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Synthesis, crystal structure and redox properties of μ-oxo-bis(μ-acetato)-diruthenium(III) complexes having 2,2′-bipyridine and imidazole bases as terminal ligands

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Three diruthenium(III) complexes, $[\{Ru(bipy)L\}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2][ClO_4]_2$, have been prepared and characterized (L = imidazole, 1- or 4-methylimidazole; bipy = 2,2′-bipyridine). The crystal structure of the 1-methylimidazole complex $[Ru_2O(O_2CMe)_2(bipy)_2(1\text{-mim})_2][ClO_4]_2\cdot H_2O\cdot MeOH$ has been determined. The complex has a $Ru_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2{}^{2+}$ core with terminal unidentate 1-mim and bidentate chelating bipy ligands. The imidazole is *trans* to the oxide ligand. The Ru ··· Ru distance and Ru–O–Ru angle are 3.285(2) Å and 121.5(3)°. The ^1H NMR spectra of the complexes are consistent with this crystal structure. The complexes show an intense charge-transfer band near 600 nm. They are redox active and display reversible one-electron oxidation and reduction processes. On addition of weak proton-donor imidazole bases the complexes undergo a one-step two-electron reduction process $Ru^{III}Ru^{III}$–$Ru^{II}Ru^{II}$ along with the $Ru^{III}Ru^{III}$–$Ru^{III}Ru^{IV}$ oxidation couple.

Of the variety of transition-metal complexes having a μ-oxo-bis(μ-carboxylato)dimetal core[1–15] those of ruthenium are redox active and undergo successive reversible oxidation and reduction of the core. Among the redox couples, those involving one-step multielectron transfer processes are of special importance considering their relevance to the multi-electron redox reactions occurring at the dinuclear active sites in several non-haem metalloproteins.[1,16] In this paper we report the synthesis, structure and electrochemical properties of three diruthenium(III) complexes, $[Ru_2O(O_2CMe)_2(bipy)_2L_2][ClO_4]_2$ [bipy = 2,2′-bipyridine; L = imidazole (Him) **1a**, 1-methylimidazole (1-mim) **1b** or 4-methylimidazole (4-mim) **1c**]. During the course of our investigation a preliminary report on the electrochemical properties of the PF_6 salt of the 1-methylimidazole complex was made by Kikuchi *et al.*[15]

Experimental

All reagents and chemicals were from commercial sources and used as received. Tetrabutylammonium perchlorate was prepared by treating tetrabutylammonium bromide with perchloric acid in water. The solid thus obtained was recrystallized twice before drying at 100 °C under vacuum. Acetonitrile used for electrochemical studies was purified by the conventional method.

Preparation of $[Ru_2O(O_2CMe)_2(bipy)_2L_2][ClO_4]_2$ (L = Him 1a, 1-mim 1b or 4-mim 1c)

The complexes were prepared by following a general procedure[10a] in which $RuCl_3\cdot 3H_2O$ (100 mg, *ca.* 0.4 mmol) in a water (8 cm^3)–$MeCO_2H$ (6 cm^3)–EtOH (3 cm^3) was heated to 70 °C for 10 min and then treated with 2,2′-bipyridine (170 mg, *ca.* 1 mmol). The reaction was continued for 15 min at 90 °C after which the appropriate imidazole base (L) (400 mg, *ca.* 5 mmol) was added. The reaction was continued for 15 min, then the solution was cooled to ambient temperature and concentrated to ≈20 cm^3. The product was precipitated on adding cold aqueous solution (50 cm^3) of $NaClO_4$ (500 mg, *ca.* 4 mmol). The crude green solid was filtered off, dried and purified by column chromatography using a basic alumina column (40 × 1 cm diameter) to remove an uncharacterized yellow species present as a minor product (yield ≈80%). The blue diruthenium complex **1** was eluted from the column using $CHCl_3$–MeOH (10:1 v/v) as eluent. The yield of the column-purified **1** was ≈50% (Found: C, 37.0; H, 3.2; N, 11.2. $C_{30}H_{30}Cl_2N_8O_{13}Ru_2$ **1a** requires C, 36.6; H, 3.1; N, 11.4. Found: C, 38.6; H, 3.5; N, 11.3. $C_{32}H_{34}Cl_2N_8O_{13}Ru_2$ **1b** requires C, 38.0; H, 3.4; N, 11.1. Found: C, 38.5; H, 3.4; N, 11.1. $C_{32}H_{34}Cl_2N_8O_{13}Ru_2$ **1c** requires C, 38.0; H, 3.4; N, 11.1%). Single crystals of **1b**, suitable for X-ray studies, were obtained on cooling a solution of the complex in MeCN–MeOH–Et_2O.

CAUTION: perchlorate salts of metal complexes containing organic ligands are potentially explosive and should be handled with great care using only small amounts of material.

Physical measurements

Elemental analyses were done on a Heraeus CHN-O Rapid instrument. Electronic and ^1H NMR spectra were recorded on Hitachi U-3400 and Bruker AC(AF)-200 MHz spectrometers, respectively. Conductivity measurements were done on a Century CC603 digital conductivity meter. Cyclic and differential pulse voltammetric measurements were made at 25 °C on a PAR model 174 A polarographic analyser connected to a Houston Instruments Omnigraphic X-Y recorder. In a three-electrode set-up, a platinum-inlay working, a platinum-wire auxilliary and a saturated calomel reference electrode (SCE) were used. Measurements were made in MeCN containing 0.1 mol dm^{-3} $[NBu^n{}_4][ClO_4]$. The data reported are uncorrected for junction potentials. Ferrocene was used as an internal standard to verify the potentials against the SCE and to obtain the electron-transfer stoichiometries of the redox process by peak-current measurements. Constant-potential electrolysis were performed to determine the nature of the redox processes. The ferrocene–ferrocenium couple in MeCN–0.1 mol dm^{-3} $[NBu^n{}_4][ClO_4]$ appeared at 0.43 V *vs.* SCE (ΔE_p = 60 mV at 50 mV s^{-1} scan rate).

Crystallography

Crystal data. $C_{33}H_{40}Cl_2N_8O_{15}Ru_2$, **1b**·$H_2O$·MeOH, M = 1061.8, monoclinic, space group $P2_1/c$ (no. 14), a = 18.633(5), b = 13.174(4), c = 19.236(8) Å, β = 115.85(3)°, U = 4249(3) $Å^3$, $F(000)$ = 2144, Z = 4, D_c = 1.66 g cm^{-3}, Mo-Kα radiation, λ = 0.7107 Å, μ(Mo-Kα) = 8.96 cm^{-1}, T = 290 K, transmission coefficients 0.99–1.17.

Data collection and processing. A bluish crystal of dimensions 0.4 × 0.3 × 0.3 mm was mounted on a glass fibre. The unit-cell parameters were obtained by least-squares treatment of 25 reflections in the range $16 < 2\theta < 28°$. Intensity data were collected within $4 \leqslant 2\theta \leqslant 50°$ using ω–2θ scans on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo-Kα radiation. The data were corrected for Lorentz-polarization and absorption effects.[17]

Structure solution and refinement. There were 6275 unique data of which 4381 with $F_o > 5\sigma(F_o)$ were used for structure determination using the Patterson method which revealed the position of the ruthenium atoms in the crystallographic asymmetric unit. The remaining atoms were located from Fourier-difference maps and refined by the least-squares technique. Three oxygen atoms of one perchlorate anion were positionally disordered and six peaks each with a site occupancy factor of 0.5 were refined for them. There were three additional peaks in the Fourier-difference map: one was refined for a water oxygen, the other two for a methanol. The source of water could be the solvents used for crystallization. All non-hydrogen atoms except those positionally disordered were refined anisotropically. The hydrogen atoms of the complex cation were placed in calculated positions and used only for structure-factor calculations. The full-matrix least-squares refinement converged to $R = 0.0522$ and $R' = 0.0527$ with a weighting scheme $w = 1.0/[\sigma^2|F_o| + 0.000\,692|F_o{}^2|]$ using 537 parameters. The highest peak in the final Fourier-difference map was 0.80 e Å^{-3}. All calculations were carried out using a VAX88 computer at the computer centre of the Indian Institute of Science using the SHELX system of programs.[18] Atomic scattering factors were taken from ref. 19.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/112.

Results and Discussion

The complexes were prepared by following a general synthetic route involving facile formation of a μ-oxo-bis(μ-acetato)diruthenium(III) core having bidentate chelating 2,2′-bipyridine and a unidentate imidazole base (Him, 1-mim or 4-mim) as terminal ligands. The molecular structure of the 1-methylimidazole complex has been determined by X-ray crystallography. An ORTEP[20] view of the complex cation is shown in Fig. 1. The metal centres have a near-octahedral co-ordination. The Ru···Ru, Ru–O (oxo) distances and Ru–O–Ru angle in the cationic complex $[(1\text{-mim})(\text{bipy})\text{Ru}(\mu\text{-O})(\mu\text{-O}_2\text{CMe})_2\text{Ru}(\text{bipy})(1\text{-mim})]^{2+}$ are 3.285(2), 1.882(6) Å and 121.5(3)° (Table 1). Due to the *trans* influence of the oxide ligand and considerable Ru–O (oxo) double-bond character, the Ru–N (1-mim) distance is much longer than the Ru–N (bipy) distances. The observed *trans* geometry of the imidazole base in **1b** is unusual as the unidentate ligand in related complexes $[\text{Ru}_2\text{O}(\text{O}_2\text{CR})_2(\text{PPh}_3)_2(\text{en})_2]^{2+}$ (en = ethane-1,2-diamine), $[\text{Mn}_2\text{O}(\text{O}_2\text{CMe})_2(\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$, $[\text{Fe}_2\text{O}(\text{O}_2\text{CMe})_2(\text{bipy})_2\text{Cl}_2]$, $[\text{Mn}_2\text{O}(\text{O}_2\text{CR})_2\text{X}_2(\text{bipy})_2]^{n+}$ (R = Ph or Me; X = Cl^-, $\text{N}_3{}^-$ or H_2O; n = 0 or 2) and $[\text{Mn}_2\text{O}(\text{O}_2\text{CMe})_2(\text{bipy})_2(\text{H}_2\text{O})(\text{S}_2\text{O}_8)]\cdot\text{H}_2\text{O}$ has a *cis* disposition with respect to the μ-oxo ligand.[13h,21–24]

Physicochemical data for complexes **1a**–**1c** are given in Table 2. The complexes are 1 : 2 electrolytes in MeCN. Their electronic spectra show a strong visible band near 600 nm, diagnostic of a $[\text{Ru}_2(\mu\text{-O})(\mu\text{-O}_2\text{CR})_2]^{2+}$ core and due to a charge-transfer transition involving ruthenium(III) d_π and oxygen(oxo) p_π orbitals. The complexes are essentially diamagnetic as evidenced from the ^{1}H NMR spectra. The bipyridine, acetate and imidazole ligands are present in a 1 : 1 : 1 ratio. The ^{1}H NMR data show that the two rings of the bipyridine ligand are equivalent and the imidazole base is *trans* to the μ-oxo ligand.

The redox behaviour of the complexes has been studied by cyclic and differential-pulse voltammetric techniques. The complexes undergo reversible one-electron oxidation near 0.80 V and reduction in the range −0.5 to −0.9 V *vs.* SCE along with an irreversible reduction. The reversible electron-transfer processes are assignable to the $\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}$–$\text{Ru}^{\text{III}}\text{Ru}^{\text{IV}}$ and $\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}$–$\text{Ru}^{\text{III}}\text{Ru}^{\text{II}}$ couples. The origin of the irreversible reduction process is not clear for **1a** and **1c** as free imidazole or 4-methylimidazole shows a quasi-reversible cyclic voltammetric response at −1.4 V (ΔE_p = 200 mV at 50 mV s^{-1}) in MeCN–0.1 mol dm^{-3} $[\text{NBu}^n{}_4][\text{ClO}_4]$. The cyclic and differential pulse voltammograms of **1a** are shown in Fig. 2.

The effect of protonation of the μ-oxo ligand in [Ru$_2$O-

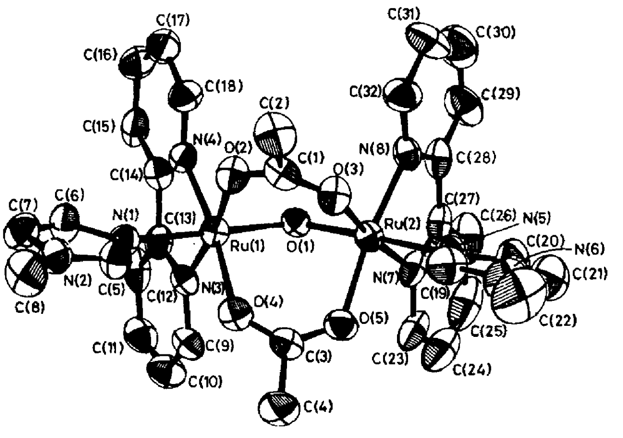

Fig. 1 Molecular structure and atom numbering scheme of the cationic complex in $[\text{Ru}_2\text{O}(\text{O}_2\text{CMe})_2(\text{bipy})_2(1\text{-mim})_2][\text{ClO}_4]_2\cdot\text{H}_2\text{O}\cdot\text{MeOH}$ showing 50% probability thermal ellipsoids

Table 1 Selected bond distances (Å) and angles (°) in $[\text{Ru}_2\text{O}(\text{O}_2\text{CMe})_2(\text{bipy})_2(1\text{-mim})_2][\text{ClO}_4]_2\cdot\text{H}_2\text{O}\cdot\text{MeOH}$ with estimated standard deviations in parentheses

Ru(1)···Ru(2)	3.285(2)	Ru(2)–O(1)	1.881(5)
Ru(1)–O(1)	1.883(7)	Ru(2)–O(3)	2.082(6)
Ru(1)–O(2)	2.072(5)	Ru(2)–O(5)	2.079(6)
Ru(1)–O(4)	2.088(5)	Ru(2)–N(5)	2.124(6)
Ru(1)–N(1)	2.125(9)	Ru(2)–N(7)	2.018(8)
Ru(1)–N(3)	2.037(5)	Ru(2)–N(8)	2.035(7)
Ru(1)–N(4)	2.030(5)	O(4)–C(3)	1.264(10)
O(2)–C(1)	1.261(9)	O(5)–C(3)	1.245(12)
O(3)–C(1)	1.252(12)	C(3)–C(4)	1.505(13)
C(1)–C(2)	1.508(13)		
Ru(1)–O(1)–Ru(2)	121.5(3)	O(1)–Ru(2)–O(3)	96.7(2)
O(1)–Ru(1)–O(2)	94.8(2)	O(1)–Ru(2)–O(5)	94.7(2)
O(1)–Ru(1)–O(4)	95.5(2)	O(1)–Ru(2)–N(5)	178.7(2)
O(1)–Ru(1)–N(1)	177.8(3)	O(1)–Ru(2)–N(7)	88.4(3)
O(1)–Ru(1)–N(3)	91.6(3)	O(3)–Ru(2)–O(5)	89.8(2)
O(1)–Ru(1)–N(4)	90.7(2)	O(3)–Ru(2)–N(5)	83.4(3)
O(2)–Ru(1)–N(3)	171.4(2)	O(3)–Ru(2)–N(7)	172.5(2)
O(2)–Ru(1)–N(4)	93.8(2)	O(3)–Ru(2)–N(8)	95.3(3)
N(1)–Ru(1)–N(3)	90.6(3)	O(5)–Ru(2)–N(5)	84.0(3)
N(1)–Ru(1)–N(4)	89.8(3)	O(5)–Ru(2)–N(7)	95.3(3)
N(3)–Ru(1)–N(4)	80.3(2)	O(5)–Ru(2)–N(8)	172.7(2)
O(4)–Ru(1)–N(1)	84.2(3)	N(5)–Ru(2)–N(8)	91.3(3)
O(4)–Ru(1)–N(3)	94.4(2)	N(7)–Ru(2)–N(8)	79.2(3)
O(4)–Ru(1)–N(4)	172.0(2)	Ru(2)–O(3)–C(1)	131.6(6)
Ru(1)–O(2)–C(1)	128.4(5)	Ru(2)–O(5)–C(3)	128.4(5)
Ru(1)–O(4)–C(3)	131.9(6)	O(4)–C(3)–C(4)	116.4(8)
O(2)–C(1)–O(3)	126.7(8)	O(4)–C(3)–O(5)	126.9(8)
O(2)–C(1)–C(2)	115.6(8)	O(5)–C(3)–C(4)	116.7(8)
O(3)–C(1)–C(2)	117.8(8)		

Table 2 Physicochemical data for $[Ru_2O(O_2CMe)_2(bipy)_2L_2][ClO_4]_2$ (L = Him **1a**, 1-mim **1b** or 4-mim **1c**)

	1a	**1b**	**1c**
$\Lambda_M{}^a/\Omega^{-1}$ cm^2 mol^{-1}	240	250	220
λ_{max}/nm (ε/dm^3 mol^{-1} cm^1)	608 (19 500)[a]	608 (22 600)[a]	603 (18 600)[b]
^{1}H NMR (δ)[c]			
CH_3 (acetate)	2.06 (s, 6 H)	2.18 (s, 6 H)	2.04 (s, 6 H)
CH_3 (imidazole base)		4.04 (s, 6 H)	2.29 (s, 6 H)
CH (imidazole ring)	7.04 (s, 2 H), 7.72 (s, 2 H), 8.15 (s, 2 H)	7.24 (s, 2 H), 7.92 (s, 2 H), 8.16 (s, 2 H)	6.71 (s, 2 H), 7.94 (s, 2 H)
CH (bipyridine)	6.06 (d, 4 H), 7.23 (t, 4 H), 7.95 (t, 4 H), 8.87 (d, 4 H)	6.12 (d, 4 H), 7.21 (t, 4 H), 7.95 (t, 4 H), 8.65 (d, 4 H)	6.06 (d, 4 H), 7.21 (t, 4 H), 7.92 (t, 4 H), 8.86 (d, 4 H)
$E_{\frac{1}{2}}$/V (ΔE_p/mV)[d]			
$Ru^{III}Ru^{IV}$–$Ru^{III}Ru^{III}$	0.77 (60)	0.77 (60)	0.77 (60)
$Ru^{III}Ru^{III}$–$Ru^{III}Ru^{II}$	−0.85 (100)	−0.57 (60)	−0.84 (80)
$Ru^{III}Ru^{II}$–$Ru^{II}Ru^{II}$	−1.56[e]	−0.90[e]	−1.56[e]
$Ru^{III}Ru^{III}$–$Ru^{II}Ru^{II}$ [f]	−0.62 (50)	−0.40 (50)	−0.60 (50)

[a] In MeCN. [b] In MeOH. [c] In CD_3CN–$SiMe_4$ for complex **1b**, $(CD_3)_2SO$–$SiMe_4$ for **1a** and **1c**; s = singlet, d = doublet, t = triplet. The NH protons in **1a** and **1c** were not observed. [d] In MeCN–0.1 mol dm^{-3} $[NBu^n{}_4][ClO_4]$ with SCE as reference electrode; $E_{\frac{1}{2}} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials. Scan rate 50 mV s^{-1} at a platinum working electrode; $\Delta E_p = E_{pa} - E_{pc}$. [e] The cathodic peak potentials of the irreversible reduction process. [f] This couple was observed on addition of imidazole for complex **1a**; benzimidazole for **1b** and 4-methylimidazole for **1c**.

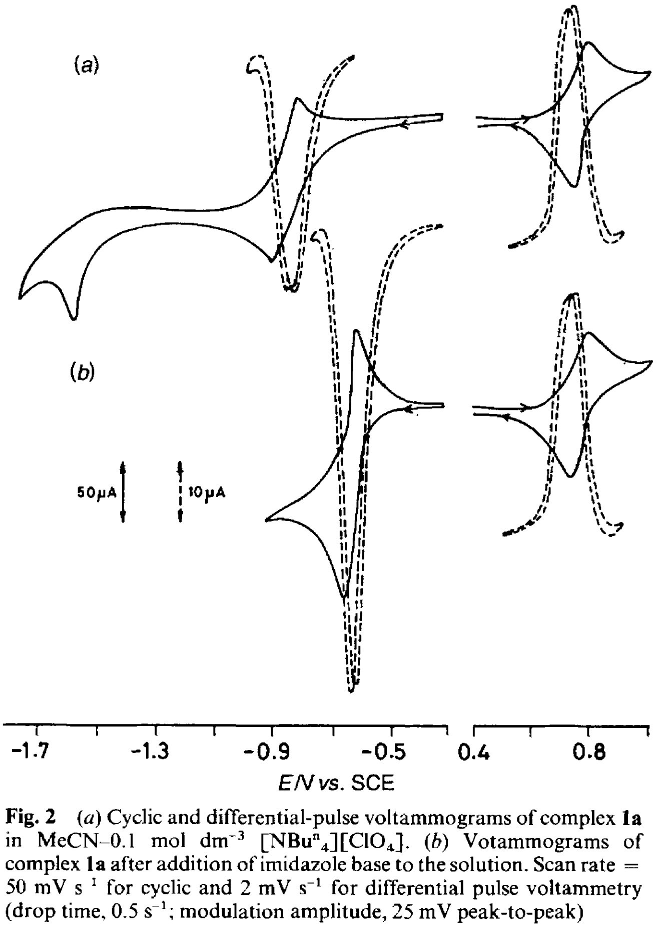

Fig. 2 (*a*) Cyclic and differential-pulse voltammograms of complex **1a** in MeCN–0.1 mol dm^{-3} $[NBu^n{}_4][ClO_4]$. (*b*) Votammograms of complex **1a** after addition of imidazole base to the solution. Scan rate = 50 mV s^{-1} for cyclic and 2 mV s^{-1} for differential pulse voltammetry (drop time, 0.5 s^{-1}; modulation amplitude, 25 mV peak-to-peak)

$(O_2CMe)_2(bipy)_2(1\text{-mim})_2][PF_6]_2$ has recently been reported by Kikuchi *et al.*[15] We have observed that the oxidation couple remains unaffected on addition of a weak proton-donor imidazole base. However, the reduction process shows a dramatic shift in potential as well as the nature of the electron stoichoimetry. Addition of imidazole to a solution of complex **1a** resulted in a one-step two-electron-transfer redox couple $Ru^{III}Ru^{III}$–$Ru^{II}Ru^{II}$ at −0.625 V (ΔE_p = 50 mV at 50 mV s^{-1}) (Fig. 2). A similar reduction process is observed at −0.4 V (ΔE_p = 50 mV at 50 mV s^{-1}) for **1b** on addition of benzimidazole. Complex **1c** also displays a two-electron transfer process at −0.6 V (ΔE_p = 50 mV at 50 mV s^{-1}) in the presence of 4-methylimidazole. This couple appears 200 mV to positive potential of that observed for the $Ru^{III}Ru^{III}$–$Ru^{III}Ru^{II}$ couple, indicating the possibility of formation of a protonated μ-hydroxo species during electrochemical reduction of the $Ru_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2{}^{2+}$ core in the presence of a weak proton-donor base.

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