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Structural and Spectroscopic Properties of $[\{Ru(bipy)_2\}_2(\mu\text{-}OR)_2]^{2+}$ (R = Me or Et, bipy = 2,2′-bipyridine), a New Class of Strongly Interacting Bridged Binuclear Ruthenium Complexes

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The new alkoxide-bridged binuclear ruthenium(II) complexes $[\{Ru(bipy)_2\}_2(\mu\text{-}OR)_2][PF_6]_2$ (R = Me **1** or Et **2**, bipy = 2,2′-bipyridine) have been prepared and characterised, and the crystal structure of $\mathbf{2}\cdot Et_2O\cdot 2MeCN$ determined; both undergo two one-electron oxidations to the $Ru^{II}Ru^{III}$ and $Ru^{III}Ru^{III}$ states with substantial separations (0.55 and 0.57 V) between the successive redox potentials, allowing preparation of stable mixed-valence species which have a strong intervalence charge-transfer band in the electronic spectrum.

Binuclear ruthenium complexes in which the metal centres are directly linked by a bridging ligand have attracted much attention due to the possibility of studying electron transfer and delocalisation in mixed-valence $Ru^{II}Ru^{III}$ species. The most famous example is the Creutz-Taube ion $[\{Ru(NH_3)_5\}_2(\mu\text{-}NC_4H_4N)]^{5+}$,[1] and numerous similar examples are known with a very wide variety of bridging ligands.[2] Oxo-bridged ruthenium(III) complexes of the type $[\{Ru(bipy)_2X\}_2(\mu\text{-}O)]^{n+}$ (X = Cl or NO_2, $n = 2$; X = H_2O, $n = 4$; bipy = 2,2′-bipyridine) are also known[3] and permit access to $Ru^{III}Ru^{IV}$ mixed-valence states, but these have been less extensively studied. In this communication we report the syntheses and the electrochemical, spectroscopic and structural properties of $[\{Ru(bipy)_2\}_2(\mu\text{-}OR)_2][PF_6]_2$ (R = Me **1** or Et **2**), the first members of a new class of binuclear ruthenium(II) complexes with two alkoxide bridges.

Reaction of $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ with KOH in methanol followed by treatment with NH_4PF_6 afforded **1** in 84% yield.†‡ In contrast, reaction of $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ with ethanolic KOH at reflux under N_2 only afforded **2** in small amounts. However reaction of **1** with NaOEt in EtOH at reflux gave **2** in good yield by exchange of the bridging alkoxide groups.† The formulations of **1** and **2** were confirmed by fast-atom bombardment mass spectrometry, a peak cluster corresponding to the mass of the binuclear cation appearing in each case. In addition the ^1H NMR spectra of both complexes show eight well defined resonances of equal intensity in the aromatic region, indicating that all four bipyridyl ligands are equivalent. The resonances clearly split into two sets of four, one set for the pyridyl rings which are *trans* to the alkoxy ligands and one for the pyridyl rings which are *trans* to other pyridyl rings.

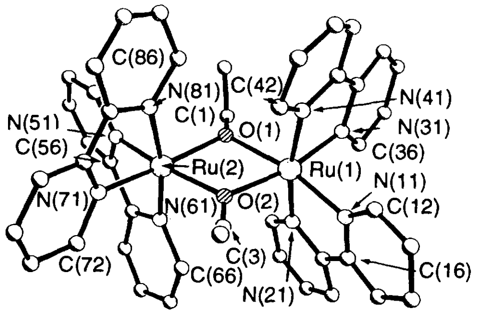

Fig. 1 Molecular structure of the dication of **2**. Dimensions: Ru(1)–O(1) 2.097(7), Ru(1)–O(2) 2.114(7), Ru(1)–N(11) 2.033(8), Ru(1)–N(21) 2.060(8), Ru(1)–N(31) 2.037(8), Ru(1)–N(41) 2.058(8), Ru(2)–O(1) 2.104(7), Ru(2)–O(2) 2.110(7), Ru(2)–N(51) 2.036(8), Ru(2)–N(61) 2.062(8), Ru(2)–N(71) 2.033(8), Ru(2)–N(81) 2.048(8) Å; N(11)–Ru(1)–N(21) 78.7(3), N(31)–Ru(1)–N(41) 78.6(4), N(51)–Ru(2)–N(61) 78.8(3), N(71)–Ru(2)–N(81) 79.3(3), Ru(1)–O(1)–Ru(2) 104.4(3), Ru(1)–O(2)–Ru(2) 103.5(3)°

Crystals of **2** were grown from acetonitrile–diethyl ether; the structure of the cation is shown in Fig. 1.§ Each binuclear cation has approximate non-crystallographic C_2 symmetry and is optically active, with both ruthenium atoms having the same configuration; the crystal is racemic, with opposite enantiomers related by an inversion centre. This arrangement is necessitated by overlap of near-parallel sections of the bipyridyl ligands, resulting in π-stacking interactions,[7] with average separations of 3.3 Å between the parallel, overlapping aromatic ring segments (ring 4 overlaps with ring 8, and ring 2 with ring 6, according to the numbering scheme used). The core structure is reminiscent of that of $[\{Mn(bipy)_2\}_2(\mu\text{-}O)_2]^{3+}$.[8] The rather low

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† Preparation of **1**: A mixture of $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (100 mg, 0.19 mmol) and KOH (100 mg, a large excess) in methanol (20 cm^3) was heated to reflux for 4 h under N_2, resulting in a deep purple-black solution. This was treated with aqueous NH_4PF_6 (excess) and concentrated *in vacuo* to remove the methanol. The resulting fine suspension was extracted with several portions of CH_2Cl_2 which were combined, dried ($MgSO_4$) and evaporated. The crude solid was purified by chromatography on a preparative-scale Al_2O_3 plate (Merck, article 5726) with MeCN as eluent. The final yield was 84% (Found: C, 42.8; H, 3.5; N, 9.4. Calc. for $C_{42}H_{38}F_{12}N_8O_2P_2Ru_2$: C, 42.9; H, 3.2; N, 9.5%).

Preparation of **2**: A mixture of **1** (200 mg, 0.17 mmol) and NaOEt (0.85 mmol) in dry ethanol (20 cm^3) was heated to reflux under N_2 for 4 h. The dark solution was treated with aqueous NH_4PF_6, and worked up and purified as above to give **2** in 64% yield (Found: C, 43.4; H, 3.5; N, 9.2. Calc. for $C_{44}H_{42}F_{12}N_8O_2P_2Ru_2$: C, 43.8; H, 3.5; N, 9.3%).

‡ It was reported a while ago[4] that reaction of *cis*-$[Ru(bipy)_2(dme)]^{2+}$ (dme = 1,2-dimethoxyethane) with NaOMe in MeOH resulted in the formation of $[Ru(bipy)_2(OMe)_2]$, although it was not isolated from solution. It is likely that this species was in fact the dication of **1**, especially in view of the similarity of its reported electronic spectrum to that of **1**.

§ Crystal data for $\mathbf{2}\cdot Et_2O\cdot 2MeCN$: $C_{44}H_{42}F_{12}N_8O_2P_2Ru_2\cdot Et_2O\cdot 2MeCN$, M = 1363.2, triclinic, space group $P\bar{1}$, a = 10.422(9), b = 11.571(8), c = 24.833(16) Å, α = 93.31(5), β = 94.74(7), γ = 96.47(6)°, U = 2960(4) $Å^3$, Z = 2, D_c = 1.53 g cm^{-3}, $F(000)$ = 1380, μ(Mo-Kα) = 6.5 cm^{-1}, R = 0.058 (R' = 0.056) for 4249 unique data [293 K, Wyckoff ω-scans, $2\theta \leqslant 40°$, $F \geqslant 3\sigma(F)$]. Data were collected using a Siemens R3m/V diffractometer (Mo-Kα radiation, graphite monochromator, λ = 0.710 73 Å). The data were corrected for Lorentz, polarisation and X-ray absorption effects. The structure was solved by conventional heavy-atom methods and successive Fourier difference syntheses were used to locate all non-hydrogen atoms. Crystals of $\mathbf{2}\cdot Et_2O\cdot 2MeCN$ lose solvent of crystallisation extremely easily and that used for data collection (approximate dimensions 0.8 × 0.9 × 1.0 mm) was sealed in a capillary tube containing Et_2O–MeCN. Despite these precuations the intensities of three check reflections showed a marked loss of intensity during the course of data collection. Final refinements by full-matrix least-squares procedures were performed on a Micro Vax computer with the SHELXTL system of programs.[5] Scattering factors with corrections for anomalous dispersion were taken from ref. 6. Atomic co-ordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

chemical shifts of the methoxy protons of **1** (δ 2.25) and the ethoxy protons of **2** (δ 2.70 and 0.01) are explained by the proximity of these groups to the ring currents of the bipyridyl ligands.

The electrochemical properties of both **1** and **2** are nearly identical; the cyclic and square-wave voltammograms of **2** are shown in Fig. 2. There are two reversible, one-electron oxidations at $E_{\frac{1}{2}}$ values of −0.06 and +0.51 V *vs.* the ferrocene–ferrocenium couple; for both waves the cathodic and anodic peaks are of equal intensity and separated by 70–80 mV independent of scan rate. These are assigned to successive metal-based oxidations to give the $Ru^{II}Ru^{III}$ and $Ru^{III}Ru^{III}$ species respectively. The separation of 0.57 V between the redox couples indicates a comproportionation constant (K_c) of 6 × 10^9. The corresponding oxidation potentials of **1** are −0.09 and +0.46 V, which gives K_c = 3 × 10^9. These new complexes are therefore amongst the most strongly electrochemically interacting binuclear ruthenium(II) complexes known; by comparison K_c = 10^6 for the Creutz–Taube ion,[2] and only complexes with cyanogen,[9] $[N{\equiv}C{-}CR{-}C{\equiv}N]^-$ (ref. 10) and *p*-benzoquinone diimine[11] bridging two pentaammineruthenium centres have significantly higher K_c values. The best comparison is with $[\{Ru(bipy)_2\}_2(\mu\text{-}Cl)_2]^{2+}$,[12] which undergoes two successive one-electron Ru^{II}–Ru^{III} couples separated by 0.55 V, but the mixed-valence state is unstable and decomposes to give mononuclear products. Complex **2** also undergoes four reductions at $E_{\frac{1}{2}}$ = −1.93, −2.00, −2.31 and −2.43 V *vs.* ferrocene–ferrocenium, which are potentials characteristic of ligand-based processes (for **1**; $E_{\frac{1}{2}}$ = −1.95, −2.01, −2.29 and −2.42 V); all four bipyridyl ligands in **1** and **2** may therefore be reduced in sequence. Although the reduction waves occur in overlapping pairs in the cyclic voltammogram, the $E_{\frac{1}{2}}$ values could be determined by square-wave voltammetry.

The electronic spectrum of **1** in CH_2Cl_2 is shown in Fig. 3(*a*). The broad absorption in the visible region (λ_{max} = 579 nm) and the band at 364 nm we assign to $Ru(d_\pi) \longrightarrow bipy(\pi^*)$ metal-to-ligand charge transfers (m.l.c.t.). The more intense bands at 298 and 246 nm are characteristic of ligand-centred π–π* transitions. The spectrum of **2** is very similar (λ_{max} = 575, 370, 295 and 245 nm in CH_2Cl_2). The lower m.l.c.t. energies of **1** and **2** compared to, for example, $[Ru(bipy)_3]^{2+}$ are consistent with the weaker ligand field of the alkoxides resulting in a smaller separation between the $Ru(d_\pi)$ and the bipy(π*) levels.

Bulk electrolysis of **1** in MeCN at +0.2 V *vs.* ferrocene–ferrocenium at room temperature (n = 0.97 e^- mol^{-1}) resulted in slow cleavage of the dimer to give $[Ru(bipy)_2(MeCN)_2]^{2+}$ (λ_{max} = 426 nm);[13] in this respect **1** behaves similarly to $[\{Ru(bipy)_2\}_2(\mu\text{-}Cl)_2]^{2+}$.[12] However at 240 K in MeCN electrochemical oxidation produced a stable mixed-valence species $[Ru_2(bipy)_2(\mu\text{-}OMe)_2]^{5+}$ which could be re-reduced to **1** without significant decomposition. The electronic spectrum of this species [Fig. 3(*b*)] shows a strong intervalence charge transfer (i.v.c.t.) transition at *ca.* 1800 nm (ε ≈ 5000 dm^3 mol^{-1} cm^{-1}) (it is difficult to measure accurately as the peak maximum is partly obscured by sharp IR overtone bands from the solvent), which disappeared on further oxidation to the +3/+3 state. A full spectroelectrochemical study to determine whether the mixed-valence state is class-II or -III is being undertaken and will be reported in due course.

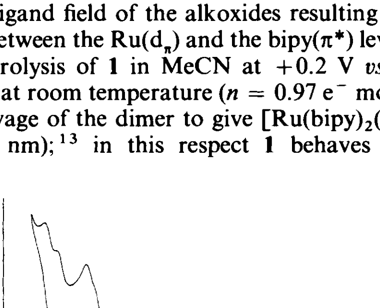

Fig. 2 Cyclic voltammogram and square-wave voltammogram of **2** in MeCN at a scan rate of 0.2 V s^{-1}

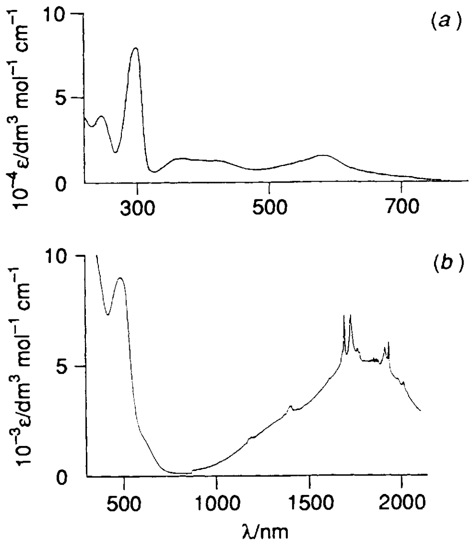

Fig. 3 UV/VIS spectrum of **1** ($Ru^{II}Ru^{II}$) (*a*) and of its one-electron oxidation product ($Ru^{II}Ru^{III}$) (*b*)

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