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Expanded ligands: bis(2,2′:6′,2″-terpyridine carboxylic acid)ruthenium(II) complexes as metallosupramolecular analogues of dicarboxylic acids†

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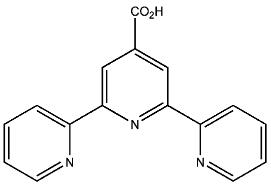
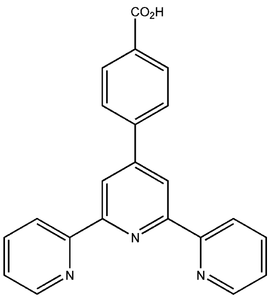
Ligands in which multiple metal-binding domains are linked by a metal-containing moiety rather than a conventional organic group are described as "expanded ligands". The use of 4,4′-difunctionalised {Ru(tpy)$_2$} units provides a linear spacer between metal-binding domains and we have extended this motif to expanded ligands containing two carboxylic acid metal-binding domains. In this paper, we describe the synthesis and structural characterisation of ruthenium(II) complexes of 2,2′:6′,2″-terpyridine-4′-carboxylic acid and 4′-carboxyphenyl-2,2′:6′,2″-terpyridine. The ability of the ruthenium(II) centre to charge compensate deprotonation of the carboxylic acid leads to Zwitterionic complexes and three representative compounds have been structurally characterised.

Introduction

We have recently been developing the concept of "expanded ligands" in which metal-binding domains are linked through metal-containing scaffolds.[1–8] Typical scaffolds are {M(bpy)$_3$}[9] and {M(tpy)$_2$}[10–12] moieties (bpy = 2,2′-bipyridine, tpy = 2,2′:6′,2″-terpyridine), which possess different topological and topographical properties as well as potentially different numbers of attached metal-binding domains.[13,14]



H1



H2

This paper is concerned with ruthenium complexes of the carboxylic acid ligands **H1** and **H2**. The origin of the term "expanded ligands" is seen in Fig. 1 which presents the ideal carboxylic acid C⋯C distances in oxalic acid, terephthalic acid, and the complexes [Ru(H**1**)$_2$]$^{2+}$ and [Ru(H**2**)$_2$]$^{2+}$. The C⋯C distance increases by about 20 Å or over 1000% on moving from oxalic acid to [Ru(H**2**)$_2$]$^{2+}$.

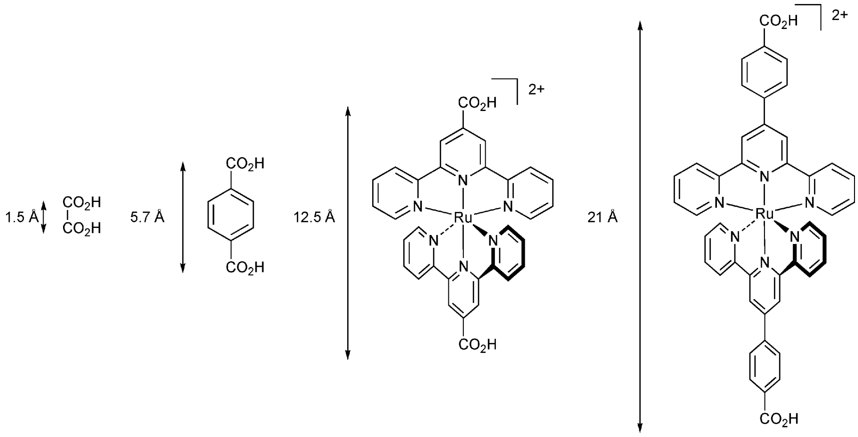


Fig. 1 The concept of an expanded ligand exemplified by the comparison of oxalic and terephthalic acids with the complex cations bis[Ru(H1)$_2$]$^{2+}$ and [Ru(H**2**)$_2$]$^{2+}$.

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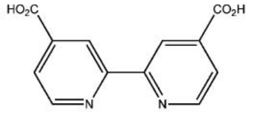
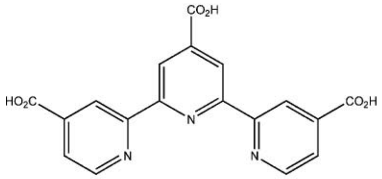
Di- and polycarboxylic acids are widely used as bridging ligands for the construction of coordination polymers and networks and have been shown to form a wide variety of one-, two- and three-dimensional simple or interpenetrated structures.[15] Carboxylic acid derivatives of oligopyridines are a reasonably well-known class of ligands and ruthenium complexes of 2,2′-bipyridine-4,4′-dicarboxylic acid $H_2\mathbf{3}$ and 2,2′:6′,2″-terpyridine-4,4′,4″-tricarboxylic acid $H_3\mathbf{4}$ have found widespread application in dye-sensitised photovoltaic cells.[16] Our scaffolds of choice are kinetically inert d^6 ruthenium(II) complexes and although a number of structural determinations of ruthenium complexes of 2,2′-bipyridine 4-[17–27], 5-[28] and 6-carboxylic acids[29–31] have been reported, the only example of a structurally characterised 2,2′:6′,2″-terpyridine carboxylic acid complex is found for $[NEt_4]_2[Ru(H_2\mathbf{4})(NCS)_3]$[32,33] which is the active dye for the preparation of one popular class of dye-sensitized solar cells. In these structurally characterised species, the inherent ambiguity in the protonation state of the carboxylic acid substituents is clearly demonstrated. The structural complexity arising from the use of bidentate bpy ligands, which typically results in trifurcated or hexafurcated structures, has led us to concentrate upon $\{Ru(tpy)_2\}$ scaffolds. We have, therefore, investigated the behaviour of the linearly expanded ligand acids $[Ru(H\mathbf{1})_2]^{2+}$ and $[Ru(H\mathbf{2})_2]^{2+}$ each of which can generate $[Ru(H\mathbf{1})_2]^{2+}$, $[Ru(H\mathbf{1})(\mathbf{1})]^{+}$ or $[Ru(\mathbf{1})_2]$ units in the crystal, where **HL** represents **H1** or **H2**. In this paper we report the synthesis of these complexes and describe the hydrogen bonding interactions that characterise the solid state species.



$H_2\mathbf{3}$

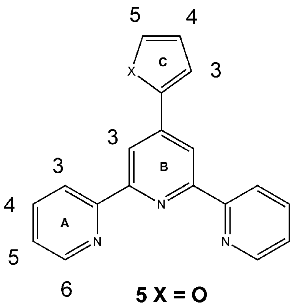


$H_3\mathbf{4}$

Results and discussion

Synthesis of $[Ru(H\mathbf{1})_2][PF_6]_2$

2,2′:6′,2″-Terpyridine-4′-carboxylic acid **H1** is not readily accessible[34–36] and we have developed a new and convenient synthesis of the complex cation $[Ru(H\mathbf{1})_2]^{2+}$. The key intermediate is 4′-(2-furyl)-2,2′:6′,2″-terpyridine **5**[37–39] which has been obtained from 2-acetylpyridine and 2-furaldehyde under various conditions. We have optimised the reaction conditions and obtain **5** in 86% yield from the reaction of 2-acetylpyridine with furaldehyde in ethanol in the presence of ammonia at 60 °C. Beley and coworkers have shown that the furyl substituent in the complex $[Ru(\mathbf{5})(\mathbf{6})]^{2+}$ can be oxidised to give the complex $[Ru(H\mathbf{1})(\mathbf{6})]^{2+}$ directly[38] and we have extended this reaction to the oxidation of $[Ru(\mathbf{5})_2]^{2+}$ to $[Ru(H\mathbf{1})_2]^{2+}$.



5 X = O

6 X = S

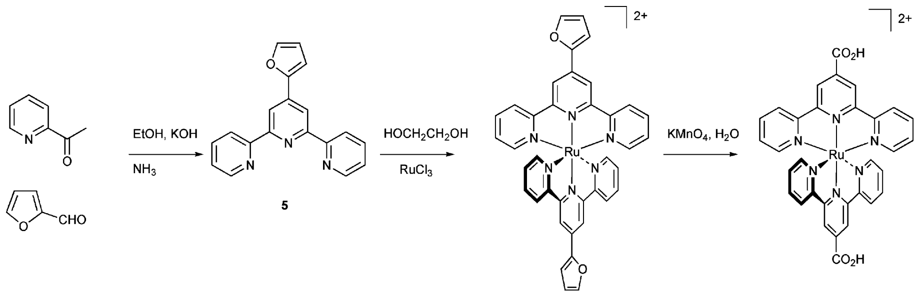
The complex $[Ru(\mathbf{5})_2][PF_6]_2$ was conveniently prepared in the one pot reaction of commercial $RuCl_3\cdot 3H_2O$ with two equivalents of **5** in ethane-1,2-diol under microwave heating conditions. After recrystallisation, the compound was obtained analytically pure as a red microcrystalline solid in 49% yield. The complex was fully characterised by conventional spectroscopic methods. A comparison of the free ligand **5** and the complex $[Ru(\mathbf{5})_2][PF_6]_2$ revealed the typical upfield shifting of H^{6A} upon coordination. The furyl protons are all shifted downfield upon coordination and the assignment of the furyl H^{3C}, which was initially based upon the $^3J_{3,4}$ coupling constant was confirmed by the observation of a cross peak between H^{3B} and H^{3C} in the NOESY spectrum (Fig. 2)

After investigating a variety of conditions for the oxidation of $[Ru(\mathbf{5})_2]^{2+}$ to $[Ru(H\mathbf{1})_2]^{2+}$ we finally developed a protocol involving oxidation in neutral aqueous solution with $KMnO_4$. The reaction can be followed by TLC and additional portions of $KMnO_4$ are added until no trace of the starting complex is observed. After work-up and recrystallisation, the complex $[Ru(H\mathbf{1})_2][PF_6]_2$ was obtained in 48% yield as a red crystalline solid. The ^1H NMR spectrum of the complex indicates that the furyl substituent is no longer present and the carboxylic acid CO_2H protons are observed as a broad singlet at δ 10.66 ppm in CD_3CN solution. The synthetic transformations are summarised in Scheme 1.

We note that although $[Ru(\mathbf{5})_2]^{2+}$ is stable in the solid state, some decomposition occurs when a CD_3CN solution of $[Ru(\mathbf{5})_2][PF_6]_2$ is exposed to sunlight over several days. Most NMR signals of the tpy remained unaffected, while the signals of the furanyl group were absent in the decomposition product, whose NMR spectra was nevertheless different from that of $[Ru(\mathbf{5})_2]^{2+}$. We have not investigated this reaction in detail, but note that the changes are in accord with partial oxidation of the furan.

Synthesis of $[Ru(H\mathbf{2})_2][PF_6]_2$ and related compounds

A number of reports have appeared describing ester[40] and amide[41–44] derivatives of 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine **H2** together with descriptions of iridium[45] and ruthenium[40,46–49] complexes and the use of the ruthenium complexes as carboxylate donor ligands in dirhodium complexes.[47] We have investigated a number of methods for the optimal preparation of $[Ru(H\mathbf{2})_2]^{2+}$. We originally considered the synthesis of the free ligand **H2** from the ester **7**, which was prepared in modest yield from 2-acetylpyridine and 4-methoxycarbonylbenzaldehyde using the solvent free conditions introduced by Raston and coworkers[50] followed by cyclisation with ammonium acetate in ethanol. The ester **7** was obtained in 25% yield after recrystallisation which represents an improvement over our previously reported 15% yield



Scheme 1

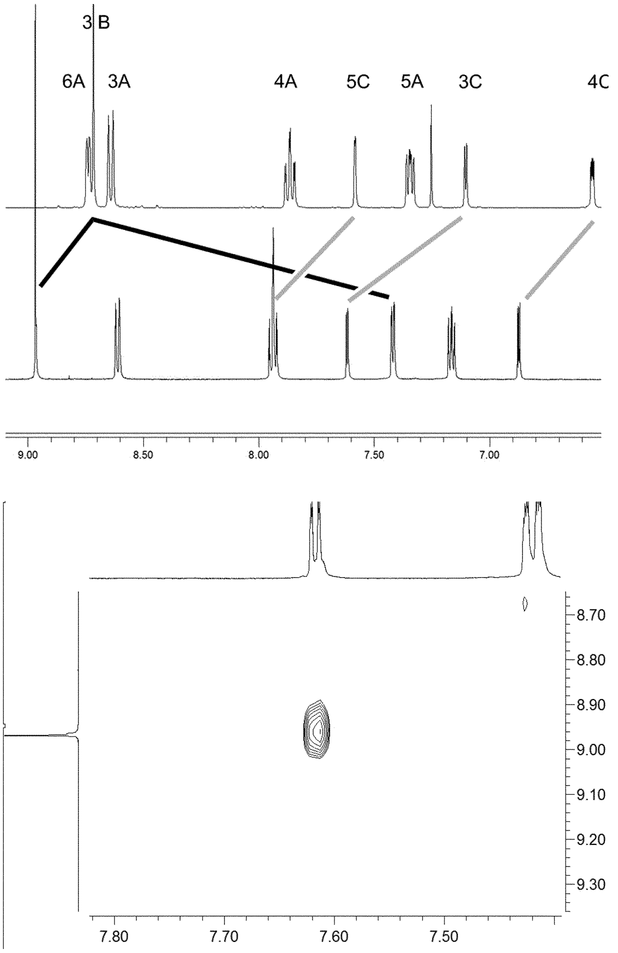


Fig. 2 Coordination shifts of ligand **5** on changing from the free ligand (upper trace, in $CDCl_3$, 400 MHz) to [Ru(**5**)$_2$][PF$_6$]$_2$ (middle trace, CD_3CN, 500 MHz). The typical upfield shift of H^{6A} (black) is observed, together with a downfield shifting of all the furyl protons (grey) and H^{3B} (black). The lower spectrum shows the cross peak between H^{3B} and H^{3C} in the NOESY spectrum of [Ru(**5**)$_2$][PF$_6$]$_2$ confirming the assignment of H^{3C}.

in a two step reaction.[40] The ligand was fully characterised by conventional spectroscopic and analytical methods.

We then considered two alternative routes for the preparation of [Ru(H**2**)$_2$]$^{2+}$ derivatives. Firstly, the direct hydrolysis of **7** to give the free acid H**2** with subsequent coordination to ruthenium and, secondly, the preparation and subsequent hydrolysis of [Ru(**7**)$_2$]$^{2+}$.

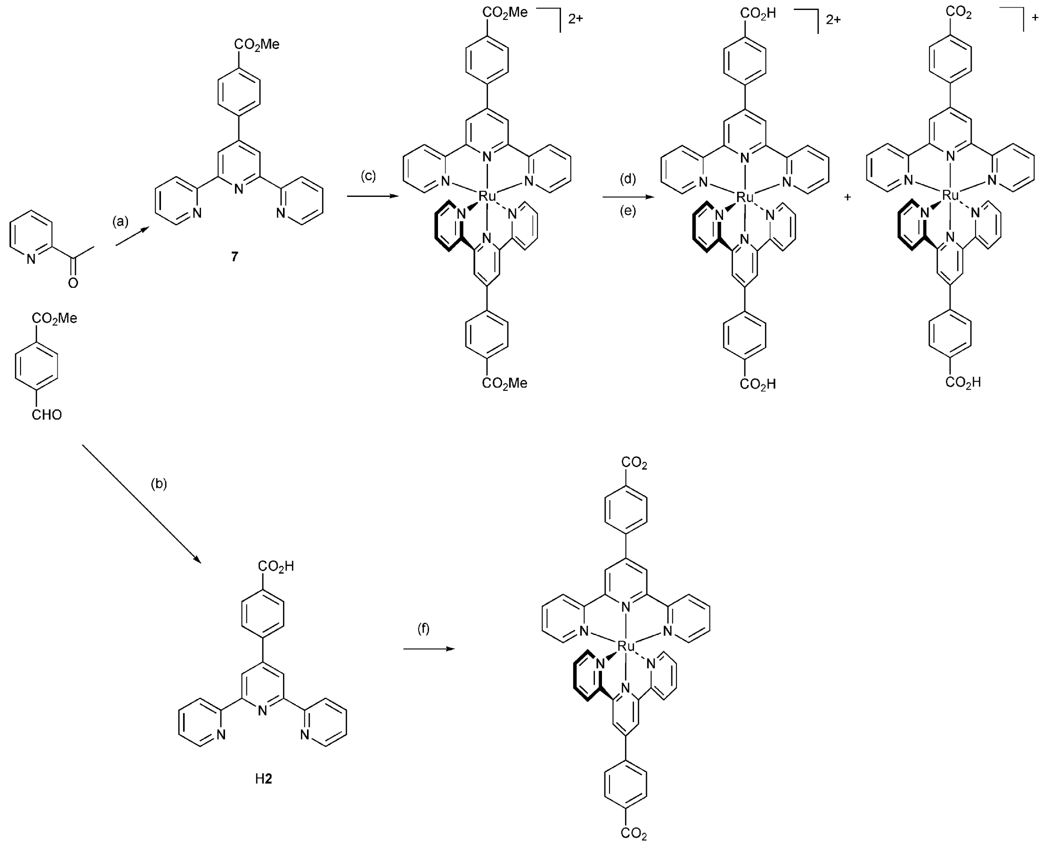
We experienced severe difficulties in defining reproducible conditions for the hydrolysis of the free ligand **7** and under apparently identical reaction conditions obtained yields varying between 0 and 80%. We have, however, found a reproducible method for the preparation of the free acid H**2** from 2-acetylpyridine and 4-methoxycarbonylbenzaldehyde in aqueous ethanol containing ammonia and NaOH. After acidic work-up, the desired acid is obtained in 49% yield as a white microcrystalline material. The overall yield of 12% over two steps is lower than the 22% reported by Campagna[45] but using a conventional ("non-Green") preparation of ester **7**[40,48] the overall yield is raised to >25%. We speculate that the low yields associated with the preparation of **7** might be associated with concurrent ester hydrolysis, although we have not isolated any acid from the reaction conditions reported in the experimental section.

The reaction of two equivalents of H**2** with commercial ruthenium trichloride in a pressure vessel in basic ethanol, followed by work-up in basic conditions gave the fully deprotonated complex [Ru(**2**)$_2$] as a deep red solid. The work-up of the complex is critical to the protonation state and under various conditions it is possible to obtain [Ru(**2**)$_2$], [Ru(**2**)(H**2**)]$^+$ or [Ru(H**2**)$_2$]$^{2+}$.

An alternative strategy for the synthesis of derivatives of [Ru(H**2**)$_2$]$^{2+}$ involves the preliminary synthesis of the ester complex [Ru(**7**)$_2$]$^{2+}$ and subsequent hydrolysis directly to complexes of H**2**. The ester complexes [Ru(**7**)$_2$][PF$_6$]$_2$ and [Ru(**7**)$_2$]Cl$_2$ were prepared in acceptable yield by standard methods (microwave synthesis in ethane-1,2-diol or thermal reaction in methanol) and isolated as red crystalline solids. The reaction of [Ru(**7**)$_2$][PF$_6$]$_2$ with sodium hydroxide in aqueous acetonitrile gave the salt [Ru(H**2**)$_2$][PF$_6$]$_2$ as a red solid in 64% yield. After drying *in vacuo* an approximately 8 : 2 mixture of [Ru(H**2**)$_2$][PF$_6$]$_2$ and [Ru(H**2**)(**2**)][PF$_6$] was obtained. Although the two tpy ligands of this complex are formally different, proton transfer is apparently fast in DMSO-d$_6$ (the only suitable solvent) and a single set of tpy signals are observed in the ^{1}H NMR spectrum. The synthetic transformations are summarised in Scheme 2.

Structural characterisation of ruthenium complexes of carboxylic acid derivatives

We have structurally characterised the precursor ester complex [Ru(**7**)$_2$]Cl$_2$·4H$_2$O and hydrates of [Ru(**1**)$_2$] and [Ru(**2**)$_2$], the latter being obtained from reactions aiming at the formation of coordination polymers or metal organic frameworks by reaction with additional metal salts in basic conditions.[51]



Scheme 2 (a) (i) KOH (ii) EtOH, NH_4OAc (b) (i) NH_3, H_2O, NaOH (ii) HCl (c) $RuCl_3\cdot 3H_2O$, $HOCH_2CH_2OH$, *N*-ethylmorpholine, microwave or $RuCl_3\cdot 3H_2O$, MeOH, 150 °C (d) NaOH, MeCN (e) HCl, NH_4PF_6 (f) $RuCl_3\cdot 3H_2O$, NEt_3, EtOH.

The ester complex $[Ru(\mathbf{7})_2]Cl_2\cdot 4H_2O$

The ester complex $[Ru(\mathbf{7})_2]^{2+}$ provides an excellent model for the carboxylic acid complexes without the ambiguity of protonation state and without a very strong hydrogen bond acceptor or donor in the coordination unit. X-Ray quality crystals of $[Ru(\mathbf{7})_2]Cl_2\cdot 4H_2O$ were obtained directly from the reaction mixture upon cooling.

The structure of the two crystallographically independent but chemically very similar cations is presented in Fig. 3 and confirms the expected $\{Ru(tpy)_2\}$ structural motif with pendant methoxycarbonylphenyl groups. The $\{Ru(tpy)_2\}$ motifs are typical with the tpy ligands being essentially coplanar and the least squares planes angles between any two bonded pyridine rings not being greater than 7° and most being below 4°. Bond lengths and angles within the coordination sphere and within the ligands are typical. The methoxycarbonylphenyl substituents show a rather different behaviour; two of the phenyl substituents are almost coplanar with the pyridine rings to which they are attached (rings containing N5 and N8, least squares planes angles 5 and 4°) whilst the other two make least squares planes angles of 36 and 40° with the directly bonded pyridine rings. The near coplanar phenyl substituents are π-stacked with a terminal pyridine of the independent cation, the one attached to the ring containing N8 with that containing N6, and that attached to the ring containing N5 with that containing N7. The stacked rings are offset and near coplanar with distances of atoms in one ring from the least squares plane of the other being in the range 3.3 – 3.6 Å. The presence of the additional aromatic ring at the 4′-position results in a lattice in which there are no typical tpy embraces.[52–54]

The second principal packing motif is a hydrogen bonding network involving the lattice water molecules, the chloride counterions and the carbonyl oxygen atoms. Each of the cations is hydrogen bonded to two water molecules through each of the carbonyl groups (O4 · · · O10, O8 · · · O11, O2 · · · O13 and O6 · · · O15: O · · · O, 2.80–2.95 Å; ∠O–H · · · O, 137–165°). The water and chloride ions form two distinct types of motif in the lattice. The first is a one dimensional hydrogen-bonded chain in the sequence Cl1 · · · O9 · · · Cl2 · · · O11 · · · O12 · · · O13 · · · Cl1A with typical Cl · · · O distances in the range 3.10–3.22 Å and O · · · O distances 2.73, 2.92 Å (Fig. 4). The remaining water and chloride ions have some positional disorder, but form discrete clusters with further hydrogen bonds to the cation carbonyl oxygen atoms.

The deprotonated complex $[Ru(\mathbf{1})_2]\cdot 4H_2O$

Dark red rhombic crystals of the complex $[Ru(\mathbf{1})_2]\cdot 4H_2O$ were obtained from a reaction of $[Ru(H\mathbf{1})_2][PF_6]_2$ with zinc nitrate in aqueous DMF under autoclave conditions.

The structure of the neutral $[Ru(\mathbf{1})_2]$ molecule is shown in Fig. 5. The $\{Ru(tpy)_2\}$ motif is very much as expected and the Ru–N distances are very similar to those in the ester complex $[Ru(\mathbf{7})_2]Cl_2$ discussed above. The carboxylate substituent is planar and near

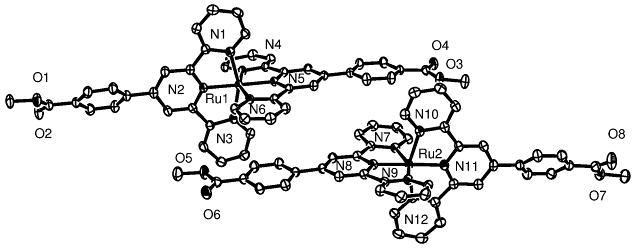


Fig. 3 The two crystallographically independent $[Ru(\mathbf{7})_2]^{2+}$ cations present in the lattice of $[Ru(\mathbf{7})_2]Cl_2{\cdot}4H_2O$. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are plotted at 50% probability. Selected bond lengths (Å) and angles (°): Ru1–N1, 2.067(3); Ru1–N2, 1.969(2); Ru1–N3, 2.064(3); Ru1–N4, 2.069(3); Ru1–N5, 1.971(2); Ru1–N6, 2.069(3); Ru2–N7, 2.076(3); Ru2–N8, 1.973(3); Ru2–N9, 2.068(3); Ru2–N10, 2.058(3); Ru2–N11, 1.971(3); Ru2–N12, 2.066(3); N1–Ru1–N2, 78.85(10); N1–Ru1–N3, 158.27(10); N2–Ru1–N3, 79.41(10); N1–Ru1–N4, 94.50(10); N2–Ru1–N4, 101.32(10); N3–Ru1–N4, 89.81(10); N1–Ru1–N5, 100.04(10); N2–Ru1–N5, 178.82(10); N3–Ru1–N5, 101.69(10); N4–Ru1–N5, 79.15(10); N1–Ru1–N6, 91.07(10); N2–Ru1–N6, 100.52(10); N3–Ru1–N6, 92.81(10); N4–Ru1–N6, 158.12(10); N5–Ru1–N6, 79.04(10); N7–Ru2–N8, 78.50(10); N7–Ru2–N9, 157.45(10); N8–Ru2–N9, 79.13(10); N7–Ru2–N10, 92.99(10); N8–Ru2–N10, 101.91(11); N9–Ru2–N10, 88.85(10); N7–Ru2–N11, 101.89(10); N8–Ru2–N11, 178.75(11); N9–Ru2–N11, 100.54(10); N10–Ru2–N11, 79.28(11); N7–Ru2–N12, 91.99(10); N8–Ru2–N12, 100.14(11); N9–Ru2–N12, 94.69(10); N10–Ru2–N12, 157.94(10); N11–Ru2–N12, 78.67(11).

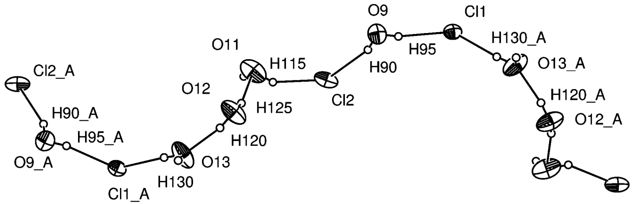


Fig. 4 The one dimensional chain of chloride ions and water molecules in the lattice of $[Ru(\mathbf{7})_2]Cl_2{\cdot}4H_2O$. The chain is linked to the cations through additional hydrogen bonds from O13 and O11. The symmetry description refers to atoms generated by the symmetry operator $x + 1/2, -y, z$.

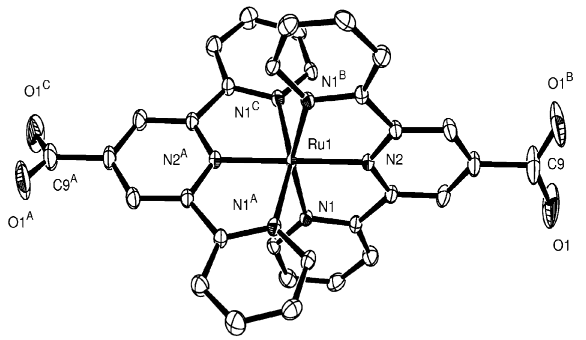


Fig. 5 The structure of $[Ru(\mathbf{1})_2]$ in the compound $[Ru(\mathbf{1})_2]{\cdot}4H_2O$. Selected bond lengths (Å) and angles (°): Ru1–N1, 2.0667(19); Ru1–N2, 1.9768(16); C9–O1, 1.226(2); N1–Ru1–N2, 78.84(5); N2–Ru1–N2A, 180.0(0); N1–Ru1–N1A, 92.148(17); N1–Ru1–N1B, 157.67(9); N2–Ru1–N1A, 101.16(5); O1–C9–O1B, 127.0(3). The symmetry labels A, B and C refer to the symmetry operators $(y, -x, -z)$, $(-x, -y, z)$ and $(-y, x, -z)$. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids at 50% probability level.

coplanar with the central ring of the terpyridine to which it is attached (least squares planes, 20°). The carboxylate C–O bonds are equal with a bond length of 1.226(2) Å and O–C–O of 127.0(3)° fully consistent with a delocalised carboxylate.

The lattice comprises hydrogen bonded sheets of water molecules and carboxylate groups separated by layers of the $\{Ru(tpy)_2\}$ units. Fig. 6a shows a view of the hydrogen-bonded sheet along *c* and illustrates the formation of a net of 12-membered (non-hydrogen atoms) rings. Reducing the network to a nodal representation, the sheets are an example of the (6, 3) network in which the three-connected nodes are the lattice water molecules. The corrugated water–carboxylate sheets separate the $\{Ru(tpy)_2\}$ motifs as shown in Fig. 6b.

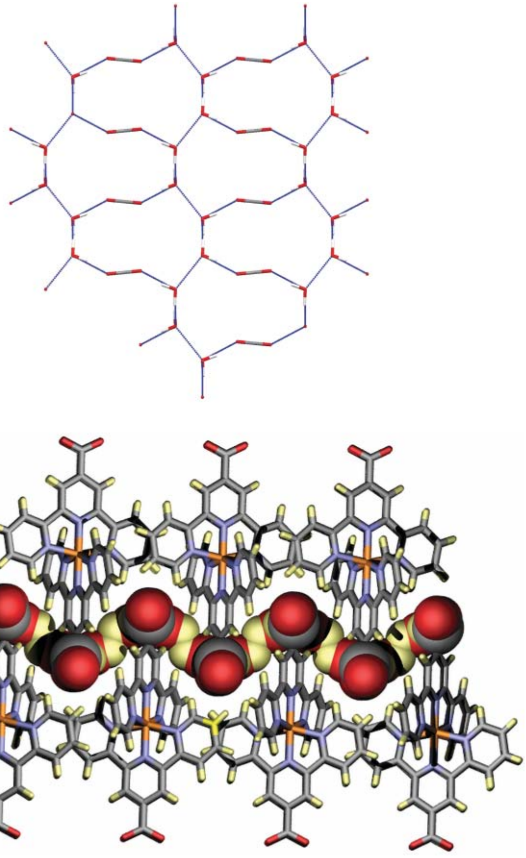


Fig. 6 (a) The (6, 3) net formed in the hydrogen-bonded sheets of water molecules and carboxylate in the lattice of $[Ru(\mathbf{1})_2]{\cdot}4H_2O$ and (b) a projection orthogonal to part a showing the alternating layers of water sheets and $\{Ru(tpy)_2\}$ motifs.

The deprotonated complex $[Ru(\mathbf{2})_2]{\cdot}5H_2O$

X-Ray quality crystals of the complex $[Ru(\mathbf{2})_2]{\cdot}5H_2O$ were obtained from the reaction of the complex $[Ru(H\mathbf{2})_2][PF_6]_2$ with europium(III) nitrate in aqueous DMF in an autoclave. The compound is topologically equivalent to $[Ru(\mathbf{1})_2]$ discussed above, although the incorporation of the 1,4-phenylene residue is expected to increase the C-carboxylate-to-C-carboxylate distance from ~13 Å to ~21 Å. This expansion of the ligand is expected to result in differences in packing consistent with the Kitaigorodsky close packing model.[55] The structure of the neutral $[Ru(\mathbf{2})_2]$

species present in the lattice is presented in Fig. 7. The typical features of the $\{Ru(tpy)_2\}$ core are present and the structural features of the coordination unit closely resemble those in $[Ru(\mathbf{7})_2]Cl_2\cdot4H_2O$. Once again, there is no significant influence of the remote charged carboxylate substituent on the Ru–N distances. The average Ru–$N_{terminal}$ and Ru–$N_{central}$ distances for $[Ru(\mathbf{7})_2]Cl_2\cdot4H_2O$ are 2.07 Å and 1.97 Å and for $[Ru(\mathbf{2})_2]\cdot5H_2O$ 2.07 Å and 1.97 Å respectively. The phenylene rings are not coplanar with the pyridine to which they are bonded but make least squares planes angles of 19° (ring bonded to pyridine with N5) and 29° (ring bonded to pyridine with N2). As in $[Ru(\mathbf{1})_2]\cdot4H_2O$, the carboxylate substituent is planar and near coplanar with the ring to which it is bonded (least squares planes, 17 and 10°). The carboxylate C–O bonds are equivalent with a bond lengths in the range 1.25–1.26 Å and O–C–O of 125.4(3) and 125.7(3)° fully consistent with a delocalised carboxylate.

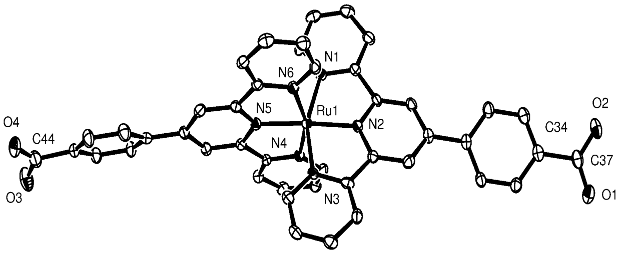


Fig. 7 The $[Ru(\mathbf{2})_2]\cdot5H_2O$ unit present in $[Ru(\mathbf{2})_2]\cdot5H_2O$ showing the partial numbering scheme adopted. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–N1, 2.080(2); Ru1–N2, 1.978(2); Ru1–N3, 2.065(2); Ru1–N4, 2.063(2); Ru1–N5, 1.971(2); Ru1–N6, 2.067(2); C37–O1, 1.252(4); C37–O2, 1.256(4); C44–O3, 1.265(4); C44–O4, 1.256(4); N1–Ru1–N2, 78.56(9); N1–Ru1–N3, 157.39(9); N2–Ru1–N3, 78.88(9); N1–Ru1–N4, 91.73(9); N2–Ru1–N4, 98.99(9); N3–Ru1–N4, 93.24(9); N1–Ru1–N5, 104.46(9); N2–Ru1–N5, 176.23(10); N3–Ru1–N5, 98.14(9); N4–Ru1–N5, 78.79(10); N1–Ru1–N6, 91.70(9); N2–Ru1–N6, 103.30(10); N3–Ru1-N6, 92.02(9); N4–Ru1–N6, 157.69(9); N5–Ru1–N6, 79.01(10); C34–C37–O2, 116.6(3); O3–C44–O4, 125.4(3). Thermal ellipsoids at 50% probability level.

As in $[Ru(\mathbf{1})_2]\cdot4H_2O$, the carboxylate oxygen and water molecules build a complex hydrogen bonded network. Two separate substructures are present. The first is a two-dimensional sheet (Fig. 8a) which exhibits the net structure (4.8^2) constructed from water and carboxylate residues. The formation of the (4.8^2) net is a remarkable validation of the expanded ligand concept as exactly this motif is found in the tetra-*n*-butylammonium terephthalate hydrate.[56] The second motif is a one dimensional chain (Fig. 8b). The two motifs are bridged by the $[Ru(\mathbf{2})_2]$ molecules and the end result is a 3D lattice (Fig. 9a). In the same way that $[Ru(\mathbf{1})_2]$ may be regarded as an expanded terephthalate ligand in which the C-carboxylate ··· C-carboxylate distance has been increased from ~6 to ~13 Å, $[Ru(\mathbf{2})_2]$ may be seen as a super-expanded terephthalate or as an expanded $[Ru(\mathbf{1})_2]$, in which the C-carboxylate ··· C-carboxylate distance has further increased from ~13 to ~21 Å. The incorporation of longer spacers is expected to lead to increasingly porous structures and eventually lead to interpenetrating sub-lattices[57–63] as shown by Yaghi for terephthalate analogues.[64] As Fig. 9b shows, the introduction of the 1,4-phenylene spacer into the expanded ligand results in the formation of large voids, resulting in the formation of three identical interpenetrating nets (Fig. 9c).

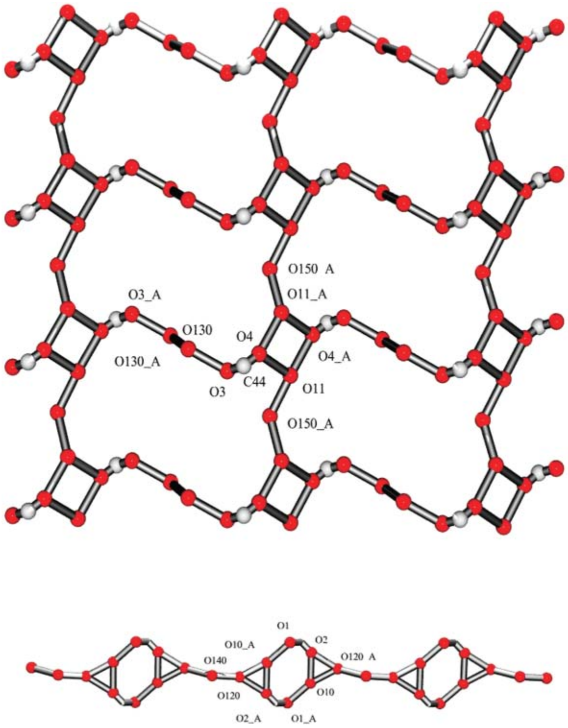


Fig. 8 The two hydrogen-bonding motifs involving carboxylate and water found in $[Ru(\mathbf{2})_2]\cdot5H_2O$. (a) The (4.8^2) sheets constructed from water molecules containing O130, O150 and O11 and carboxylate oxygen atoms O3 and O4 and (b) the chains constructed from water molecules containing O120, O140 and O10 and carboxylate oxygen atoms O1 and O2. The nets have been idealised by the omission of symmetry related atoms from half occupancy positions.

Conclusions

We have shown that the expanded ligands $[Ru(H\mathbf{1})_2]^{2+}$ and $[Ru(H\mathbf{2})_2]^{2+}$ may be prepared and that they behave as analogues of phthalic acids. The ability of the ruthenium(II) centre in these compounds to charge compensate the deprotonation of the carboxylic acid has been established and the solid state structures of two Zwitterionic compounds have been determined. The introduction of a 1,4-phenylene spacer between the tpy and the carboxylic acid leads to a significantly more open sub-lattice which gives a three-fold interpenetrated structure.

The expanded ligand principle can be a powerful tool in supramolecular chemistry and crystal engineering allowing a subtle control over the topological and topographical properties of molecular and extended constructs to be achieved. In this paper, we have shown that the combination of metal-containing and hydrogen-bonding motifs gives access to significant solid state diversity and offers new approaches to the construction of network structures.

Experimental

General

Infrared spectra were recorded on a Shimadzu FTIR-8400 S spectrophotometer with samples as solids using a Golden Gate ATR accessory. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance DRX 500 or 400 spectrometers and chemical shifts are

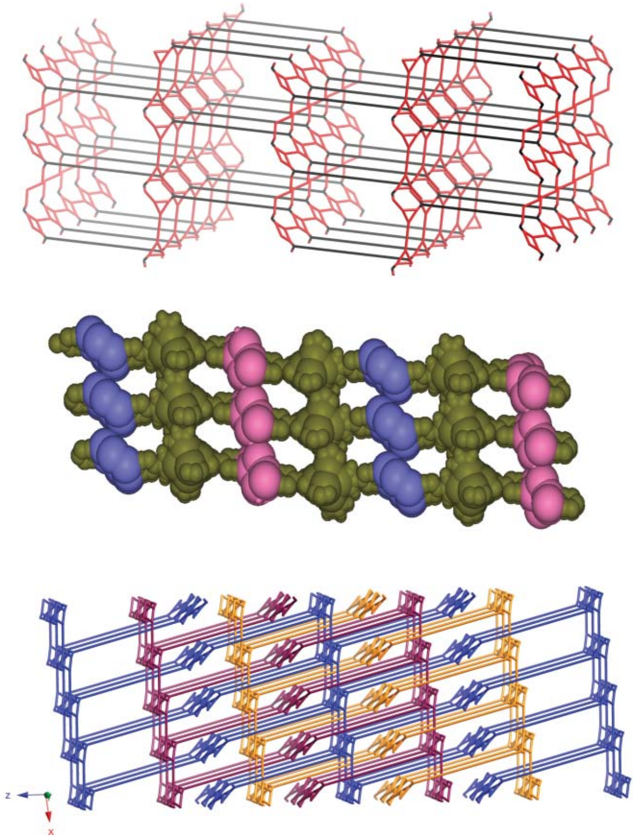


Fig. 9 (a) The construction of an interpenetrating net in which the water–carboxylate sheets and chains are connected by the central complex core (represented schematically by the black lines between carboxylate carbon atoms). (b) Space filling representation of a single net, with hydrogen bonded sheets shown in pink, and hydrogen bonded chains shown in blue. The voids into which the interpenetrating networks fit are clear. (c) The three interpenetrating networks, with complexes shown schematically as in part (a).

referenced with respect to residual solvent peaks (CD_3CN, δ_H 1.49 ppm δ_C 1.24 ppm; DMSO-d_6, δ_H 2.50 ppm, δ_C 39.43 ppm) and quoted with respect to TMS = δ 0 ppm. MALDI-TOF mass spectra were recorded using Finnigan MAT LCQ and PerSeptive Biosystems Voyager mass spectrometers, respectively. Electronic absorption spectra were recorded on a Varian-Cary 5000 spectrophotometer.

Syntheses

Method 1. 2-Furaldehyde (1.0 mL, 12 mmol), 2-acetylpyridine (2.7 mL, 24 mmol) and aqueous ammonia solution (28–30%, 5 mL, 80 mmol) were dissolved in ethanol (40 mL) and a solution of NaOH (1.0 g, 25 mmol) in H_2O (1 mL) added to the yellow mixture. The resulting dark yellow–brown solution was stirred vigorously open to the air and after 30 min a white precipitate started to appear. Stirring in air was continued for 2 d, after which the precipitate was isolated by filtration and washed with H_2O to give **5** as an off-white powder (2.36 g, 7.89 mmol, 65%).

Method 2. Sodium hydroxide (1.09 g, 27 mmol) was dissolved in ethane-1,2-diol (50 mL) and 2-furaldehyde (1.0 mL, 12 mmol), 2-acetylpyridine (2.7 mL, 24 mmol) and aqueous ammonia solution (28–30%, 5 mL, 80 mmol) were added to the solution, which was then heated to 80 °C and stirred vigorously at that temperature for 24 h in a flask open to air. The brown solution so obtained was poured into water (200 mL) and cooled to ambient temperature. The slightly brown precipitate was isolated by filtration, washed with water and recrystallised from hot ethanol (100 mL) at −20 °C to yield **5** as off-white needles (1.46 g, 4.88 mmol, 41%).

Method 3. 2-Furaldehyde (1.92 g, 0.02 moles) and 2-acetylpyridine (4.84 g, 0.0400 moles) were dissolved in EtOH (100 mL). To this was added, KOH (3.08 g, 0.055 moles) and aqueous ammonia solution (60 mL, 25%). The solution was then stirred at 60 °C for 24 h after which about half of the solvent was removed under reduced pressure and the solution filtered yielding an off-white solid. Recrystallisation from EtOH–MeOH gave **5** as white needles. (5.12 g, 0.0171 mmol, 86%).

(Found: C, 76.16; H, 4.32; N, 13.92. $C_{19}H_{13}N_3O$ requires C, 76.24; H, 4.38; N, 14.04%); δ_H/ppm (400 MHz, $CDCl_3$): 8.74 (d, 2H, J = 4.8 Hz, H^{6A}), 8.72 (s, 2H, H^{3B}), 8.64 (d, 2H, J = 8.0 Hz, H^{3A}), 7.87 (dt, 2H, J = 1.9, 7.8 Hz, H^{4A}), 7.59 (d, 1H, J = 1.2 Hz, H^{5C}), 7.35 (ddd, 2H, J = 1.0 , 4.8, 7.4 Hz, H^{5A}), 7.11 (d, 1H, J = 3.2 Hz, H^{3C}), 6.57 (dd, 1H, J = 1.8, 3.4 Hz, H^{4C}); δ_C/ppm (100 MHz, $CDCl_3$): 156.1, 155.9, 151.9, 149.1, 143.7, 139.5, 136.8, 123.8, 121.3, 115.1, 112.1, 109.1; m/z (EIMS) 299 (M^+, 100%), 271 (26%), 192 (6%), 149.5 (M^{2+}, 5%), 78 ($[C_5H_4N]^+$, 5%).

$[Ru(5)_2][PF_6]_2$. $RuCl_3{\cdot}3H_2O$ (100 mg, 0.38 mmol), 4′-(2-furyl)-2,2′;6′,2″-terpyridine (250 mg, 0.84 mmol) and *N*-ethylmorpholine (8 drops) were dissolved in ethane-1,2-diol (50 mL) and the suspension homogenized in an ultrasonic bath. Heating to reflux in the microwave oven (6 min, 400 W) yielded a red solution, which was treated with excess ammonium hexafluorophosphate in water (0.4 M, 9.5 mL) while still hot. After cooling to ambient temperature the suspension was filtered over Celite, washed several times with ethanol and ether and extracted with acetonitrile. After evaporation of the solvent, the residue was recrystallised from methanol–acetone (1 : 1) to yield $[Ru(\mathbf{5})_2][PF_6]_2$ as a red, microcrystalline powder (185 mg, 0.187 mmol, 49%); (Found: C, 46.13; H, 2.92; N, 8.30. $C_{38}H_{26}F_{12}N_6O_2P_2Ru$ requires C, 46.12; H, 2.65; N, 8.49%); δ_H/ppm (500 MHz, CD_3CN): 8.97 (s, 4H, H^{3B}), 8.61 (ddd, 4H, J = 0.8, 1.3, 8.3 Hz, H^{3A}), 7.94 (m, 4H, $^{\mathrm{H4A,H5C}}$), 7.62 (dd, 2H, J = 0.5, 3.5 Hz, H^{3C}), 7.42 (ddd, 4H, J = 0.5, 1.5, 5.5 Hz, H^{6A}), 7.17 (ddd, 4H, J = 1.5, 5.5, 7.5 Hz, H^{5A}), 6.88 (dd, 2H, J = 1.5, 3.5 Hz, H^{4C}); δ_C/ppm (100 MHz, CD_3CN): 159.0, 156.5, 153.5, 151.3, 147.0, 139.1, 138.2, 128.5, 125.5, 118.4, 114.4, 113.1; m/z (FABMS) 845 (82%, $[M - PF_6]^+$), 700 (100%, $[M - 2PF_6]^+$).

$[Ru(H1)_2][PF_6]_2$. $RuCl_3{\cdot}3H_2O$ (381 mg, 1.46 mmol), **5** (873 mg, 2.92 mmol) and *N*-ethylmorpholine (14 drops) were suspended in ethanol (40 mL) and the mixture heated to reflux for 24 h after which the suspension turns bright red. After evaporation of the solvent a red–violet precipitate was obtained, which was transferred into a round bottom flask containing a solution of $KMnO_4$ (450 mg) in water (50 mL). After stirring for 3 h at room temperature TLC analysis showed significant amounts of the $[Ru(\mathbf{5})_2]^{2+}$ remained (SiO_2, CH_3CN –saturated aqueous KNO_3 – H_2O 7 : 1 : 0.5, R_f = 0.45) and another portion of $KMnO_4$ (500 mg) was added. A further portion of $KMnO_4$ (1100 mg) was added after an additional 3.5 h as TLC analysis still showed the presence of $[Ru(\mathbf{5})_2]^{2+}$. After stirring overnight, no $[Ru(\mathbf{5})_2]^{2+}$could be detected by TLC, but still two red spots remained in the TLC (assumed to be $[Ru(\mathbf{5})(H\mathbf{1})]^{2+}$ and the desired $[Ru(H\mathbf{1})_2]^{2+}$. $KMnO_4$ (1.54 g) was added over a period of 2 h and stirring continued for an additional 7 h, after which the suspension was filtered and washed with water. The residue was extracted with aq. H_2SO_4 (2 M) and reacted with NH_4PF_6 (0.4 M aq. solution, 10 mL) to yield a red precipitate. The suspension was stirred overnight, filtered over Celite, washed with aqueous NH_4PF_6 solution (0.02 M) and a little water and extracted with acetonitrile. After evaporation of the solvent, $[Ru(H\mathbf{1})_2][PF_6]_2$ was obtained as a red microcrystalline solid (667 mg, 0.0704 mmol, 48%); (Found: C, 40.18; H, 2.50; N, 8.78. $C_{32}H_{22}F_{12}N_6O_4P_2Ru$ requires C, 40.65; H, 2.35; N, 8.89%); δ_H/ppm (400 MHz, CD_3CN): 10.66 (br s, 2H, CO_2H), 9.21 (s, 2H, H^{3B}), 8.65 (d, 2H, J = 8.4 Hz, H^{3A}), 7.94 (dt, 2H, J = 1.5 Hz, 7.9, H^{4A}), 7.33 (d, 2H, J = 4.8 Hz, H^{6A}), 7.18 (ddd, 2H, J = 1.3, 5.7, 7.5 Hz, H^{5A}); m/z (ESMS) 801 (7%, $[M - PF_6]^+$), 655 (12%, $[M - 2PF_6]^+$).

4′-(4-Methoxycarbonylphenyl)-2,2′:6′,2″-terpyridine 7. Powdered potassium hydroxide (2.5 g, 44 mmol), 4-methoxycarbonylbenzaldehyde (6.82 g, 42 mmol) and 2-acetylpyridine (9.2 mL, 82 mmol) were ground together in a pestle and mortar for 15 min to give a sticky yellow solid, which was left standing for 30 min, ground again and dispersed in water. The solid was collected by filtration, washed with water and dried in air for 1 h. The off-white precipitate was dispersed in a suspension of ammonium acetate (16.0 g, 208 mmol) in ethanol (125 mL) and the mixture stirred for 8 d at room temperature in a flask open to air and the resulting precipitate isolated by filtration and recrystallised twice from hot ethanol to give 4′-(4-methoxycarbonylphenyl)-2,2′:6′,2″-terpyridine **7** as very pale yellow fibres (3.85 g, 10.1 mmol, 25%); (Found: C, 74.21; H, 4.66; N, 11.29. $C_{23}H_{17}N_3O{\cdot}0.25H_2O$ requires C, 74.28; H, 4.74; N, 11.30%); δ_H/ppm (400 MHz, $CDCl_3$): 8.76 (2H, s, H^{3B}), 8.74 (2H, d, J = 4.8 Hz, H^{6A}), 8.68 (2H, d, J = 8.0 Hz, H^{3A}), 8.18 (2H, d, J = 8.0 Hz, H^{3C}), 7.97 (2H, d, J = 8.4 Hz, H^{2C}), 7.89 (2H, dt, J = 1.7, 7.7 Hz, H^{4A}), 7.37 (2H, ddd, J = 1.0,4.8,7.4 Hz, H^{5A}), 3.97 (3H, s, Me); δ_C/ppm (125 MHz, $CDCl_3$): 166.8, 156.1, 156.0, 149.2, 149.18, 142.9, 136.9, 130.5, 130.2, 127.4, 124.0, 121.4, 118.9, 52.2; m/z (EIMS) 367 (M^+, 100%).

4′-(4-Carboxyphenyl)-2,2′:6′,2″-terpyridine H2. 30% NH_3 solution (1 mL) and NaOH (0.488 g, 12.2 mmol) dissolved in a minimum amount of water were added to a solution of 4-methoxycarbonylbenzaldehyde (1.0 g, 6.1 mmol) and 2-acetylpyridine (1.37 mL, 12.2 mmol) in ethanol (25 mL). After the addition of the NaOH, the solution turned yellow and after about 1 h red. The solution was stirred vigorously at room temperature in a flask open to air for 17 h, after which a yellow suspension was obtained. Water (50 mL) was added to the solution, which was then neutralized with conc. HCl to yield a slightly yellow precipitate and a red solution. The precipitate was collected by filtration and washed with water. For further purification it was refluxed for 1 h in 50 mL EtOH, and the solid collected by filtration and dried in vacuum. (1.06 g, 3.00 mmol, 49%); (Found: C, 74.41; H, 4.25; N, 11.68. $C_{22}H_{15}N_3O_2$ requires C, 74.78; H, 4.28; N, 11.89%); δ_H/ppm (400 MHz, DMSO-d_6): 13.2 (br s, 1H, CO_2H), 8.77 (d, 2H, J = 4.8 Hz, H^{6A}), 8.76 (s, 2H, H^{3B}), 8.69 (d, 2H, J = 8.0 Hz, H^{3A}), 8.14 (d, 2H, J = 8.4 Hz, H^{3C}), 8.07 (d, 2H, J = 8.8 Hz, H^{2C}), 8.05 (dt, 2H, J = 1.7, 7.7 Hz, H^4), 7.54 (ddd, 2H, J = 1.2, 4.8, 7.6 Hz, H^{5A}); m/z (EIMS) 353 (M^+, 100%), 308 ($[M - CO_2H]^+$, 26%).

$[Ru(\mathbf{7})_2][PF_6]_2$. $RuCl_3{\cdot}3H_2O$ (100 mg, 0.38 mmol), **7** (281 mg, 0.76 mmol) and N-ethylmorpholine (8 drops) were dissolved in ethane-1,2-diol (50 mL) and heated to reflux in a microwave oven (6 min, 400 W). The resulting red solution was cooled to room temperature and treated with excess aqueous ammonium hexafluorophosphate. The red suspension so obtained was collected over Celite, washed several times with water and extracted with acetonitrile. After evaporation of the MeCN, the residue was purified by column chromatography (SiO_2, CH_3CN – saturated aqueous KNO_3 – H_2O 7 : 1 : 0.5). The collected fractions were concentrated and treated with ammonium hexafluorophosphate to give $[Ru(\mathbf{7})_2][PF_6]_2$ as a red microcrystalline powder (318 mg, 0.275 mmol, 73%); (Found: C, 46.06; H, 3.00; N, 7.07. $C_{46}H_{34}F_{12}N_6O_4P_2Ru.4H_2O$ requires C, 46.12; H, 3.53; N, 7.02%); δ_H/ppm (500 MHz, CD_3CN): 9.06 (s, 4H, H^{3B}), 8.67 (d, 4H, J = 7.5 Hz, H^{3A}), 8.37 (d, 4H, J = 9.0 Hz, H^{3C}), 8.31 (d, 4H, J = 8.5 Hz, H^{2C}), 7.96 (dt, 4H, J = 1.7, 7.6 Hz, H^{4A}), 7.44 (dd, 4H, J = 1.3, 5.3 Hz, H^{6A}), 7.19 (ddd, 4H, J = 1.5, 5.8, 7.5 Hz, H^{5A}), 3.99 (s, 6H, CH_3); m/z (MALDI-TOF MS) 838 ($[M + H]^+$, 100%).

$[Ru(\mathbf{7})_2]Cl_2$. $RuCl_3{\cdot}3H_2O$ (100 mg, 0.38 mmol) and **7** (337 mg, 0.76 mmol) were suspended in methanol (5 mL) and the suspension heated in a Teflon-lined Parr reaction vessel for 15 h to 150 °C and then cooled slowly to room temperature. The microcrystalline material (suitable for X-ray diffraction study) was isolated by filtration and extracted with methanol. Evaporation of the solvent gave $[Ru(\mathbf{7})_2]Cl_2$ as a red microcrystalline powder (234 mg, 0.250 mmol, 66%); (Found: C, 55.44; H, 4.37; N, 8.19. $C_{46}H_{34}Cl_2N_6O_4Ru{\cdot}5H_2O$ requires C, 55.42; H, 4.45; N, 8.43%); δ_H/ppm (400 MHz, DMSO-d_6): 9.56 (s, 4H, H^{3B}), 9.13 (d, J = 8.0 Hz, 4H, H^{3A}), 8.59 (d, J = 8.4 Hz, 4H, H^{3C}), 8.33 (d, J = 8.4 Hz, 4H, H^{2C}), 8.08 (dt, J = 1.3, 7.9 Hz, 4H, H^{4A}), 7.57 (d, J = 6.0 Hz, 4H, H^{6A}), 7.29 (ddd, J = 0.7, 5.5, 7.7 Hz, 4H, H^{5A}), 3.98 (s, 6H, Me); m/z (FABMS) 871 ($[M - Cl]^+$, 24%).

$[Ru(\mathbf{2})_2]$. H**2** (342 mg, 0.97 mmol), $RuCl_3{\cdot}3H_2O$ (126.5 mg, 0.48 mmol), and NEt_3 (0.3 mL, 2.2 mmol) were suspended in ethanol (3 mL) and heated in a Teflon-lined Parr-vessel for 18 h to 150 °C. After cooling to ambient temperature the precipitate formed is filtered over Celite, and washed with ethanol (5 mL), water containing 10 drops of 2 M NaOH (10 mL), and water (10 mL). The remaining residue was extracted with boiling methanol (350 mL) and evaporation of the solvent yielded $[Ru(\mathbf{2})_2]$ as a red powder (254 mg, 0.315 mmol, 65%); (Found: C, 63.71; H, 4.30; N, 10.23. $C_{44}H_{28}N_6O_4Ru{\cdot}1.25H_2O$ requires C, 63.76; H, 3.77; N, 10.14%); δ_H/ppm (400 MHz, DMSO-d_6): 9.53 (4H, s, H^{3B}), 9.14 (4H, d, J = 8.0 Hz, H^{3A}), 8.48 (4H, d, J = 8.4 Hz, H^{3C}), 8.24 (4H, d, J = 8.4 Hz, H^{2C}), 8.06 (4H, dd, J = 7.4, 14.6 Hz, H^{4A}), 7.56 (4H, d, J = 6.0 Hz, H^{6A}), 7.28 (4H, t, J = 6.6 Hz, H^{5A}).

$[Ru(H\mathbf{2})_2][PF_6]_2$. Aqueous sodium hydroxide (2 M, 5 mL) was added to a suspension of $[Ru(\mathbf{7})_2][PF_6]_2$ (150 mg, 0.13 mmol) in acetonitrile (80 mL) and the mixture refluxed overnight. After cooling to room temperature, 2 M hydrochloric acid (5 mL) and aqueous ammonium hexafluorophosphate (0.4 M, 5 mL, 2 mmol) were added to the suspension, which was then filtered over Celite, washed with water and extracted with acetonitrile and methanol.

The solvents were evaporated to yield "[Ru(**2**)$_2$][PF$_6$]$_2$" as a red solid of variable constitution between [Ru(H**2**)(**2**)][PF$_6$] and [Ru(H**2**)$_2$][PF$_6$]$_2$ (88 mg, 0.080 mmol, 61%); δ_H/ppm (400 MHz, DMSO-d$_6$): 9.57 (4H, s, H^{3B}), 9.15 (4H, d, J = 8.0 Hz, H^{3A}), 8.58 (4H, d, J = 8.4 Hz, H^{3C}), 8.30 (4H, d, J = 8.4 Hz, H^{2C}), 8.09 (4H, dt, J = 0.9, 7.7 Hz, H^{4A}), 7.57 (4H, d, J = 5.2 Hz, H^{6A}), 7.29 (4H, t, J = 6.2 Hz, H^{5A}); m/z (FABMS) 953 ([M − PF$_6$]$^+$, 808 ([M − 2PF$_6$]$^+$).

Crystal structure determination†

Data were collected on an Enraf Nonius Kappa CCD instrument; data reduction, solution and refinement used the programs COLLECT,[65] SIR92[66] and CRYSTALS.[67]

CCDC reference numbers 651821–651823.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709557k

[Ru(7)$_2$]Cl$_2$·4H$_2$O. Crystals were obtained on cooling the solution from the preparation of the compound in methanol at 150 °C. Crystal data for: $C_{46}H_{62}Cl_2N_6O_8Ru$, M = 977.84, monoclinic, space group $P2/c$, a = 25.857(3), b = 8.8662(13), c = 39.775(4) Å, β = 106.393(7)°; U = 8747.7(2) Å^3, Z = 8, D_c = 1.485 Mg m^{-3}, μ(Mo-Kα) = 0.542 mm^{-1}, T = 173 K, 22 134 reflections collected. Refinement of 11 491 reflections (1158 parameters) with $I > 3.0\sigma(I)$ converged at final $R1$ = 0.0367 (0.0784 all data), $wR2$ = 0.0388 (0.0576 all data), gof = 1.081.

[Ru(1)$_2$]·4H$_2$O. [Ru(H**1**)$_2$][PF$_6$]$_2$ (10 mg, 10.6 µmol) and Zn(NO$_3$)$_2$·6H$_2$O (31.5 mg, 106 µmol) was dissolved in a glass vessel in DMF (1.5 mL). The vessel was placed in a Teflon-lined Parr autoclave and heated to 150 °C for 1 d, after which the vessel was slowly cooled to ambient temperature to give red rhombic crystals.

Crystal data: $C_{32}H_{28}N_6O_8Ru$, M = 725.68, tetragonal, space group $I\bar{4}2d$, a = 8.6013(4), b = 8.6013(4), c = 40.033(2) Å; U = 2961.7(2) Å^3, Z = 4, D_c = 1.627 Mg m^{-3}, μ(Mo-Kα) = 0.595 mm^{-1}, T = 173 K, 2158 reflections collected. Refinement of 1455 reflections (116 parameters) with $I > 3.0\sigma(I)$ converged at final $R1$ = 0.0211 (0.0418 all data), $wR2$ = 0.0218 (0.0304 all data), gof = 1.093.

[Ru(2)$_2$]·5H$_2$O. [Ru(H**2**)][PF$_6$]$_2$, (4.7 mg) and Eu(NO$_3$)$_3$·5 H$_2$O (2.7 mg) were dissolved in DMF and heated in a glass vessel to 180 °C in a Teflon-lined Parr autoclave for 1 d. After cooling to ambient temperature red crystals were isolated from the solution by filtration.

Crystal data: $C_{44}H_{32}N_6O_9Ru$, M = 889.84, triclinic, space group $P\bar{1}$, a = 8.6945(2), b = 13.4822(3), c = 16.5345(4) Å, α = 93.118(1), β = 97.373(1), γ = 90.915(2)°; U = 1918.80(8) Å^3, Z = 2, D_c = 1.540 Mg m^{-3}, μ(Mo-Kα) = 0.477 mm^{-1}, T = 123 K, 9123 reflections collected. Refinement of 5963 reflections (580 parameters) with $I > 2.0\sigma(I)$ converged at final $R1$ = 0.0393 (0.0730 all data), $wR2$ = 0.0364 (0.1043 all data), gof = 1.144.

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Notes and references

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