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The first solid state structure of a triruthenium polypyridyl complex

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The first trinuclear ruthenium polypyridyl complex to be characterised by X-ray diffraction is reported along with evidence of stereospecific complexation during its formation.

Ruthenium polypyridyl complexes are studied extensively due to their exceptional photophysical properties and their functionality when incorporated into light-activated devices.[1] The prototypical $[Ru(bpy)_3]^{2+}$ complex (bpy = 2,2′-bipyridine) is luminescent at room temperature and is stable to a wide range of oxidative and reductive conditions.[2] The parent $[Ru(bpy)_3]^{2+}$ complex is also photostable with respect to its ligands, and derivatives thereof have been included into various functional devices and sensors.[3–5] The complexes have been studied by numerous techniques to elucidate their photophysical properties.[1,2] However, there is a lack of solid state structures of higher nuclearity polypyridyl complexes even though they are important benchmarks for computational studies. Our interest in the solid-state structure of these complexes relates to their use in building up large polymetallic complexes, however, they also give accurate metal–metal distances for physical studies, such as the interaction of polymetallic complexes with surfaces and DNA.[6]

Triruthenium complex **1** was synthesized by allowing a slight excess of $Ru(bpy)_2Cl_2$ to react overnight with pyridyl-pyrimidine ligand **2**[5] and 2 eq. of $AgNO_3$ in refluxing $EtOH/H_2O$ (Scheme 1). An excess of the $[Ru(bpy)_2(solvent)_2]^{2+}$ reagent is required to avoid complicated mixtures of mono- and di-ruthenium complexes. The green triruthenium complex can be isolated by adding NH_4PF_6 to the reaction mixture followed by filtration.† Purification by column chromatography on silica gel affords **1** in 58% yield. Elemental analysis confirmed the constitutional purity of **1**.

A single crystal of **1** suitable for X-ray diffraction studies was grown from acetonitrile by vapor diffusion of diisopropylether.‡ The cation contains three $[Ru(bpy)_2]^{2+}$ moieties attached to one bridging ligand **2** (Fig. 1). Each of the Ru cations is in a pseudo-octahedral coordination geometry. The bond lengths and angles in each of the bipyridines are as expected for Ru-bipyridyl complexes. The pyridine N-to-Ru bond lengths of the terminal pyridines in ligand **2** (N8-Ru2 = 2.053(8) Å, N20-Ru3 = 2.065(8) Å) also fall in the range of pyridine N-to-Ru bond lengths for the bipyridines. The pyrimidine N to peripheral Ru bond lengths are similar to their pyridine N-to-Ru equivalents. The pyrimidine N-to-Ru bond lengths, however, differ from central to peripheral sites. The pyrimidine N-to-Ru1 bond lengths (N1 = 2.096(7) Å and N13 = 2.067(7) Å) are slightly longer than those found to Ru2 (N3 = 2.044(7) Å) and Ru3 (N15 = 2.062(7) Å), which may be due to steric hindrance in the central site.

Each Ru centre is stereogenic, with the possibility of Λ or Δ enantiomers.[7] Complex **1** has dissymetrical Λ,Λ,Δ stereochemistry, in which Ru2 and Ru3 have opposite configurations (Fig. 1a). However the antipodal Δ,Δ,Λ stereoisomer also crystallizes in the unit cell (not shown).

The stereochemistry of the Ru centres in **1** gives rise to a complicated mixture of stereoisomers based on the racemic $Ru(bpy)_2Cl_2$ starting material. Complete interpretation by ^1H NMR of **1** is precluded due to the large number of proton resonances in the 7–10 ppm range. However, two discernable sets of singlets above 9 ppm can be assigned to the pyrimidine protons (Fig. 2). The 2-pyrimidyl protons are the farthest downfield due to deshielding from the adjacent N atoms and the $[Ru(bpy)_2]^{2+}$ moieties, while those clustered around 9.2 ppm are due to the 5-pyrimidyl protons. The four peaks for each resonance corresponds to the three stereoisomers that formed during the reaction. The use of deuterated bipyridine (approximently 95% isotopic purity) allows the protons of ligand **2** to be seen in the 7.0–8.5 ppm region.[8]

Some information about the relative amount of each stereoisomer can also be gleaned from these peaks. Although the peaks were not completely assigned, the dissymetrical Λ,Λ,Δ isomer is assignable due to the inequivalence of the two pairs of pyrimidyl protons. The three isomers should form in a 1 : 2 : 1 ratio (Λ,Λ,Λ : Λ,Λ,Δ = Δ,Λ,Λ : Λ,Δ,Λ), respectively. However, a 4 : 9 : 1 ratio is observed, suggesting diastereoselectivity in the reaction.[9]

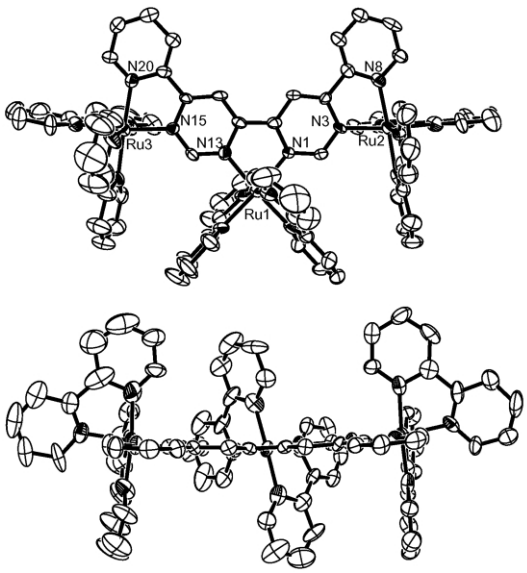
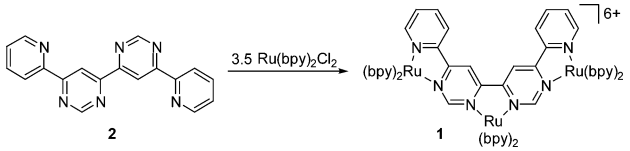


Fig. 1 X-ray crystal structure of **1**: a) top-view, exposing the chirality of the metal centres; b) side-view, showing the planarity of ligand **2**. Six acetonitrile of solvation, the H atoms, and the PF_6 anions have been omitted for clarity.



Scheme 1 Synthesis of triruthenium complex **1** from ligand **2**; a) EtOH/H_2O, 7 $AgNO_3$, reflux, 2 h; b) NH_4PF_6

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The ^{99}Ru NMR of **1** in acetonitrile at 300 K displays only one broad resonance (1 kHz). The chemical shift of 4679 ppm is in agreement with that observed for a related di-Ru(bpy)$_2$ complex of 6-(2-pyridyl)-4′-(2-pyridyl)-4,5′-bipyrimidine, containing two pyridyl-pyrimidine chelating motifs.[10] On heating to 343 K, the resonance is shifted to higher frequency at 4753 ppm as was previously observed for the above mentioned complex. However, contrary to expectations, the signal neither sharpens nor splits with increasing temperature. Therefore, the observed line width results not only from the rapid relaxation of the quadrupolar ^{99}Ru nucleus (broad signals are expected for such a large complex) but also the overlap of the signals of the different Ru nuclei in the different diastereomers.[11]

The cyclic voltammogram of **1** exhibits three reversible one-electron oxidations, which occur at +1.51, +1.59 and +1.96 V *vs.* NHE. The first two processes are ascribed to the oxidation of the two peripheral Ru centres, followed by the oxidation of the central Ru centre at a substantially more positive value. In comparison, a previously reported diruthenium complex of ligand **2** with a vacant central site has a single broad two-electron process at +1.41 V.[12] The diruthenium complex of 2,2′:4′,4″:2″,2‴-quaterpyridine also exhibits a similar broad process for the first and second oxidation at +1.31 V.[13] The larger separation of the first two oxidation potentials in **1** (80 mV) indicates enhanced communication between the two peripheral ruthenium ions. Although the two ruthenium ions are spaced 11.0 Å apart, the restricted rotation around the pyrimidine–pyrimidine bond may be allowing greater overlap between the molecular orbitals on the adjacent pyrimidine rings. The three Ru(II) ions also facilitate the reduction of bridging ligand **2** (−0.09 V) as compared to its diruthenium complex with only peripheral Ru(II) ions (−0.58 V).[12]

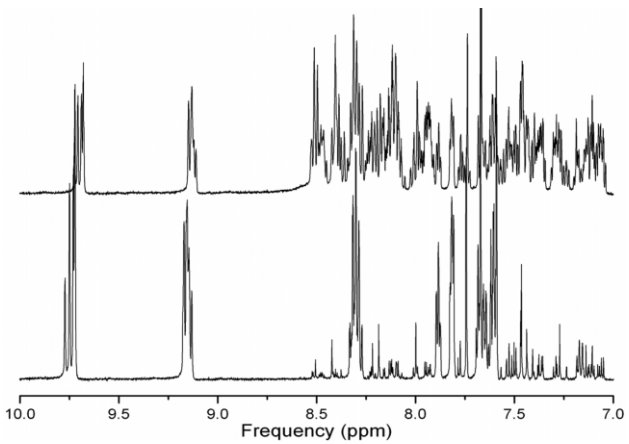

Fig. 2 ^{1}H NMR of **1** in the 7–10 ppm region: top; (**2**-H$_{12}$)Ru$_3$(bipy-H$_8$)$_6$, bottom; (**2**-H$_{12}$)Ru$_3$(bipy-D$_8$)$_6$.

We have reported the first solid-state structure of a triruthenium polypyridyl complex, which displays an enhanced stereospecificity in its formation. We are currently investigating the role that thermal- and photo-processes may play in the formation of the most abundant stereoisomer.

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Notes and references

† In acetonitrile, λ_{max}/nm (ε/L mol^{-1}cm^{-1}); **1**: 635 (23700), 567 (16300), 425 (30900), 353 (27400), 282 (127000).

‡ *Crystal data* for **1,** $C_{80}H_{54}N_{18}Ru_3.6PF_6.6CH_3CN$ were collected on a Bruker APEX at 150 K using Mo–Kα radiation (λ = 0.71073 Å). Full-matrix, least squares refinements on F_2 using all data. 19390 reflections, M = 2683.16, triclinic, space group $P\bar{1}$, a = 12.406(3), b = 22.388(6), c = 22.576(6) Å, α = 116.385(6), β = 95.147(6), γ = 96.653(6)°, U = 5509(3) Å^3, Z = 2, μ(MoKα) = 0.610, $R1$ [$I > 2s(I)$] = 9.66, wR^2 (all 19390 data) = 18.5. CCDC 228758. See http://www.rsc.org/suppdata/cc/b4/b401276c/ for crystallographic data in .cif or other electronic format.

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