Redox Behaviour of the Oxo-bridged Diruthenium(III) Complex, $[Ru_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2(bpy)_2(mim)_2]^{2+}$ in Acetonitrile in the Presence of Various Proton Donors (bpy = 2,2′-bipyridine, mim = 1-methylimidazole)

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Redox potentials of the $Ru_2^{III,III}$–$Ru_2^{III,II}$ and $Ru_2^{III,II}$–$Ru_2^{II,II}$ processes of $[Ru_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2(bpy)(mim)_2]^{2+}$ in acetonitrile, move to the positive direction remarkably on addition of a strong acid such as toluene-*p*-sulfonic acid, while two processes are coalesced to show apparent one-step two-electron reduction on addition of weaker proton donors.

Electron-transfer reactions associated with protonation–deprotonation at oxide bridges of dinuclear complexes, in particular proton-coupled one-step multi-electron transfer reactions, are considered to have primary importance in understanding enzymatic reactions involving dinuclear metal centres such as haemerythrin, catalase, ribonucleotide reductase, and photosystem II, and also in constructing multi-electron transfer hydrogenation catalysts.[1] Proton-coupled one-step two- and three-electron transfer systems have been reported for some oxo and nitrido ruthenium, osmium[2] and rhenium complexes in aqueous media.[3] Redox reactions coupled with protonation at oxide bridges have been reported for some dinuclear complexes of ruthenium[4–6] and manganese.[7] Information is insufficient to elucidate characteristics of the redox behaviour of the oxide-bridged complexes, however, due to the limited accessible pH range over which the complexes are stable. We report here that the addition of various proton sources with different pK_a values to the aprotic solvent acetonitrile can control the effective pH and provide useful information on redox processes associated with protonation at oxide bridges. This study concerns oxo–diacetato bridged dinuclear ruthenium complexes.[8–14]

A new dinuclear ruthenium(III) complex, $[Ru_2(\mu\text{-}O)(\mu\text{-}MeCO_2)(bpy)_2(mim)_2]^{2+}$ (bpy = 2,2′-bipyridine; mim = 1-methylimidazole) **1** (Fig. 1) has been prepared according to the method described for the similar complex, $[Ru_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2(bpy)_2(py)_2][PF_6]_2$,[8b] and isolated as a PF_6^- salt. The complex shows a characteristic strong band at 608 nm (ε = 21800 dm^3 mol^{-1} cm^{-1}). The ^1H NMR spectrum of **1** in CD_3CN shows that the two pyridyl rings of the bpy ligands are equivalent. Thus the unidentate ligands, mim, occupy positions *trans* to the oxide bridge.

Fig. 2 shows cyclic voltammograms of **1** in acetonitrile in the absence and presence of proton donors of different acidities. In the absence of a proton donor, complex **1** shows two consecutive one-electron reduction waves, the first one being reversible and the second one irreversible, and a one-electron oxidation wave [Fig. 2(*a*)]. On successive addition of toluene-*p*-sulfonic acid as a strong proton donor, two new reduction peaks appear at the expense of the original two reduction peaks† and at a ratio of one equivalent of the acid to **1**, the original reduction peaks disappear completely. The extent of the shifts amounts to 0.82 V (−0.55 to +0.27 V *vs.* Ag–AgCl) and 0.89 V (−1.16 to −0.27 V *vs.* Ag–AgCl)‡ for the first and second reduction waves, respectively, with considerable increase of the chemical reversibility for the second reduction process [Fig. 2(*b*)]. This is due to protonation at the oxide bridges in the reduced states $Ru_2^{II,III}$ and $Ru_2^{II,II}$. The protonation is stoichiometric, indicating that the $Ru_2^{II,III}$ and $Ru_2^{II,II}$ complexes are strong bases in the aprotic acetonitrile solvent.§ Proton-coupled redox reactions between $Ru_2^{III,IV}$ and $Ru_2^{III,III}$ states have already been reported for some μ-O–μ-$(RCO_2)_2$ type complexes in aqueous media,[4] and protonation at the oxide bridge has been established by the X-ray structural analysis of a $Ru_2^{III,III}$–μ-OH–μ-$(MeCO_2)_2$[14] and $Ru_2^{II,III}$–μ-OH_2–μ-$(MeCO_2)_2$ complexes.[11d] The oxidation wave corresponding to the $Ru_2^{III,IV}$–$Ru_2^{III,III}$

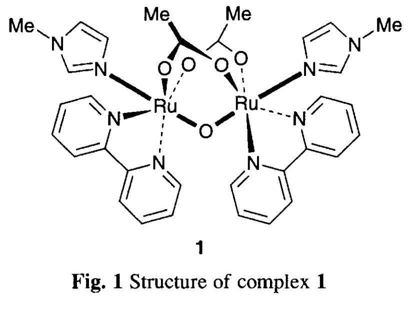

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Fig. 1 Structure of complex **1**

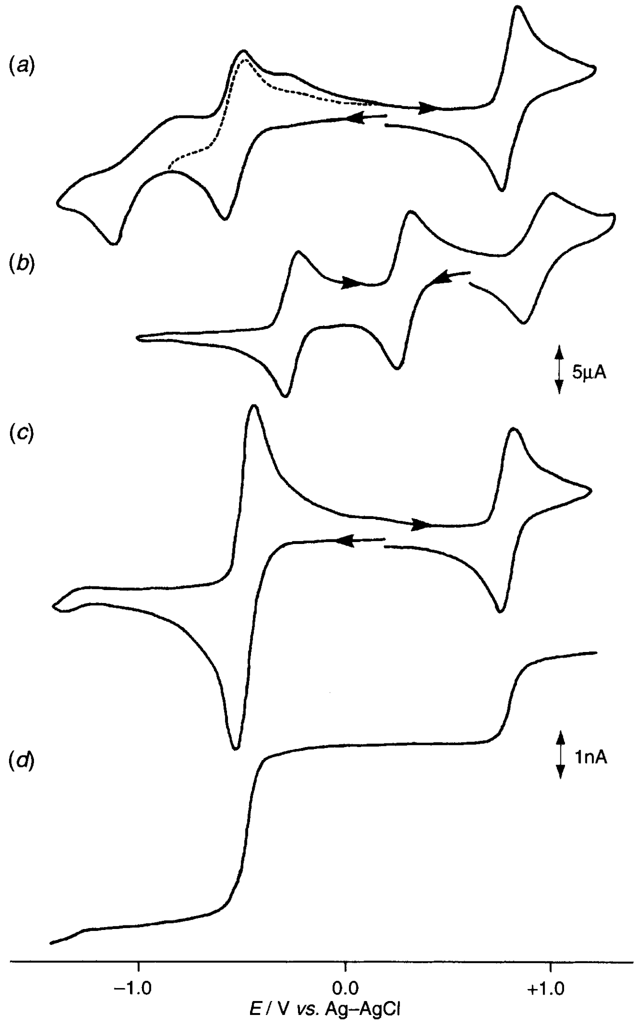

Fig. 2 Cyclic [(*a*)–(*c*)] and steady-state (*d*) voltammograms of **1** in acetonitrile (0.1 mol dm^{-3} NBu_4PF_6) solution (glassy carbon working electrode at a scan rate of 50 mV s^{-1} at room temp.). (*a*) Without added acid, (*b*) on addition of 1 equivalent of toluene-*p*-sulfonic acid and (*c*), (*d*) on addition of 1 equiv. of benzimidazole.

couple of **1** in acetonitrile is not affected by the addition of acid.

The correlation shown in Figs. 2(*a*) and 2(*b*) indicates that the reduction to $Ru_2^{II,II}$ in the presence of acid occurs at a *more* positive potential than the reduction to $Ru_2^{II,III}$ in the absence of acid. It is therefore possible to obtain a single two-electron transfer by adding a proton donor with lower acidity than the oxide bridge of the $Ru_2^{II,III}$ state but stronger than that in the $Ru_2^{II,II}$ state. This is indeed observed on addition of imidazole or benzimidazole as weak proton donors [Fig. 2(*c*)].¶,‖ The two reduction waves, $Ru_2^{III,III}$–$Ru_2^{II,III}$ and $Ru_2^{II,III}$–$Ru_2^{II,II}$ have now collapsed because the oxide bridge in the $Ru_2^{II,II}$ state is a very strong base and accepts a proton from the very weak proton donor imidazole, while that of the $Ru_2^{II,III}$ state does not. The involvement of two electrons at this step is apparent from the relative peak current compared with that for the $Ru_2^{III,III}$–$Ru_2^{III,IV}$ process. Controlled potential coulometry at −0.8 V confirms the collapsed reduction to be a two-electron step.

Various proton donors can be classified into four groups as follows:** (*i*) positively shifted $Ru_2^{III,III}$–$Ru_2^{III,II}$ and $Ru_2^{III,II}$–$Ru_2^{II,II}$ potentials for toluene-*p*-sulfonic acid (pK_a = 1.7), trifluoroacetic acid (*ca.* 0), trichloroacetic acid (*ca.* 0.7), and dichloroacetic acid (*ca.* 1.3); (*ii*) coalesced apparent two-electron processes at potentials between −0.55 and −0.27 V for chloroacetic acid (*ca.* 2.7), formic acid (*ca.* 3.6), benzoic acid (*ca.* 4.2), β-naphthol (*ca.* 9.4), ethyl acetoacetate (*ca.* 10.7), benzimidazole (*ca.* 12.3), and diethylmalonate (*ca.* 13.5); (*iii*) coalesced two-electron processes at −0.55 V for imidazole (*ca.* 14.4); (*iv*) no effect on the potentials for cyclohexanone and acetophenone ($pK_a > 20$). From the $E^{0\prime}$ *vs.* pH profile of **1** in aqueous solution[16] and the present observation, it is suggested that the pK_a values for the oxide bridges of the $Ru_2^{III,II}$ and $Ru_2^{II,II}$ states in aqueous media are *ca.* 14 and 20, respectively.

The present results show that pK_a of added proton donor can control the redox behaviour of the oxide-bridged complexes and lead to apparent one-step two-electron transfer under certain conditions in aprotic solvent acetonitrile.

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Footnotes

† On further addition of the acid, the $Ru_2^{II,III}$–$Ru_2^{II,II}$ wave showed further potential shifts to positive direction ($E^{0\prime}$ = −0.12 V) which is completed upon addition of two equivalents of acid.

‡ Against the Ag–AgCl electrode, the half-wave potential of Fc^+–Fc [$E_{1/2}(Fc^{+/0})$] *vs.* Ag–AgCl] was +0.43 V.

§ Observation of two waves for the single redox process in the presence of < 1 equivalent of the acid, has been reproduced by a simulation under the assumption of a very large protonation constant for the oxide bridge of the $Ru_2^{II,III}$ state (estimated to be *ca.* 10^{15} dm^3 mol^{-1} as judged by the potential shift of *ca.* 0.9 V) and the establishment of rapid protonation equilibrium as indicated by the good reversibility of the redox process of the protonated form.

¶ The substitution of added imidazole for 1-methylimidazole is slow and is not significant in the present measurements.[15]

‖ A similar CV to Fig. 2(*c*) has been reported recently for $[Ru_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2(mim)_6]^{2+}$ in acetonitrile in the absence of any added proton source.[11e] No explanation is given for this observation which we have confirmed and further found that addition of toluene-*p*-sulfonic acid causes the separation of the two-electron wave. It appears that the complex in the $Ru_2^{II,II}$ state is a strong enough base to remove protons from traces of water and shows a one-step two-electron transfer.

** The pK_a values given here are those in aqueous media. These values should be taken as approximate ones, since conditions such as temperatures and ionic strengths are different. It has been suggested that values in aqueous media and acetonitrile are related by $pK_a(MeCN) = pK_a(H_2O) + 7.5$.[17]

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