LI})_3]^{2+}$ (0.60–0.61 Å), lying more in the range of the Os–N(ligand) bond distances, which indeed corresponds to a chemically reasonable situation if the Os–N bonds are characterised by considerable $\pi_{\text{M}}-\pi_{\text{L}}$ orbital overlap. This explanation for the much larger values of the correction term $\Delta G_{\text{DA}}^{\text{tot}}$ required for Os^{II} complexes when compared with Ru^{II} analogues is further supported by the photophysical evidence from the ¹MLCT and ³MLCT energy differences ΔE_{ST} . A more than two-fold increase is observed for ΔE_{ST} on going from $[\text{Ru}(\text{LI})_3]^{2+}$ ($\Delta E_{\text{ST}} \approx 1700 \pm 500$ cm⁻¹)^{10b} to $[\text{Os}(\text{LI})_3]^{2+}$ ($\Delta E_{\text{ST}} \approx 5400 \pm 500$ cm⁻¹) which, as previously noted for the $[\text{M}(\text{L})_3]^{2+}$ ($\text{M} = \text{Ru}^{\text{II}}, \text{Os}^{\text{II}}$;

L = bipy and derivatives), suggests much greater extension of Os^{II} d⁵ orbitals onto those of the ligand than in the analogous Ru^{II} complexes.^{13b} Consequently, the simple approach of Lever and coworkers,²⁸ which is so attractive for a straightforward global interpretation of the electrochemical and optical properties of Ru^{II} complexes, is not applicable for the related Os^{II} complexes.

Emission properties of *mer*-[Os(L1)₃](PF₆)₂, **1**(PF₆)₂, and *fac*-[Os(L1)₃](PF₆)₂, **2**(PF₆)₂

As is apparent from the quantum yield Φ and lifetime τ data listed in Table 4, room temperature emissions from the ³MLCT states in complexes **1**(PF₆)₂ and **2**(PF₆)₂ are both weaker and shorter lived than their Ru^{II} analogues. The lifetime attenuation is partly due to spin–orbit coupling which imparts some allowedness to the classically spin-forbidden triplet–singlet transition and which is known to have a more pronounced impact on both radiative and non-radiative decay rates for Os^{II} systems.^{2a,27e} Lower quantum yields arise from more efficient coupling of the excited state(s) with the ground state vibrational modes, a process which is fortified by lower emission energies (according to the energy gap law) and has also been suggested to result from the substantial $\pi_{\text{sa}}-\pi_{\text{L}}$ orbital overlap in [Os^{II}(α,α' -diimine)₃]²⁺ complexes (*vide supra*).^{13b} Excited state lifetimes for **1**(PF₆)₂ and **2**(PF₆)₂ show a similar dependence on temperature to those of polypyridyl complexes of Os^{II}.^{2a} Plots of τ vs T in the temperature range $10 \leq T \leq 150$ K (Fig. S4, ESI†) evidence a smooth decrease in lifetime with increasing temperature, consistent with the presence of several close lying ³MLCT states, each with a unique radiative and non-radiative deactivation rate constant, whose populations reflect available thermal energy. Of particular note is the comparative effect that reducing temperature has on the excited state lifetimes τ of the respective Ru^{II} and Os^{II} complexes of **L1**. The same decrease in temperature causes an increase of two orders of magnitude for τ in the Ru^{II} complexes, and only one order of magnitude in **1** and **2**. Indeed, the existence of low-lying d–d states was implicated in the large changes observed in τ for *mer*- and *fac*-[Ru(L1)₃]²⁺; estimated to lie only *ca.* 2500 cm^{−1} higher in energy than the emitting ³MLCT level, the Ru^{II} d–d levels are efficiently populated at room temperature, providing thermally activated non-radiative deactivation pathways from the excited state(s).^{10b} In contrast, we do not expect such processes to feature in complexes **1** and **2** since an increase of *ca.* 30% in ligand-field splitting occurs on going from Ru^{II} to Os^{II}.^{2a} Based on the zero-point energies (zpe) E° of the d–d states in *mer*- and *fac*-[Ru(L1)₃]²⁺ $\approx 19\,500$ cm^{−1}, we thus estimate zpes of $E^\circ \approx 25\,000$ cm^{−1} for d–d states in **1** and **2**. Consequently, the energy difference ΔE° between emitting ³MLCT and d–d states can be obtained according to $\Delta E^\circ \approx E^\circ - h\nu_{\text{max(em)}} - \chi_{\text{r(em)}} \approx 25\,000 - 12\,300 - 1150 = 11\,550$ cm^{−1}. A difference of this magnitude is clearly too large for thermal deactivation *via* population of the d–d states to be a significant factor for **1** and **2** and likewise accounts for the high kinetic inertness of these complexes under the same conditions which led to photochemical degradation of their Ru^{II} analogues.

Synthesis and characterization of the bimetallic triple-stranded helicate *HHH*-[OsLu(L2)₃](CF₃SO₃)₅

The preparation of hybrid d–f helicates based on **L2** using thermodynamic self-assembly has been reported for a number of

different metal combinations (Fig. 1).^{10,25,31} Extending this family of compounds to include the more inert Os^{II} ion is clearly not accomplishable using this approach, but we have nonetheless explored the possibility of templating the formation of *HHH*-[OsLu(L2)₃](CF₃SO₃)₅ by reacting a 3 : 1 molar ratio of **L2** and Os salt in the presence of Lu(CF₃SO₃)₃. As reported for the analogous Ru^{II} system,^{10b} ¹H NMR spectra of the crude products obtained by simply reacting 3 : 1 molar ratios of ligand and osmium salt (OsCl₃ or [Os^{II}Cl₂(DMSO)₄]) in ethylene glycol (180 °C, 48 h) were highly complex, indicating the presence of an intricate mixture of species of varying symmetry and stoichiometry. Adding one equivalent of Lu(CF₃SO₃)₃ at the beginning of the reaction did little to improve on this situation; ¹H NMR and electrospray ionisation mass spectra (ESI-MS) still provided little evidence for the formation of significant quantities of the desired complex *HHH*-[OsLu(L2)₃]⁵⁺. Given the ability of the flexible ethylene glycol chain to chelate Ln^{III} ions and thereby diminish its affinity for the tridentate site of **L2**, we have resorted to a series of test runs, screening the same osmium salts and conditions as those used for **L1** in ethanol. Despite the apparently limited scope of this solvent as established for the analogous reactions with **L1** (see above), stirring a 3 : 1 : 1 molar ratio of **L2**/OsCl₃/Lu(CF₃SO₃)₃ in a pressure vessel at 160 °C (*ca.* 8–10 bar, [**L2**]_{tot} = 10 mM) for 48 h finally gave encouraging results. In the morass of ¹H NMR peaks which raises the baseline of the aromatic region in the crude product, one set can be clearly discerned above the rest (Fig. 10a). Peak integrals are of limited value here, but of particular note are the two singlets appearing at δ 4.85 and 5.43 which, by comparison with the diamagnetic Ru^{II10b} and Zn^{II31c} analogues, can be confidently assigned to aromatic protons H⁶ and H⁹ in the C₃-symmetric helicate *HHH*-[OsLu(L2)₃]⁵⁺ (see Fig. 1c for numbering), their diagnostic upfield shifts a result of their being held within the shielding regions of adjacent ligand strands in the helical structure. From the large number of peaks present elsewhere in the spectrum it is clear that the crude material still contains a number of other species. The ESI mass spectra show a similar (complicated) picture in the gas-phase, but with intense molecular ions at m/z 536.8, 765.0 and 1222.2, corresponding to [OsLu(L2)₃(CF₃SO₃)₄]⁴⁺, [OsLu(L2)₃(CF₃SO₃)₂]³⁺ and [OsLu(L2)₃(CF₃SO₃)₃]²⁺ respectively, also evidence significant quantities of the desired complex. Upon partitioning the crude product between CH₂Cl₂ and an aqueous solution of sodium triflate, the low-field resonances of H⁶ and H⁹ shift to higher frequency; H⁶ by *ca.* 1 ppm and H⁹ by *ca.* 2.5 ppm (Fig. 10b). Such changes are typical of lanthanide decomplexation from the nine-coordinate N₆O₃ site, which results in the partial unwrapping of the helicate structure and consequent relocation of these protons with respect to the shielding influence of adjacent ligand strands.³⁰ The ¹H NMR spectrum of the organic phase now shows a set of relatively well-resolved peaks whose chemical shifts correspond to those of the free ligand (Fig. 10b), which suggests that the reaction did not go to completion (as previously observed for reactions of **L1** with Os^{II} salts in ethanol). Subjecting the crude product to several cycles of column chromatography on alumina allowed complete removal of the free ligand and other impurities. The ¹H NMR spectrum of the dark red solid obtained (Fig. 10c) shows a major set of 12 aromatic resonances, corresponding to the C₃-symmetric tripod *fac*-[Os(L2)₃]²⁺, in addition to a more complicated set of less intense peaks which can be assigned to the C₁-symmetric

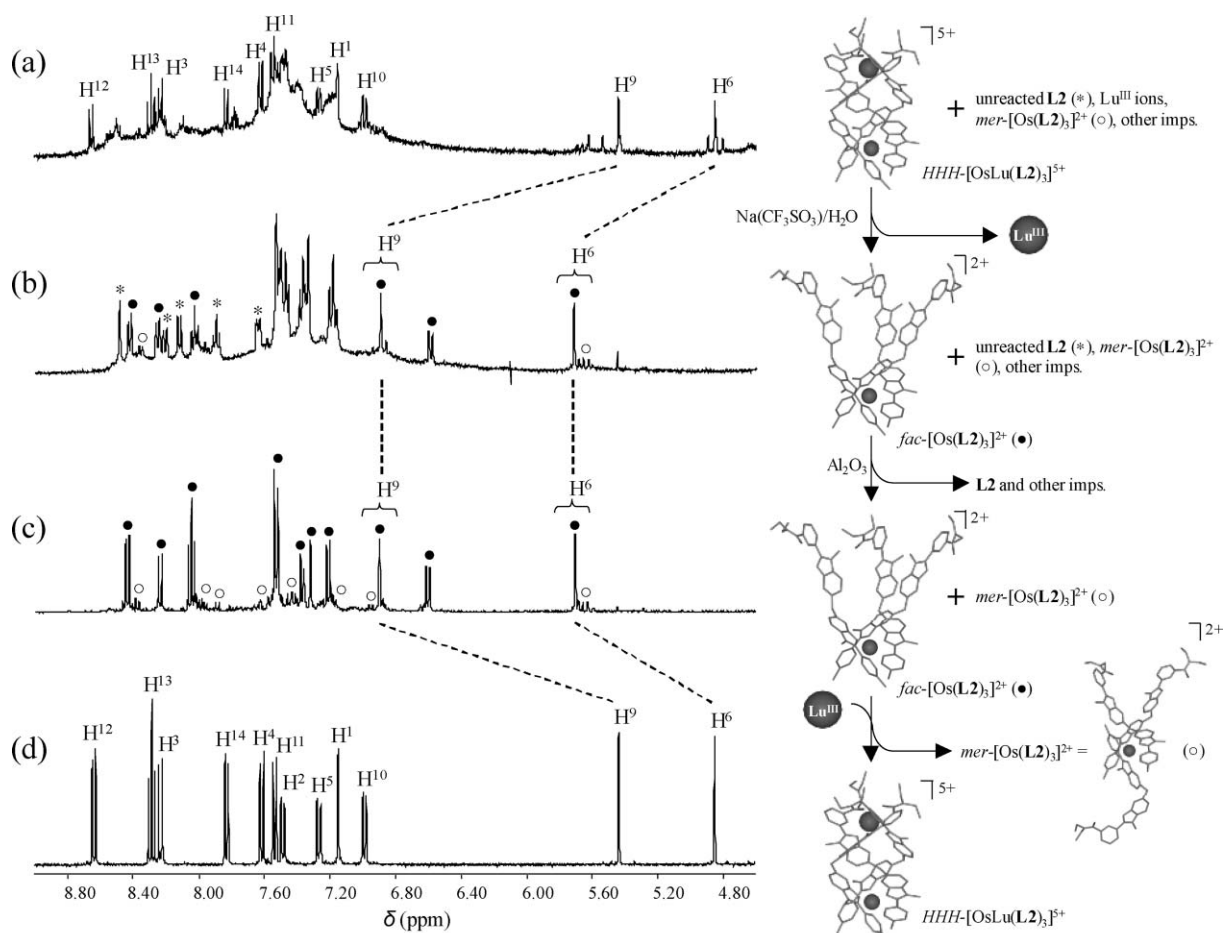


Fig. 10 Successive stages in the purification of $HHH-[OsLu(L2)_3]^{5+}$ with corresponding 1H NMR spectra (CD_3CN , 298 K, numbering as in Fig. 1c). (a) The crude reaction mixture, (b) after partitioning between $Na(CF_3SO_3)_{aq}/CH_2Cl_2$, (c) after chromatography on alumina and (d) pure $HHH-[OsLu(L2)_3]^{5+}$. Peaks due to $fac-[Os(L2)_3]^{2+}$ (●), $mer-[Os(L2)_3]^{2+}$ (○) and free ligand (*) are highlighted where possible.

$mer-[Os(L2)_3]^{2+}$ complex. Of particular note, the ratio of $fac-/mer-[Os(L2)_3]^{2+}$ is *ca.* 3:1 in favour of the *fac* isomer, compatible with a significant templating effect of the Lu^{3+} ion operating during the reaction. Further exploiting the fact that the Lu^{3+} ion will preferentially coordinate a tripodal receptor $fac-[Os(L2)_3]^{2+}$ over its less pre-organised dipodal counterpart $mer-[Os(L2)_3]^{2+}$, recombination with one equivalent of $Lu(CF_3SO_3)_3$ (per part of $fac-[Os(L2)_3]^{2+}$) followed by recrystallisation in hot ethanol then allowed isolation of pure $HHH-[OsLu(L2)_3](CF_3SO_3)_5$ as a black microcrystalline powder (Fig. 10d). On recombination with Lu^{3+} , the recovery of the $HHH-[OsLu(L2)_3]^{5+}$ complex is confirmed by resonances for H^6 and H^9 , which are restored to their initial upfield positions, and the splitting patterns of proton-pairs $H^{7,8}$, $H^{17,18}$ and $H^{15,16}$ which become diastereotopic in the helicate structure. Interstrand NOEs between $H^5 \cdots Me^3$, $H^{10} \cdots Me^2$ and $H^9 \cdots Me^3$ furthermore evidence tight wrapping of the strands around the central $Os \cdots Lu$ axis, as observed for other isostructural systems. That the 1H NMR spectrum remains unchanged after standing for months in CD_3CN indicates a high degree of resilience towards complex degradation in polar solvents. Efforts are under way to optimise the current *ca.* 6–10% yield.

Solid-state and molecular structures of $HHH-[OsLu(L2)_3]-(CF_3SO_3)_5 \cdot MeOH \cdot 2MeCN$, $3(CF_3SO_3)_5 \cdot MeOH \cdot 2MeCN$

The crystal structure of $HHH-[OsLu(L2)_3](CF_3SO_3)_5 \cdot MeOH \cdot 2MeCN$ $3(CF_3SO_3)_5 \cdot MeOH \cdot 2MeCN$ displays the expected complex cation $HHH-[OsLu(L2)_3]^{5+}$ (3) together with ionic triflates and interstitial solvent molecules. The molecular structure of the cation and its atomic numbering scheme are shown in Fig. 11 whilst selected bond lengths and angles are given in Table 7. The complex cation is typical of this family of compounds (Fig. S5, ESI†): three ligand strands are arranged in a *HHH*-fashion around the central internuclear axis, each coordinating the Os and Lu centres *via* the bidentate and tridentate segments, respectively. The resulting arrangement of donor atoms around the metals imparts pseudo-octahedral geometry around Os^{II} and distorted tricapped trigonal prismatic geometry around the Lu^{3+} ion (Table S2, ESI†). The classical geometric treatment for (qualitatively) assessing the pitches P_j of helical progressions in 3^{1b} gives similar values to those obtained for $HHH-[RuLu(L2)_3]^{5+}$ (Table S3 and Scheme S3, ESI†) in accordance with the marginal changes in molecular structure expected on exchanging Ru^{II} for isoelectronic Os^{II} (effective ionic radii for Ru^{II} and Os^{II} are 0.62 and 0.63 Å respectively).²⁴

Table 7 Selected bond lengths (Å) and bite angles (°) for $HHH-[OsLu(L2)_3]^{3+}$ (**3**) and, for comparison, $HHH-[RuLu(L2)_3]^{5+}$.^{10b} Values for the restrained model of **3** are listed between square brackets

	<i>HHH</i> -[OsLu(L2) ₃] ⁵⁺ (3), M = Os			<i>HHH</i> -[RuLu(L2) ₃] ⁵⁺ , M = Ru		
M...Lu	9.0885(8) [9.0874(13)]			9.0794(9)		
	Ligand a	Ligand b	Ligand c	Ligand a	Ligand b	Ligand c
M–N1	2.248(8) [2.071(2)]	2.103(6) [2.064(2)]	1.922(8) [2.059(2)]	2.064(6)	2.060(5)	2.055(5)
M–N2	2.148(6) [2.068(2)]	1.879(8) [2.061(2)]	2.254(8) [2.073(2)]	2.051(5)	2.044(5)	2.057(5)
Lu–N4	2.788(7) [2.657(8)]	2.269(9) [2.379(8)]	2.517(8) [2.477(8)]	2.534(6)	2.469(6)	2.514(5)
Lu–N6	2.675(7) [2.556(9)]	2.314(6) [2.439(8)]	2.814(8) [2.577(8)]	2.518(4)	2.531(5)	2.515(4)
Lu–O1	2.031(6) [2.226(8)]	2.338(8) [2.330(8)]	2.616(7) [2.402(8)]	2.345(5)	2.284(5)	2.326(4)
N1–M–N2	69.1(3)[72.7(3)]	90.3(3)[80.2(2)]	72.0(3)[73.2(3)]	77.8(2)	77.5(2)	77.9(2)
O1–Lu–N4	127.4(2)[124.2(4)]	132.2(2)[135.9(4)]	125.0(2)[128.7(4)]	128.2(1)	128.7(2)	129.6(2)
O1–Lu–N6	76.9(2)[68.0(4)]	59.6(3)[62.8(3)]	55.1(2)[59.3(4)]	63.8(2)	64.2(2)	65.2(1)
N4–Lu–N6	50.6(2)[56.2(4)]	72.6(3)[73.2(4)]	69.9(2)[69.3(4)]	64.5(2)	64.5(2)	64.7(2)

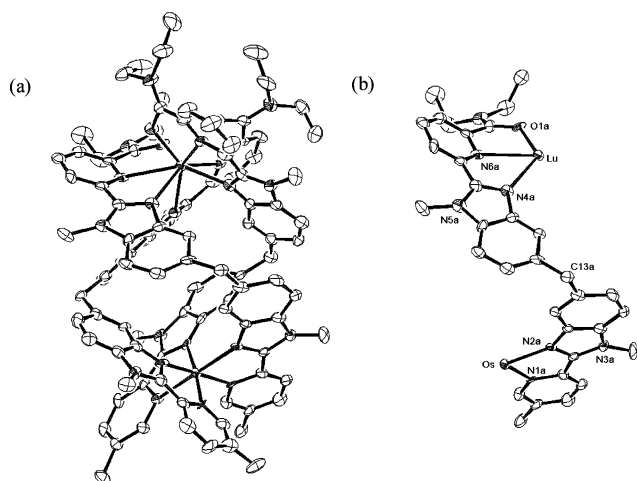


Fig. 11 (a) Solid-state structure of the complex cation $HHH\text{-[OsLu(L2)}_3\text{]}^{5+}$ (**3**). (b) Atom numbering scheme for ligand strand a (strands b and c are numbered identically). Hydrogens, anions and solvent moieties have been omitted for clarity. Thermal ellipsoids are shown at a 50% probability level.

Close inspection of the complex micro-architecture, however, reveals some significant structural distortions in the solid-state. The Os–N bond distances are distributed over the rather large range 1.879(8)–2.254(8) Å, in contrast to both those observed for mononuclear complexes **Λ-1** and **2** (Os–N: 2.043(7)–2.079(7) Å, Table 2) and the isostructural Ru^{II} complex *HHH*–[RuLu(**L2**)₃]⁵⁺ (Ru–N: 2.044(5)–2.064(6) Å, Table 7). Similar anisotropies are observed for the Lu–N/O bonds, which lie in the range 2.031(6)–2.814(8) Å (*cf.* 2.284(5)–2.534(6) Å for *HHH*–[RuLu(**L2**)₃]⁵⁺) and even for the covalent bonds in the ligand strands.

Alarminglly, the distribution of *e.g.* Os–N bonds (average: 2.09(16) Å) in **3** is even larger than that observed for all 51 structures containing octahedral OsN₆ units in the CSD (average: 2.05(3) Å), a fact which suggests that the distortions are more likely artefacts of data contamination by systematic errors than genuine structural phenomena. Several other features support this; although refinements against absorption corrected intensities (on either F_o or F_o^2) converged to a very satisfactory final R value of *ca.* 5% (Table 8), many of the anisotropic thermal parameters are disc-like and similarly orientated, showing principle displacements

coplanar with the (-110) plane. It is possible that this is caused by preferential alignment of sub-domains within the crystal with respect to the crystallographic $[111]$ direction (the pseudo-hexagonal axis), an explanation which is also supported by the high observed mosaic spread of the data (0.015). These problems aside, the result (the best of several attempts) does unambiguously confirm the connectivity of the complex cation. A model in which all 1,2- and 1,3-distances have been restrained has also been refined (the more chemically sensible geometric parameters of which are listed in Table 7), though agreement statistics for the latter are considerably worse (Table 8).

Photophysical properties of $HHH-[OsLu(L2)_3](CF_3SO_3)_5 \cdot MeOH \cdot 2MeCN$, $3(CF_3SO_3)_5 \cdot MeOH \cdot 2MeCN$

From the value of $\log \beta_{11}^{\text{RuLu}} = 5.2(2)$, estimated for the *fac*- $[\text{Ru}(\text{L2})_3]^{2+} + \text{Lu}^{\text{III}} \rightleftharpoons \text{HHH}-[\text{RuLu}(\text{L2})_3]^{5+}$ equilibrium in the isostructural Ru^{II} system (MeCN),³⁰ we expect 80–90% decomplexation of the helicate $\text{HHH}-[\text{OsLu}(\text{L2})_3]^{5+}$ for the micromolar concentration at which the optical density is appropriate for luminescence emission measurements. We thus consider photophysical data obtained from measurements on solutions of $\text{HHH}-[\text{OsLu}(\text{L2})_3]^{5+}$ *without* and *with* an excess of $\text{Lu}(\text{CF}_3\text{SO}_3)_3$ to be representative, respectively, of the uncomplexed tripodal receptor *fac*- $[\text{Os}(\text{L2})_3]^{2+}$ and the bimetallic helicate $\text{HHH}-[\text{OsLu}(\text{L2})_3]^{5+}$. The absorption and emission spectra of both species are shown in Fig. 12 and selected data are summarised in Table 4. Values are, by and large, similar to those of the **L1** analogues **1** and **2**, except for larger extinction coefficients in the ligand $\pi-\pi^*$ transitions—a fact easily explained by there being twice as many absorbing aromatic rings in **L2**—and slightly longer lifetimes τ for emission from the ³MLCT state at 77 K, in particular for *fac*- $[\text{Os}(\text{L2})_3]^{2+}$. The much larger increase (*ca.* an order of magnitude) in room temperature τ observed on going from $[\text{Ru}(\text{L1})_3]^{2+}$ to $\text{HHH}-[\text{RuLu}(\text{L2})_3]^{5+}$ is once again related to the relative energies of the d–d states in each complex.

Structural contraction caused by complexation of the Lu^{III} ion to the *fac*-[Ru(**L2**)₃]²⁺ tripod was suggested to be mechanically coupled to the Ru^{II} site, increasing the ligand field splitting in the helicate with respect to that in mononuclear complexes of **L1**.^{10b} Though this effect may still operate in the Os^{II} complexes, it is reasonable that it does not manifest itself in the excited state lifetimes since the ligand field splitting is sufficiently large

Table 8 Selected refinement parameters for Λ -*mer*-[Os(L1)₃](PF₆)₂·1.5MeCN (Λ -I(PF₆)₂·1.5MeCN), *fac*-[Os(L1)₃](PF₆)₂ (2(PF₆)₂) and [OsLu(L2)₃](CF₃SO₃)₅·MeOH·2MeCN (3(CF₃SO₃)₅·MeOH·2MeCN)

Complex	Λ -I(PF ₆) ₂ ·1.5MeCN	2(PF ₆) ₂	3(CF ₃ SO ₃) ₅ ·MeOH·2MeCN
Empirical formula	[Os(C ₁₄ H ₁₃ N ₃) ₃](PF ₆) ₂ ·(CH ₃ CN) _{1.5}	[Os(C ₁₄ H ₁₃ N ₃) ₃](PF ₆) ₂	[OsLu(C ₃₃ H ₃₃ N ₇ O ₃)](CF ₃ SO ₃) ₅ ·(CH ₃ OH)·(CH ₃ CN) ₂
Formula weight	1211.7	1150.0	2855.9
Temperature/K	150	100	150
Wavelength/Å	0.7107	0.7107	0.7107
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	12.9021(6)	43.243(9)	17.813(2)
<i>b</i> /Å	26.518(2)	10.705(2)	19.120(2)
<i>c</i> /Å	14.0363(6)	20.753(4)	19.124(2)
<i>a</i> /°	90	90	75.385(9)
<i>β</i> /°	91.535(5)	117.243(2)	79.682(10)
<i>γ</i> /°	90	90	69.095(10)
Volume/Å ³	4800.7(4)	8541(3)	5859.3(10)
<i>Z</i> (<i>Z'</i>)	4 (2)	8 (1)	2 (1)
Density (calcd)/g cm ^{−3}	1.676	1.789	1.619
Absorption coefficient/mm ^{−1}	2.82	3.16	2.11
<i>F</i> (000)	2404	4544	2876
Crystal size/mm	0.13 × 0.24 × 0.30	0.075 × 0.05 × 0.01	0.055 × 0.27 × 0.48
θ range for data collection/°	4.14 < θ < 26.9	1.97 < θ < 27.48	3.55 < θ < 25.30
Index ranges	−16 ≤ <i>h</i> ≤ 16, −33 ≤ <i>k</i> ≤ 33, −17 ≤ <i>l</i> ≤ 17	−53 ≤ <i>h</i> ≤ 56, −13 ≤ <i>k</i> ≤ 13, −26 ≤ <i>l</i> ≤ 26	−21 ≤ <i>h</i> ≤ 21, −23 ≤ <i>k</i> ≤ 23, −22 ≤ <i>l</i> ≤ 22
Reflections collected	61 559	46 976	61 931
Independent reflections [<i>R</i> _{int}] ^a	20 649 [0.029]	9795 [0.092]	21073 [0.066]
Min./max. transmission	0.4798/0.7171	0.852 ^b	0.5243/0.8364
Data/restraints/parameters	17 590/0/1270	9795/0/601	12 437/82/1503 (21 073/429/888) ^c
Goodness-of-fit	1.711 ^c	0.997 ^d	1.541 ^e (1.713) ^e
Flack parameter	−0.001(6)	—	—
<i>R</i> indices	<i>R</i> = 0.029, <i>wR</i> = 0.031 ^e	<i>R</i> ₁ = 0.054, <i>wR</i> ₂ = 0.082 ^f	<i>R</i> = 0.049, <i>wR</i> = 0.048 ^e (<i>R</i> = 0.154, <i>wR</i> = 0.187 ^e) ^g
Largest diff. peak and hole/e Å ^{−3}	1.46 and −1.70	5.75 and −2.17	2.35 and −1.85 (6.56 and −2.86) ^g

^a Typical threshold of $F \geq 4\sigma(F)$. ^b The ratio of min./max. transmission is provided by SADABS.⁴³ ^c On F_o . ^d On F_o^2 . ^e Structure was refined on F_o ; $wR = [\sum[w(F_o - F_c)^2]/\sum w(F_o^2)]^{1/2}$ where $w^{-1} = [\sigma^2(F_o) + 0.0002(F_o^2)]$. ^f Structure was refined on F_o^2 using all data; the value of *R*₁ is given for comparison with older refinements based on F_o with a typical threshold of $F \geq 4\sigma(F)$. $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)]^{1/2}$ where $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$. ^g Restrained model of 3(CF₃SO₃)₅·MeOH·2MeCN.

for deactivation *via* thermal population of the d–d states to be of any consequence in both [Os(L1)₃]²⁺ and *HHH*-[OsLu(L2)₃]⁵⁺ (see previous section). Indeed, on going from *fac*-[Os(L2)₃]²⁺ to *HHH*-[OsLu(L2)₃]⁵⁺, the emission intensity maxima and lifetimes actually undergo a marginal decrease (*ca.* 20 ns at 296 K). These relatively small differences demonstrate that coordination of trivalent Lu has only a minor overall impact on the emissive properties of the Os^{II} chromophore; indeed, the photophysical properties of *HHH*-[OsLu(L2)₃]⁵⁺ are almost identical to those of the mononuclear complex *fac*-[Os(L1)₃]²⁺.

Conclusions

Using conditions typical for the preparation of tris-substituted Os^{II} complexes of bidentate α,α' -diimine ligands,³² the synthesis of the mononuclear chromophore [Os(L1)₃]²⁺ has been achieved straightforwardly and in high yield. Separation of its isomers into Δ - and Λ -*mer*-[Os(L1)₃]²⁺ and *rac-fac*-[Os(L1)₃]²⁺ on an ion-exchange resin with a chiral eluent is likewise unproblematic, and the high resilience of these complexes to isomerisation (on standing in polar solvents for months) demonstrates greater kinetic inertness than their previously reported Ru^{II} analogues.³⁰ The reaction conditions are, however, not appropriate for the preparation of the bimetallic helicates *HHH*-[OsLn(L2)₃]⁵⁺ *via* a self-assembly approach, since the templating effect of the

Ln^{III} ion is depleted in potentially chelating solvents such as glycols. The latter reaction is better achieved in ethanol at high temperature and pressure. Thus, although still limited by (i) the low reactivity of the osmium precursors, (ii) the formation of inert side products and (iii) eventual complex degradation, the inert complex *HHH*-[OsLu(L2)₃]⁵⁺ has been isolated and purified, constituting the first bimetallic d–f helicate based on Os^{II}. Photophysical and electrochemical investigations on the [Os(L1)₃]²⁺ chromophore suggest significant π_M – π_L orbital overlap combined with configurational mixing between ground and excited states. Consequently, the electrochemical data are difficult to correlate with spectroscopic properties because the incriminated electron transfer cannot be assigned to localized metal-centred or ligand-centred processes. Finally, as is clear from comparison of the photophysical properties of *fac*-[Os(L1)₃]²⁺, *fac*-[Os(L2)₃]²⁺ and *HHH*-[OsLu(L2)₃]⁵⁺, the presence of the tridentate binding unit on L2, even when occupied by an electropositive Lu^{III} ion, has little impact on the donor levels of the Os^{II} chromophore. Being connected by a saturated methylene linker, the two coordination sites in helicates *HHH*-[OsLn(L2)₃]⁵⁺ are thus isolated and with emission at $\tilde{\nu} \approx 12\,500\text{ cm}^{-1}$ the donor levels of the Os^{II} chromophore *fac*-[Os(L2)₃]²⁺ should be ideally suited for multipolar energy transfer to NIR emitters, in particular Pr^{III}, Yb^{III} and Er^{III} (low energy emissive states of 10 000 cm^{−1}, 10 200 cm^{−1} and 6500 cm^{−1} respectively).

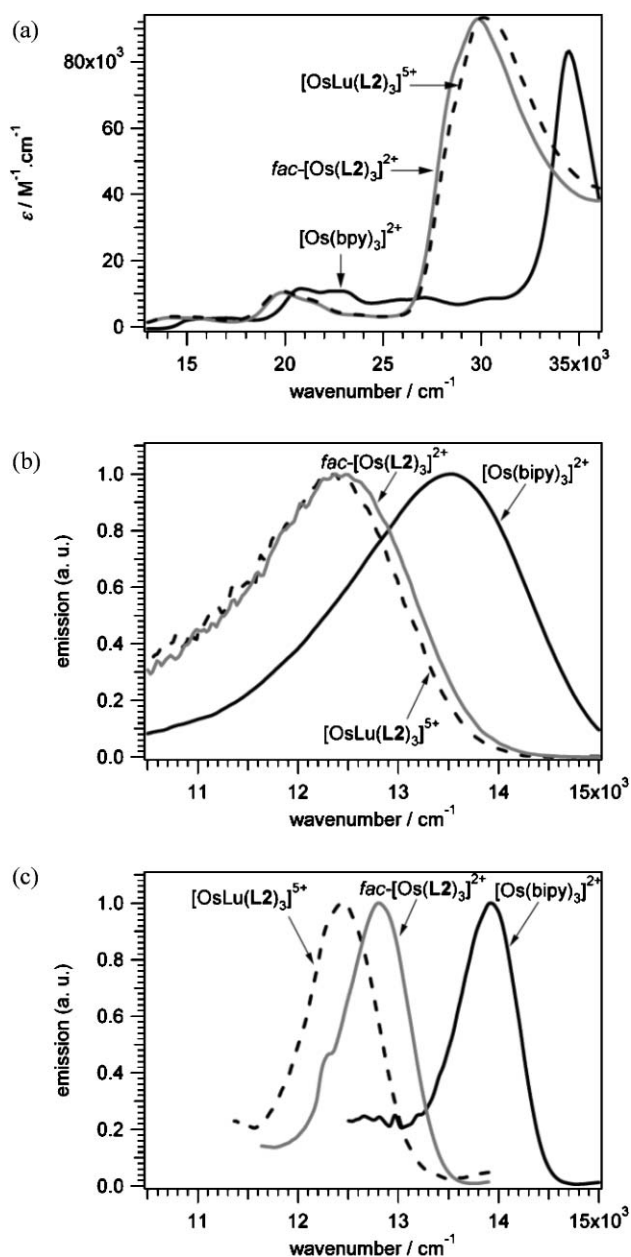


Fig. 12 (a) Room temperature absorption spectra (10^{-5} M in CH_3CN), (b) normalised room temperature emission spectra (10^{-6} M in CH_3CN) and (c) normalised 77 K emission spectra (butyronitrile–acetonitrile glass, 1 : 1 v/v) of $\text{HHH-}[\text{OsLu}(\text{L2})_3]^{5+}$ and $\text{fac-}[\text{Os}(\text{L2})_3]^{2+}$ and $[\text{Os}(\text{bipy})_3]^{2+}$.

Experimental section

Solvents and starting materials

These were purchased from Fluka AG (Buchs, Switzerland) or Acros Organics and used without further purification unless otherwise stated. Acetonitrile, dichloromethane and *N,N*-dimethylformamide were distilled from CaH_2 . The ligands 5-methyl(1-methylbenzimidazol-2-yl)pyridine **L1**,³³ 2-{6-[*N,N*-diethylcarboxamido]pyridin-2-yl}-1,1'-dimethyl-5,5'-methylene-2'-(5-methylpyridin-2-yl)bis[1*H*-benzimidazole] **L2**,^{31c} $[\text{Os}(\text{DMSO})_4\text{Cl}_2]^{16}$ and $\text{Na}_2\text{Sb}_2[+(+)\text{-C}_4\text{O}_6\text{H}_2]_2 \cdot 5\text{H}_2\text{O}$ ¹⁸ were prepared according to literature procedures. The triflate salt

$\text{Lu}(\text{CF}_3\text{SO}_3)_3 \cdot 4.6\text{H}_2\text{O}$ was prepared from the corresponding oxide (Aldrich, 99.99%).³⁴ The Lu content of solid salts was determined by complexometric titrations with Titriplex III (Merck) in the presence of urotropine and xylene orange.³⁵

Preparation of $[\text{Os}(\text{L1})_3](\text{PF}_6)_2$

A typical procedure is as follows: OsCl_3 (44 mg, 0.15 mmol) and **L1** (100 mg, 0.45 mmol, 3 equiv.) were stirred at 180 °C in ethylene glycol (20 ml) for 86 h. On cooling, a saturated aqueous solution of NH_4PF_6 (5 ml) was added to precipitate the hexafluorophosphate salt. The solid was collected on a filter, washed with cold water, dried and precipitated from Et_2O –MeCN to give $[\text{Os}(\text{L1})_3](\text{PF}_6)_2$ as a black solid, containing a ca. 3 : 1 mixture of *mer* and *fac* isomers (140 mg; yield 80%). ESI-MS m/z : 431.1 $\{[\text{Os}(\text{L1})_3]^{2+}\}$, 1006.5 $\{[\text{Os}(\text{L1})_3(\text{PF}_6)]^+\}$. Elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{39}\text{N}_9\text{P}_2\text{F}_{12}\text{Os} \cdot 2\text{H}_2\text{O} \cdot \text{MeCN}$: C 43.07, H 3.78, N 11.41; found: C 43.33, H 4.20, N 11.10.

Separation of *mer*- $[\text{Os}(\text{L1})_3](\text{PF}_6)_2$, **1**(PF_6)₂, and *fac*- $[\text{Os}(\text{L1})_3](\text{PF}_6)_2$, **2**(PF_6)₂

The mixture of *mer*- and *fac*- $[\text{Os}(\text{L1})_3](\text{PF}_6)_2$ was first converted to its chloride salt to increase solubility in water. Thus, to a solution of the crystalline powder (40 mg) in acetone (1–2 ml) was added a saturated solution of LiCl in acetone (ca. 4 ml). The resulting precipitate was collected on a membrane filter and dried. To a glass column (100 × 1.5 cm) was added SP Sephadex C25 (ca. 23 g) swollen in water. Once settled, the stationary phase was washed with water. The solid chloride salt was dissolved in water and sorbed onto the surface of the stationary phase. Elution with an aqueous solution of $\text{Na}_2\text{Sb}_2[+(+)\text{-C}_4\text{O}_6\text{H}_2]_2$ (0.09 M) then caused a dark red band to descend, which slowly separated into three fractions over time. The first two fractions are of approximately equal colour intensity and correspond to Λ - and Δ -*mer*- $[\text{Os}(\text{L1})_3]^{2+}$, the third corresponds to *rac-fac*- $[\text{Os}(\text{L1})_3]^{2+}$. After ca. 24 h all three fractions had been recovered. Saturated NH_4PF_6 (3–5 ml) was added to each and the resulting precipitates were collected on a membrane filter and washed with cold water. The solids were dried under vacuum and recrystallised from Et_2O –MeCN or Et_2O –MeOH to give microcrystals suitable for X-ray crystallography. Yields in the range 80–90% were obtained, with the relative proportions of *mer*- and *fac*- $[\text{Os}(\text{L1})_3](\text{PF}_6)_2$ depending on those of the crude material (see above).

***mer*- $[\text{Os}(\text{L1})_3](\text{PF}_6)_2$, **1**(PF_6)₂.** See Table 1 for ^1H NMR assignments. ESI-MS m/z : 431.1 $\{[\text{Os}(\text{L1})_3]^{2+}\}$, 1006.5 $\{[\text{Os}(\text{L1})_3(\text{PF}_6)]^+\}$. Elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{39}\text{N}_9\text{-P}_2\text{F}_{12}\text{Os} \cdot 2\text{H}_2\text{O} \cdot \text{MeCN}$: C 43.07, H 3.78, N 11.41; found: C 43.39, H 4.23, N 11.14.

***fac*- $[\text{Os}(\text{L1})_3](\text{PF}_6)_2$, **2**(PF_6)₂.** ^1H NMR (CD_3CN ; 400 MHz): δ = 8.33 (3H, d, J^3 = 8.4 Hz, H^3), 7.73 (3H, d, J^3 = 8.4 Hz, H^7), 7.60 (3H, dq, J^3 = 8.5 Hz, J^4 = 0.8 Hz, H^2), 7.47 (3H, overlapping ddd, J^3 = 7.4 Hz, J^4 = 1.0 Hz, H^6), 7.40 (3H, s, H^1), 6.89 (3H, overlapping ddd, J^3 = 7.4 Hz, J^4 = 1.0 Hz, H^5), 5.87 (3H, d, J^3 = 8.3 Hz, H^4), 4.46 (9H, s, Me^2), 2.26 (9H, s, Me^1). ESI-MS m/z : 431.1 $\{[\text{Os}(\text{L1})_3]^{2+}\}$, 1006.5 $\{[\text{Os}(\text{L1})_3(\text{PF}_6)]^+\}$. Elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{39}\text{N}_9\text{P}_2\text{F}_{12}\text{Os} \cdot \text{MeOH}$: C 43.69, H 3.67, N 10.66; found: C 43.98, H 3.99, N 10.85.

Preparation of [OsLu(L2)₃](CF₃SO₃)₅

OsCl₃ (18.2 mg, 0.06 mmol), **L2** (100 mg, 0.18 mmol, 3 equiv.) and Lu(CF₃SO₃)₃·4.6H₂O (43.3 mg, 0.06 mmol, 1 equiv.) were combined in ethanol (*ca.* 20 ml) and heated to *ca.* 150 < *T* < 160 °C in a pressure vessel for 48 h. On cooling, MeOH (20 ml) was added to the black solution and an insoluble black solid was removed by filtration. The filtrate was collected and the solvent removed under reduced pressure to give a dark red solid. The crude product was partitioned between Na(CF₃SO₃)_{aq} (100 ml) and CH₂Cl₂ (100 ml) (emulsion forms in the aqueous phase: leave to settle for several hours) and the aqueous phase was further washed with 2 × 100 ml portions of CH₂Cl₂. The organic phases were combined, dried and then chromatographed several times on neutral Al₂O₃ (40 × 2 cm) using 2–5% MeOH in CH₂Cl₂ (*v/v*) as eluent. The main pink fraction obtained was evaporated to dryness to give *ca.* 15 mg of a dark red solid which contained a *ca.* 3 : 1 mixture of *fac*-[Os(L2)₃]²⁺ and *mer*-[Os(L2)₃]²⁺. Based on the mass of *fac*-[Os(L2)₃]²⁺, one equiv. of Lu(CF₃SO₃)₃·4.6H₂O (*ca.* 4 mg) was added in MeCN (10 ml). After stirring for 10 min, the solvent was removed under reduced pressure and the solid dried. Recrystallisation from hot ethanol (2–3 ml) then afforded [OsLu(L2)₃](CF₃SO₃)₅ as a black microcrystalline powder (10 mg; yield 6%). ¹H NMR (CD₃CN; 400 MHz): δ = 8.64 (3H, d, *J*³ = 8.1 Hz, H¹²), 8.28 (3H, t, *J*³ = 8.1 Hz, H¹³), 8.23 (3H, d, *J*³ = 8.1 Hz, H³), 7.83 (3H, d, *J*³ = 8.1 Hz, H¹⁴), 7.61 (3H, d, *J*³ = 8.8 Hz, H⁴), 7.53 (3H, d, *J*³ = 8.8 Hz, H¹¹), 7.48 (3H, dq, *J*³ = 8.6 Hz, *J*⁴ = 0.8 Hz, H²), 7.26 (3H, dd, *J*³ = 8.5 Hz, *J*⁴ = 1.5 Hz, H⁵), 7.15 (3H, s, H¹), 6.99 (3H, dd, *J*³ = 8.4 Hz, *J*⁴ = 1.6 Hz, H¹⁰), 5.43 (3H, s, H⁹), 4.85 (3H, s, H⁶), 4.47 (9H, s, Me²), 4.43 (9H, s, Me³), 3.61 (6H, AB q, *J*² = 16.4 Hz, H^{7,8}), 3.50–3.36 (6H, m, H^{17,18}), 2.84–2.58 (6H, m, H^{15,16}), 2.14 (9H, s, Me¹), 1.05 (9H, t, *J*³ = 7.2 Hz, Me⁵), 0.68 (9H, t, *J*³ = 7.1 Hz, Me⁴). ESI-MS *m/z*: 536.8 {[OsLu(L2)₃](CF₃SO₃)₄]⁴⁺}, 765.0 {[OsLu(L2)₃](CF₃SO₃)₃]³⁺}, 910.8 {[Os(L2)₃]²⁺}, 1222.2 {[OsLu(L2)₃](CF₃SO₃)₃]²⁺}, 1971.7 {[Os(L2)₃](CF₃SO₃)₂]⁺}. High resolution ESI-MS: *m/z* 764.8728 {[OsLu(L2)₃](CF₃SO₃)₂]³⁺} (calculated 764.8765 for OsLuC₁₀₁H₉₉N₂₁O₉F₆S₂, deviation: −4.8 ppm). Elemental analysis calcd (%) for OsLuC₁₀₄H₉₉F₁₅N₂₁O₁₈S₅·1.9H₂O: C 45.00, H 3.73, N 10.59; found: C 44.97, H 3.52, N 10.59. Slow diffusion of Et₂O vapour into a solution of the complex in MeCN–MeOH (4 : 1 *v/v*) afforded single crystals of [OsLu(L2)₃](CF₃SO₃)₅·MeOH·2MeCN, the solid-state structure of which was determined by single crystal X-ray crystallography.

Spectroscopic and analytical measurements

¹H NMR spectra were recorded on a Bruker DRX-400 spectrometer at 298 K. Chemical shifts are given in ppm *versus* CD₃CN. Pneumatically-assisted electrospray (ESI-MS) mass spectra were recorded from 10^{−4} M acetonitrile solutions on a Finnigan SSQ7000 instrument. CD spectra in the UV/Vis were recorded at 298 K from 10^{−5} M solutions in acetonitrile with a JAS.CO J-815 CD spectrometer, connected to a JAS.CO PFD-350S thermostat, using quartz cells of 1 cm path length. Electronic spectra in the UV/Vis/NIR were recorded at 298 K from 10^{−5} M solutions in acetonitrile with a Cary 5000 UV/Vis/NIR spectrophotometer, using quartz cells of 0.1 and 1 cm path length. Emission and excitation spectra were measured on a Horiba Fluorolog3

fluorescence spectrometer. The emission quantum yields Φ were calculated according to:

$$\frac{\Phi_x}{\Phi_r} = \frac{[1 - \exp(-A_x(\nu))]I_x(\nu)n_x^2D_x}{[1 - \exp(-A_r(\nu))]I_r(\nu)n_r^2D_r}$$

where x refers to the sample and r to the reference, *A* is the absorbance at the excitation wavenumber used in the experiment, *I* the intensity of the excitation light, *n* the refractive index of the solvent and *D* the integrated emitted intensity. [Ru(bipy)₃](PF₆)₂ (Φ = 0.062 in acetonitrile) was used as reference for the determination of the quantum yields of the complexes. The fluorescence decay curves were recorded on a home-built set-up consisting of a single monochromator (Spex 270M) equipped with a nitrogen-cooled CCD camera (SpectrumOne Jobin Yvon-Spex) and appropriate collection optics. For excited-state lifetime measurements, samples were excited at 532 nm with the second harmonic of a pulsed Nd:YAG laser (Quintel Brillant B, 20 Hz). Emission decay curves were recorded on a digital oscilloscope (Tektronix TDS 540B) using a fast photomultiplier tube (Hamamatsu TypH957–08). The time resolution of the set-up was around 14 ns. Low-temperature glasses were produced in a custom-built sample cell inserted into a closed-cycle helium refrigeration system (Oxford Instruments CCC1100T). Samples were purged with N₂ for 15 min prior to measurement. Cyclic voltammograms were recorded by using a BAS CV-50W potentiostat connected to a personal computer. A three electrode system consisting of a stationary Pt disc working electrode, a Pt counter-electrode and a non-aqueous Ag/AgCl reference electrode was used. (nBu)₄NPF₆ (0.1 M in MeCN) served as an inert electrolyte. The reference potential (*E* = −0.16 *vs* SCE) was standardised against [Ru(bipy)₃](ClO₄)₂.³⁶ The scan speed was 100 mV s^{−1} and voltammograms were analysed according to established procedures.³⁶ Elemental analyses were performed by Dr E. Solari from the Microanalytical Laboratory of the École Polytechnique Fédérale de Lausanne. Microwave-assisted test reactions in ethanol were carried out using a focused microwave unit (Biotage InitiatorTM). The instrument consists of a continuous focused microwave power delivery system with operator selectable power output from 0–300 W. In all experiments, a constant power was applied to ensure reproducibility. Reactions were performed in glass vessels (2–5 ml) sealed with a septum. Pressure measurement is accomplished by a non-invasive sensor integrated into the cavity lid, which measures the deformation of the Teflon seal of the vessels (maximum 20 bar). Temperature control is achieved by means of an IR sensor and the indicated temperature corresponds to the maximal temperature reached during each experiment. The specified reaction time corresponds to the total irradiation time. Efficient cooling is accomplished by means of pressurized air.

X-Ray crystallography

The crystal data, intensity measurements and structure refinement parameters are collected in Table 8. The crystals were mounted on quartz fibre with protection oil. For Λ-*mer*-[Os(L1)₃](PF₆)₂·1.5MeCN (Λ-1(PF₆)₂·1.5MeCN) and [OsLu(L2)₃](CF₃SO₃)₅·MeOH·2MeCN (3(CF₃SO₃)₅·MeOH·2MeCN) cell dimensions and intensities were measured at 150 K on a Stoe IPDS image-plate diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å). Data were

corrected for Lorentz and polarisation effects and for absorption. Solutions were generated by direct methods (SIR97³⁷). Refinement by full-matrix non-linear least squares of all F data and all other calculations were performed with the XTAL³⁸ system and ORTEP³⁹ programs. For *fac*-[Os(L1)₃](PF₆)₂, 2(PF₆)₂, cell dimensions and intensities were measured at 100 K on a Bruker-AXS APEX CCD area detector diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Diffraction intensity data collection was run using SMART operating software.⁴⁰ Intensities were then integrated from several series of exposures (each exposure covering 0.3° in ω), merged and corrected for Lorentz and polarisation effects using SAINT software.⁴¹ Solutions were generated by conventional direct methods and refined by full-matrix non-linear least squares on all F^2 data, using SHELXS-97 and SHELXL software respectively (as implemented in the SHELXTL suite of programs).⁴² Empirical absorption corrections were applied based on multiple and symmetry-equivalent measurements using SADABS.⁴³ CCDC-664400 and CCDC-664401 contains the supplementary crystallographic data for **1**-(PF₆)₂ and **2**(PF₆)₂. Although the crystal structure of 3(CF₃SO₃)₅·MeOH·2MeCN unambiguously demonstrates the formation of a triple-stranded bimetallic helicate in the solid-state, the data are contaminated by systematic error (the origin of which is unknown) and the model merits no further analysis than establishing the basic connectivity of atoms in the complex cation. Allowed to refine freely, the resulting model contains chemically unreasonable bond lengths and does not justify deposition at the CCDC. The structure deposited at the CCDC (CCDC-664402) is therefore one in which all 1,2- and 1,3- (and in some cases 1,4-) distances have been restrained. Parameters for both refinements (free and restrained) are, however, listed in Table 8 and the .cif file for the unrestrained model of 3(CF₃SO₃)₅·MeOH·2MeCN is given in the ESI.†

CCDC reference numbers 664400–664402. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718885d

Acknowledgements

We are grateful to Dr John C. Jeffery at the University of Bristol for help with the X-ray crystallographic studies. We would also like to thank the European Commission for financial support under the “Directorate D – The human factor, mobility and Marie Curie activities” scheme. This work is supported through grants from the Swiss National Science Foundation.

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