Double-helical ruthenium complexes of 2,2′ : 6′,2″,2‴ : 6‴,2⁗-quinquepyridine (qpy) for multi-electron oxidation reactions

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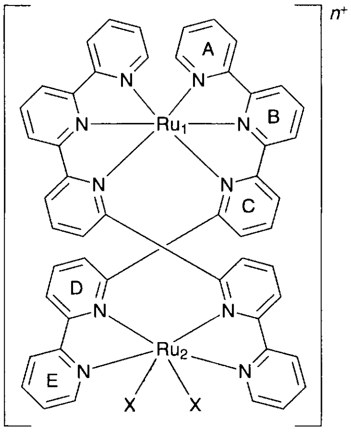
Double-helical ruthenium complexes of 2,′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (qpy) are prepared from $RuCl_3{\cdot}xH_2O$ and qpy and the crystal structure of $[Ru_2(qpy)_2(C_2O_4)][CF_3SO_3]_2{\cdot}6H_2O$ determined; chemical and electrochemical oxidations of $[Ru_2(qpy)_2(H_2O)_2]^{4+}$ in aqueous solution generate high-valent oxoruthenium complexes of qpy, which are powerful oxidants.

Two classes of ruthenium polypyridyl complexes have initiated much interest in the past two decades. The first is ruthenium(II) complexes of aromatic diimines, represented by $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine),[1] as benchmark examples in photo-induced electron-transfer reactions. The other is high-valent oxoruthenium polypyridyl complexes which have important applications in oxidation chemistry.[2] Herein is described an approach that by means of bridging oligopyridines such as qpy,[3] it is possible to bring the photoreactive ruthenium–polypyridyl and Ru=O fragments in the same molecule, and that these Ru–qpy complexes undergo interesting oxidation chemistry.

$[Ru_2(qpy)_2Cl_2]^{2+}$ **1**[†] was prepared by refluxing $RuCl_3{\cdot}xH_2O$ (1 equiv.) with qpy and LiCl in ethylene glycol and was isolated as a dark red crystalline perchlorate salt. Reaction of **1**$[ClO_4]_2$ with $AgCF_3SO_3$ in water afforded $[Ru_2(qpy)_2(H_2O)_2]^{4+}$ **2**. $[Ru_2(qpy)_2(C_2O_4)]^{2+}$ **3** and $[Ru_2(qpy)_2(py)_2]^{4+}$ **4** were prepared by the reaction of **2** with disodium oxalate and pyridine respectively. As expected, the UV-VIS absorption spectra of complexes **1**–**4** show π^* (diimine) ← $d_\pi(Ru^{II})$ charge-transfer transitions at 480–550 nm. The structure of **3**$[CF_3SO_3]_2$ has been established by a X-ray crystal analysis.[‡] As shown in Fig. 1, the structure features the first example of a double-helical ruthenium complex.[4] Both Ru atoms are in a distorted octahedral geometry with Ru(1) coordinated to two terpyridyl fragments in a *mer* configuration and Ru(2) bonds to the two bipyridyl fragments and to the bidentate oxalate. Similar to other double-helical metal complex of qpy, π–π stacking between the terpyridyl and bipyridyl fragments of the two qpy in **3** exists[3] with a close average stacking distance of 3.014 Å. A major twist of the qpy ligand occurs between the terpyridyl and bipyridyl fragments with twist angles of 114.2 and 66.4° for the two ligands. The Ru(1)···Ru(2) separation is 4.611(1) Å.



	X	*n*
1	Cl	2
2	H_2O	4
3	$^{1}/_{2}C_2O_4$	2
4	py	4
5	O/H_2O	4
6	MeCN	4

Like most ruthenium(II)–diimine complexes, these dinuclear ruthenium complexes have potential photochemical applications. For example, complex **3** shows an emission centred at 715 nm in EtOH–MeOH glass at 77 K, which is attributed to the ^{3}MLCT excited state.

Complex **2** displays interesting electrochemistry. As shown in Fig. 2, its cyclic voltammogram at pH 2.1 displays two reversible couples at 0.80 and 1.09 V *vs.* SCE, both of which are pH dependent. Constant potential electrolysis at 0.95 V established $n = 2.0 \pm 0.1$, suggesting the electrode reaction is represented by eqn. (1).

$$[Ru(1)^{II}Ru(2)^{II}(qpy)_2(H_2O)_2]^{4+} \rightleftharpoons [Ru(1)^{II}Ru(2)^{IV}(qpy)_2(H_2O)(O)]^{4+} + 2H^+ + 2e^- \qquad (1)$$

Since the couple at 1.09 V is of similar magnitude to that at 0.80 V, it is assigned to a two-electron reaction, presumably, the oxidation of $[Ru(1)^{II}Ru(2)^{IV}(qpy)_2(H_2O)(O)]^{4+}$ to $[Ru(1)^{II}Ru(2)^{VI}(qpy)_2(O)_2]^{4+}$ [eqn. (2)].

$$[Ru(1)^{II}Ru(2)^{IV}(qpy)_2(H_2O)(O)]^{4+} \rightleftharpoons [Ru(1)^{II}Ru(2)^{VI}(qpy)_2(O)_2]^{4+} + 2H^+ 2e^- \qquad (2)$$

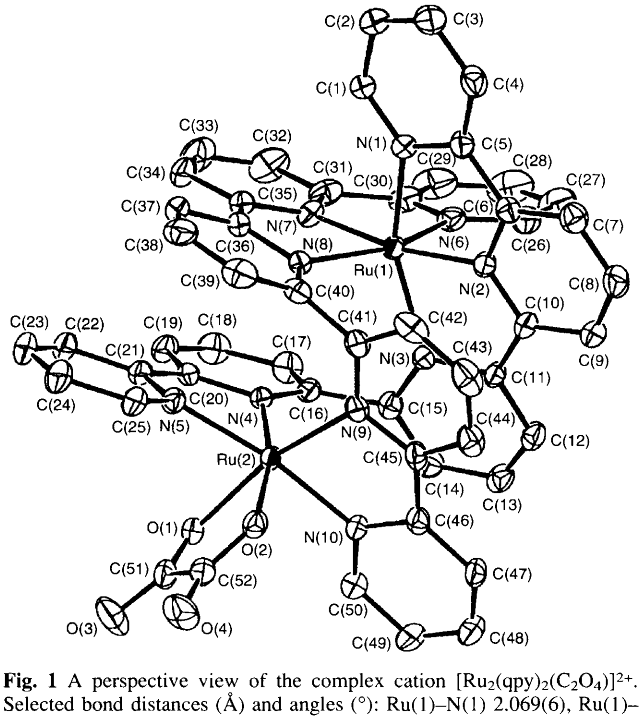


Fig. 1 A perspective view of the complex cation $[Ru_2(qpy)_2(C_2O_4)]^{2+}$. Selected bond distances (Å) and angles (°): Ru(1)–N(1) 2.069(6), Ru(1)–N(2) 1.986(6), Ru(1)–N(3) 2.139(6), Ru(1)–N(6) 2.071(6), Ru(1)–N(7) 1.982(6), Ru(1)–N(8) 2.124(6), Ru(2)–N(4) 2.055(6), Ru(2)–N(5) 2.046(6), Ru(2)–N(9) 2.085(6), Ru(2)–N(10) 2.034(6), Ru(2)–O(1) 2.081(5), Ru(2)–O(2) 2.077(5), N(1)–Ru(1)–N(3) 156.8(2), N(2)–Ru(1)–N(7) 170.3(3), N(6)–Ru(1)–N(8) 156.9(2), N(5)–Ru(2)–N(10) 171.9(2), O(1)–Ru(2)–N(9) 165.3(2), O(2)–Ru(2)–N(4) 166.9(2).

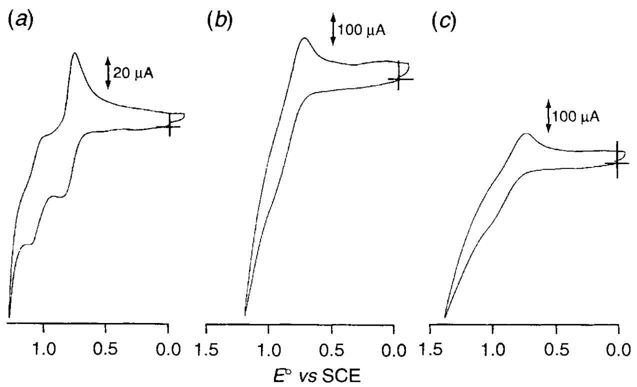


Fig. 2 Cyclic voltammograms of $[Ru_2(qpy)_2(H_2O)]^{4+}$ in (*a*) the absence of alcohols and in the presence of (*b*) 0.2 mol dm^{-3} benzyl alcohol and (*c*) 0.2 mol dm^{-3} isopropyl alcohol at pH 2.1, scan rate 50 mV s^{-1}; basal-plane pyrolytic graphite working electrode

At pH = 9.1, four poorly resolved couples with potentials at 0.14, 0.37, 0.48 and 0.59 V are observed and these are attributed to the stepwise electrochemical oxidations of *cis*-diaqua to *cis*-dioxoruthenium(VI) [eqns. (3)–(6)].

$$[Ru(1)^{II}Ru(2)^{II}(qpy)_2(H_2O)_2]^{4+} \rightleftharpoons [Ru(1)^{II}Ru(2)^{III}(qpy)_2(OH)_2]^{3+} + 2H^+ + e^- \quad (3)$$

$$[Ru(1)^{II}Ru(2)^{III}(qpy)_2(OH)_2]^{3+} \rightleftharpoons [Ru(1)^{II}Ru(2)^{IV}(qpy)_2(OH)(O)]^{3+} + H^+ + e^- \quad (4)$$

$$[Ru(1)^{II}Ru(2)^{IV}(qpy)_2(OH)(O)_2]^{3+} \rightleftharpoons [Ru(1)^{II}Ru(2)^{V}(qpy)_2(O)_2]^{3+} + H^+ + e^- \quad (5)$$

$$[Ru(1)^{II}Ru(2)^{V}(qpy)_2(O)_2]^{3+} \rightleftharpoons [Ru(1)^{II}Ru(2)^{VI}(qpy)_2(O)_2]^{4+} + e^- \quad (6)$$

In the region pH 1–9, there is no pH-independent oxidation couple suggesting that the potential required for the oxidation of Ru(1) is probably greater than 1.2 V *vs.* SCE. This is consistent with the absence of an oxidation couple in the cyclic voltammogram of **4** measured in CF_3CO_2H (0.1 mol dm^{-3}).

An oxoruthenium complex of qpy has been isolated. When an excess of $(NH_4)_2[Ce(NO_3)_6]$ was added to a solution of **2**$[ClO_4]_4$ in CF_3CO_2H (0.1 mol dm^{-3}) at 0 °C, the solution changed from deep red to reddish brown. Upon addition of $NaClO_4$, a reddish brown solid was obtained and was identified as complex **5**$[ClO_4]_4$. Its IR spectrum shows the expected $Ru^{IV}{=}O$ stretching at 776 cm^{-1}. Its UV–VIS absorption spectrum shows the characteristic $\pi^*(\text{diimine}) \leftarrow d_\pi(Ru^{II})$ transition at *ca.* 480 nm. Presumably, one of the two ruthenium sites of **5** is at the Ru^{II} state and this should be Ru(1). In acetonitrile and at room temperature, **5**$[ClO_4]$ reacted with cyclooctene and styrene to give cyclooctene oxide in 50% yield and benzaldehyde in 85% yield. The ruthenium product after the oxidation was found to be $[Ru_2(qpy)_2(MeCN)_2]^{4+}$ **6**. However, **5**$[ClO_4]_4$ does not react with cyclohexane.

Complex **2** catalyses the electrochemical oxidation of alcohols and oxidation of alkenes and alkanes by Bu^tOOH (Table 1). The cyclic voltammogram of **2** reveals electrocatalytic oxidation reactions in the presence of alcohols. As shown in Fig. 2, at pH 2.1 and in the presence of alcohols, the cyclic voltammogram reveals a large catalytic oxidative wave at *ca.* 1.0 V, which is attributed to the oxidation of alcohols by the electrogenerated high-valent oxoruthenium complexes of qpy. For the Bu^tOOH oxidations, high turnover numbers of the organic products have been found. The catalyst was robust and the turnovers of cyclohexanone increased to > 1000 after reaction for 5 d.

Table 1 Catalytic oxidation of various organic substrates (2 mmol) with Bu^tOOH (2 ml) by $[Ru_2(qpy)_2(H_2O)_2][ClO_4]_4$ (0.01 mmol) in acetone (10 ml) at 20 °C for 12 h

Substrate	Product(s)	Turnover[a]
styrene	styrene oxide	50
	benzaldehyde	126
cyclooctene	cyclooctene oxide	168
norbornene	*exo*-2,3-epoxynorborane	111
cyclohexane[b]	cyclohexanol	308
	cyclohexanone	395

[a] Based on the ratio of moles of oxidised products formed to moles of metal catalysed used. [b] Reaction conditions: cyclohexane (4 ml), TBHP (4 ml) and $[Ru_2(qpy)_2(H_2O)_2][ClO_4]_4$ (0.02 mmol) in acetone (10 ml) for 16 h.

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Footnotes

† UV–VIS [λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})] **1** (MeCN) 521 (20600), 324 (71800), 294 (63600); **2** (H_2O) 485 (14900), 300 (68400); **3** (MeOH) 485 (15900), 301 (73900); **4** (MeCN) 485 (19500), 300 (84100); **6** (MeCN) 464 (14200), 298 (71200).

‡ *Crystal data* for **3** $[CF_3SO_3]_2{\cdot}6H_2$: $C_{54}H_{34}F_6N_{10}O_{10}Ru_2S_2{\cdot}6H_2O$, M = 1471.27, monoclinic, space group $C2/c$ (no. 15), a = 30.056(6), b = 14.619(7), c = 27.33(1) Å, β = 112.68(3)°, U = 11081(8) Å^3, Z = 8, D_c = 1.764 g cm^{-3}, μ(Mo-Kα) = 7.23 cm^{-1}, $F(000)$ = 5936, T = 298 K. A purple crystal of dimensions 0.20 × 0.15 × 0.25 mm was used for data collection on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using ω–2θ scans. Intensity data were corrected for decay and for Lorentz and polarization effects. The structure was solved by Patterson methods and expanded using Fourier methods (PATTY[5]) and refined by full-matrix least squares using the software TeXsan,[6] 8526 reflections were uniquely measured, 5544 of which with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. Convergence for 820 variable parameters by least-squares refinement on F with $w = 4\,F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2)^2 = [\sigma^2(I) + (0.018F_o^2)^2]$ for 5544 reflections with $I > 3\sigma(I)$ was reached at R = 0.049, R_w = 0.056 with a goodness-of-fit of 2.06 $(\Delta/\sigma)_{max}$ = 0.04. The final difference Fourier map was featureless, with maximum positive and nevative peaks of 1.06 and 0.98 e Å^{-3} respectively.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/46.

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