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Biimidazole complexes of ML_2^{2+} [M = Ru or Os, L = 2-(phenylazo)-pyridine]. Synthesis, structure and redox properties of mono- and di-nuclear complexes‡

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A series of mono- and di-nuclear complexes of ruthenium and osmium containing the terminal ligands 2-(phenylazo)pyridine (pap), 2,2′-bipyridine (bpy) and the bridging ligand 2,2′-biimidazole(H_2biim) have been prepared. The mononuclear complex $[Ru(pap)_2(H_2biim)][ClO_4]_2\cdot 3CH_2Cl_2$ was characterised by a single-crystal structure determination. The mononuclear complexes $[M(pap)_2(H_2biim)]^{2+}$ (M = Ru or Os) act as dibasic acids and undergo deprotonation to afford $[M(pap)_2(Hbiim)]^+$ and $[M(pap)_2(biim)]$. The completely deprotonated complexes behave as reactive building units ('metal complex as ligand') which react smoothly with metal complex units to produce homo- and hetero-dinuclear complexes. The structure of the dinuclear complex $[Ru_2(bpy)_4(biim)][ClO_4]_2$ was determined. Cyclic voltammetric studies on the above complexes were performed. The quasi-reversible half-wave potentials of the oxidation processes of the dinuclear complexes are dependent on the metal as well as on the nature of the terminal ligands. These undergo two one-electron oxidation processes centered at the metal. Partial oxidation of the dinuclear complexes led to unsymmetrical bridge cleavage to form monomeric complexes. Large numbers of ligand reduction responses were observed. In some cases the first ligand reduction occurs close to zero potential (with respect to the SCE).

Di- and poly-nuclear ruthenium and osmium complexes of biimidazole (H_2biim) containing ligands have received much attention[1–4] in recent years in the context of studies of electron-transfer processes and intermetal electronic interactions.[5,6] Protonation-induced switching of metal–metal interactions in these complexes has been an area of recent activity. The biimidazole ligand requires deprotonation in order to act as a bridge and the pK_a values are quite high.[7] For this reason the complex $[Ru(bpy)_2(H_2biim)]^{2+}$ is a poor ligand for the construction[1] of polynuclear material. Against this background we focused our attention on $[M(pap)_2(H_2biim)]^{2+}$ [M = Ru or Os; pap = 2-(phenylazo)pyridine] as a possible building unit for the construction of complexes of higher nuclearity. As a terminal ligand, pap has been recognised[8] as one of the most powerful π acceptors which undergoes reversible electron transfer at low potentials on co-ordination. The very strong π-acceptor ability is expected to facilitate deprotonation[9] of $[M(pap)_2(H_2biim)]^{2+}$ and in turn make them potential building units for the construction of complexes of higher nuclearity.[10,11]

In this paper we report a comprehensive study of the synthesis and properties of the mononuclear building units $[M(pap)_2(H_2biim)][ClO_4]_2$, and their use to generate mixed-metal and mixed-ligand dinuclear complexes. The single-crystal structures of a mononuclear complex, $[Ru(pap)_2(H_2biim)][ClO_4]_2$, and a dinuclear complex, $[\{Ru(bpy)_2\}_2(biim)][ClO_4]_2$, have been analysed. Structurally characterised mono- and di-nuclear complexes of Ru/Os containing neutral terminal H_2biim or bianionic bridging, biim, are scarce.[2]

Results and Discussion

Synthesis of $[M(pap)_2(H_2biim)][ClO_4]_2$ (M = Ru or Os)

The *trans,cis* isomer[12,13] of the bis-chelated dihalogeno complexes $M(pap)_2X_2$ (X = Cl or Br) were used as starting materials. These react smoothly with $[Ag(H_2biim)]NO_3$, obtained from equimolar quantities of $AgNO_3$ and H_2biim in boiling aqueous ethanol, in 1:2 molar proportion [equations (1) and (2)]. After

$$[RuCl_2(pap)_2] + 2[Ag(H_2biim)]^+ \longrightarrow [Ru(pap)_2(H_2biim)]^{2+} + H_2biim + 2AgCl \quad (1)$$

$$[OsBr_2(pap)_2] + 2[Ag(H_2biim)]^+ \longrightarrow [Os(pap)_2(H_2biim)]^{2+} + H_2biim + 2AgBr \quad (2)$$

the removal of insoluble AgCl, aqueous sodium perchlorate was added to precipitate $[M(pap)_2(H_2biim)][ClO_4]_2$ in excellent yields (92% when M = Ru and 75% when M = Os). By application of the above synthetic strategy it was possible to synthesize $[Ru(bpy)_2(H_2biim)][ClO_4]_2$ (bpy = 2,2′-bipyridine) directly from *cis*-$[RuCl_2(bpy)_2]$ in high yield (90%).

The above silver-assisted synthetic route[14] has several advantages. This one-step and one-pot synthesis of the mixed-ligand tris chelates occurs very smoothly and rapidly (30 min). For comparison, a similar reaction starting from substitutionally labile[9] $[Ru(pap)_2(OH_2)_2]^{2+}$ and free H_2biim requires more than 2 h of reflux for completion of the reaction and the yield of $[Ru(pap)_2(H_2biim)][ClO_4]_2$ was also poor. The usefulness of this route is more recognised for the synthesis of $[Os(pap)_2(H_2biim)]^{2+}$. In this case, unlike the ruthenium congener, $[Os(pap)_2(OH_2)_2]^{2+}$ is not known. The substitution of *cis*-bromides in $[OsBr_2(pap)_2]$ by H_2biim could only be achieved by following the above route (2). As a reagent, $[Ag(H_2biim)]^+$ acts as a source of halide abstractor as well as a source of H_2biim ligand.

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[‡] *Supplementary data available*: ^{1}H NMR spectrum of $[Ru(pap)_2(H_2biim)][ClO_4]_2$. For direct electronic access see http://www.rsc.org/suppdata/dt/1998/1569/, otherwise available from BLDSC (No. SUP 57357, 3 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (http://www.rsc.org/dalton).

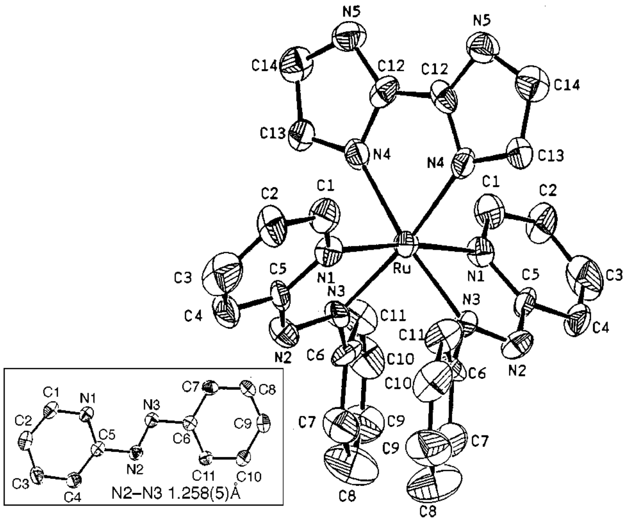


Fig. 1 An ORTEP[15] plot and atom numbering scheme for [Ru(pap)$_2$(H$_2$biim)]$^{2+}$ in [Ru(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$·3CH$_2$Cl$_2$. Inset is an ORTEP plot for [Hpap]$^+$

Table 1 Selected bond angles (°) and distances (Å)

[Ru(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$·3CH$_2$Cl$_2$			
Ru–N1	2.060(11)	Ru–N4	2.078(12)
Ru–N3	2.007(11)	N2–N3	1.271(17)
N4–Ru–N4	78.6(5)	N1–Ru–N3	99.5(5)
[(bpy)$_2$Ru(biim)Ru(bpy)$_2$][ClO$_4$]$_2$			
Ru–N1	2.140(6)	Ru–N5	2.024(6)
Ru–N2	2.143(6)	Ru–N6	2.045(6)
Ru–N3	2.035(7)	C1–C1	1.422(14)
Ru–N4	2.035(6)		
N1–Ru–N2	82.01(23)	N5–Ru–N6	79.50(3)
N3–Ru–N4	79.69(24)		

Characterisation of [M(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$ and structure of [Ru(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$

The compounds (M = Ru or Os) were formulated by elemental analysis. They are 1 : 2 electrolytes in CH$_3$CN. Their IR spectra consist of (*i*) a broad absorption at 3100 cm^{-1}, assigned to the N–H stretching mode, (*ii*) a doublet ν(N=N) at 1270–1250 cm^{-1}, (*iii*) absorptions at *ca.* 1100 (broad) and at *ca.* 620 cm^{-1} (sharp) due to the presence of ClO$_4^-$. The rest of the spectra indicate co-ordination of pap as well as H$_2$biim. The molecular geometry of the mononuclear complex cation [Ru(pap)$_2$(H$_2$biim)]$^{2+}$ with the atom numbering scheme is shown in Fig. 1. The cation is located at the crystallographic two-fold axis; only half of it occupies the asymmetric unit. Atoms given the same atom label are symmetry related. Table 1 contains selected bond distances and angles. The co-ordination geometry of the Ru^{II} is approximately octahedral involving the pap ligand in a *trans,cis* geometry and a H$_2$biim ligand. The Ru–N (H$_2$biim) distance is 2.078(12) Å and is the longest amongst the Ru–N distances present. Interestingly, the Ru–N (azo) distance, 2.007(11) Å, is shorter than the Ru–N (py) distance, 2.060(11) Å, indicating significant d$_\pi$–p$_\pi$ interactions between ruthenium (t$_{2g}$) and low-lying π*(azo) orbitals of pap. This effect is also reflected in the long[8b,16] N–N length, 1.271(17) Å, and low[8] ν(N=N). It is reasonable to compare here the N–N length in [Ru(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$ with that, 1.258(5) Å, in [Hpap][ClO$_4$]. Evidently the N–N distance in the complex is significantly longer. An ORTEP diagram of the cation [Hpap]$^+$ is shown as an inset of Fig. 1. Details of its structure and properties will be reported elsewhere.

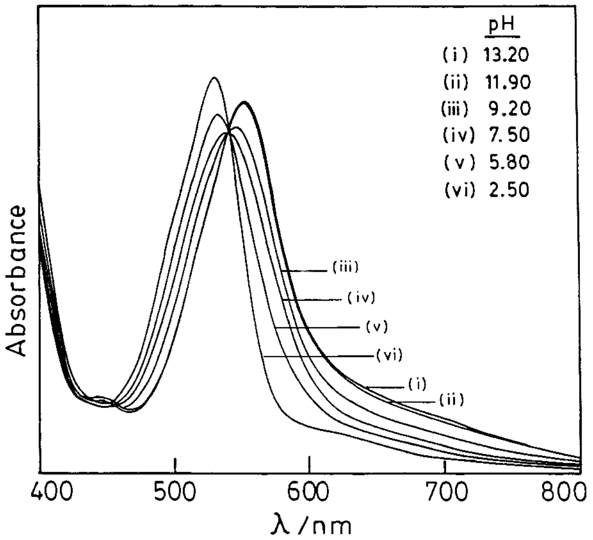


Fig. 2 Visible range spectra of [Ru(pap)$_2$(H$_2$biim)]$^{2+}$ as a function of pH in 1,4-dioxane–water (1 : 1)

The ^{1}H NMR spectra of [M(pap)$_2$(H$_2$biim)]$^{2+}$ in CD$_3$CN indicate the retention of a two-fold axis of symmetry also in solution. The characteristic proton resonances[17,18] for the complexes are: (*i*) four pyridyl proton resonances appear from δ 7.3 to 8.8, (*ii*) phenyl protons resonate in the range δ 7.0 to 7.4, (*iii*) two protons of the imidazole ring at δ 6.88 and 7.36. The ^{1}H NMR spectrum of [Ru(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$ is available as SUP 57357.

Protic equilibria

The monomeric compounds [M(pap)$_2$(H$_2$biim)]$^{2+}$ (M = Ru **1** or Os **2**) act as dibasic acids and can be titrated pH-metrically in water–1,4-dioxane (1 : 1). At 298 K we obtained pK_1 = 4.2 ± 0.1, pK_2 = 8.0 ± 0.1 for **1** and pK_1 = 3.8 ± 0.1, pK_2 = 6.5 ± 0.1 for **2**. The osmium complex is the stronger acid. Reactions (3) and (4) are reversible and each of the three species involved in the equilibria can be converted into any one of the other two simply by adjustment of pH. We have been able to isolate both [M(pap)$_2$(Hbiim)]ClO$_4$ **3** and [M(pap)$_2$(biim)] **4** in their pure state. The biim compound **4** behaves as a strong base. No crystalline ruthenium compounds containing anionic biimidazole (Hbiim$^-$ or biim^{2-}) are known. This is due to the high pK_a of the known Ru–H$_2$biim complexes. For comparison, the pK_a values[19] for the [Ru(bpy)$_2$(H$_2$biim)]$^{2+}$ complexes are: pK_1 = 7.2 and pK_2 = 12.1. Such dramatic changes of acid-dissociation constants in the pap complexes are attributed to the very high π acidity of pap compared with that of bpy.

$$[M(pap)_2(H_2biim)]^{2+} \overset{K_1}{\rightleftharpoons} [M(pap)_2(Hbiim)]^{+} + H^{+} \qquad (3)$$

$$[M(pap)_2(Hbiim)]^{+} \overset{K_2}{\rightleftharpoons} [M(pap)_2(biim)] + H^{+} \qquad (4)$$

As the pH of a solution (in 1 : 1 water–1,4-dioxane) of [Ru(pap)$_2$(H$_2$biim)]$^{2+}$ is varied from 2.5 to 13.0 the MLCT band is progressively red shifted. The pH-dependent spectra (Fig. 2) of [Ru(pap)$_2$(H$_2$biim)]$^{2+}$ show an isosbestic point at 540 nm, which indicates stepwise formation[20] of the deprotonated species with addition of OH$^-$ (increasing pH). The spectrum at pH 5.8 is that of almost pure [Ru(pap)$_2$(Hbiim)]$^+$. The pH-dependent visible range spectra of [Os(pap)$_2$(H$_2$biim)]$^{2+}$ also show a sharp isosbestic point at 550 nm in the pH range 1.5 to 8.0. At a higher pH a deviation[21] from the isosbestic point is noticed.

Table 2 The UV/VIS spectral data at 298 K

Compound	Absorption[a] λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
$[Ru(pap)_2(H_2biim)][ClO_4]_2$	618[b] (1600), 531 (14 100), 502[b] (9650), 357[b] (20 650), 287 (29 600), 218 (31 750)
$[Ru(pap)_2(Hbiim)]ClO_4\cdot H_2O$	663[b] (1200), 539 (9750), 360[b] (15 500), 313 (24 700), 218 (24 500)
$[Ru(pap)_2(biim)]\cdot 2H_2O$	692[b] (1750), 559 (11 150), 457[b] (3400), 319 (26 450), 215 (34 650)
$[Os(pap)_2(H_2biim)][ClO_4]_2\cdot 2H_2O$	630[b] (2000), 505 (12 400), 334[b] (20 800), 282 (25 000), 219 (28 700)
$[Os(pap)_2(Hbiim)]ClO_4\cdot H_2O$	660[b] (2050), 509 (12 600), 313 (26 550), 224 (32 000)
$[Os(pap)_2(biim)]\cdot 2H_2O$	670[b] (2400), 515 (12 300), 317 (21 600), 226[b] (23 750), 202 (38 400)
$[(pap)_2Ru(biim)Ru(pap)_2][ClO_4]_2\cdot 3H_2O$	526 (20 000), 450[b] (7900), 358[b] (32 500), 312 (44 000), 282[b] (36 000), 216 (61 000)
$[(pap)_2Ru(biim)Os(pap)_2][ClO_4]_2\cdot 2H_2O$	531 (22 800), 364[b] (42 250), 311 (53 000), 214 (71 000)
$[(pap)_2Ru(biim)Ru(bpy)_2][ClO_4]_2\cdot 3H_2O$	545[b] (11 500), 507 (17 000), 448[b] (8500), 322[b] (32 300), 292 (74 700), 245[b] (40 500)
$[(pap)_2Os(biim)Os(pap)_2][ClO_4]_2\cdot 2H_2O$	765[b] (1700), 508 (14 500), 309 (28 700), 221 (52 500)
$[(pap)_2Os(biim)Ru(bpy)_2][ClO_4]_2\cdot 3H_2O$	589[b] (26 250), 500 (21 200), 335 (35 000), 292 (87 500), 244 (52 500), 210 (69 300)

[a] In CH_3CN. [b] Shoulder.

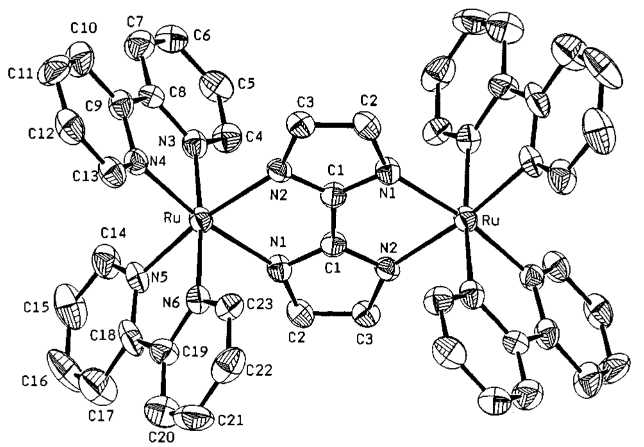
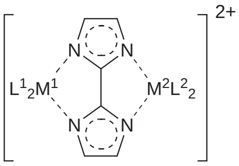


Fig. 3 An ORTEP plot and atom numbering scheme for $[\{Ru(bpy)_2\}_2(biim)]^{2+}$ in $[\{Ru(bpy)_2\}_2(biim)][ClO_4]_2$



M^1	M^2	L^1	L^2
Ru	Ru	pap	pap
Ru	Os	pap	pap
Ru	Ru	pap	bpy
Os	Os	pap	pap
Os	Ru	pap	bpy

Use of $M(pap)_2(biim)$ as a building unit

It is quite evident, from the foregoing discussion, that the neutral complex $[M(pap)_2(biim)]$ would be a potential building unit for the synthesis of polynuclear complexes. Following the strategy[22] of using it as a 'ligand' and the complex $[ML_2X_2]^{0/2+}$ [M = Ru or Os; L = pap or bpy; X = Cl, Br or CH_3CN] as 'metal' it has been possible to synthesize a group of bimetallic complexes in moderate to high yields. Examples of unsymmetrical complexes containing different metals as well as different ligands as in $[(pap)_2Os(biim)Ru(bpy)_2]^{2+}$ are very limited.[23] Here we also describe the crystal structure of $[(bpy)_2Ru(biim)Ru(bpy)_2]^{2+}$ (Fig. 3). This compound has long been known.[1] To the best of our knowledge this represents the first structural characterisation[2] of a dimeric ruthenium compound containing dianionic biim as the bridging ligand. The structure of the $[Ru_2(bpy)_4(biim)]^{2+}$ has been compared with that[18] of $[Rh_2(cod)_2(biim)]$. The asymmetric unit consists of half of the molecule which generates the dinuclear complex through a crystallographic inversion centre located at the midpoint of the C1–C1 bond. The bridging $biim^{2-}$ co-ordinates as a planar ligand in a bis-chelated four-co-ordinated manner with two $[Ru(bpy)_2]^{2+}$ moieties. The geometry about each ruthenium atom is octahedral. Selected bond angles and distances are presented in Table 1. The length of the bond C1–C1 joining the two imidazolato rings, 1.422(14) Å, is comparable to that observed in $[Rh_2(cod)_2(biim)]$ and is shorter than in the complex $[Rh_4(CO)_8(biim)_2]$.[24] The bond lengths in each imidazolato ring are in the range reported for corresponding parameters in complexes containing bidentate imidazolato ligands, $C_3H_3N_2^-$. The Ru–N (bpy) bond length, 2.035(6) Å (average) is considerably shorter than Ru–N (biim), 2.141(6) Å (average). This may be attributed to the π interaction between the $Ru(t_{2g})$ and π*(bpy) orbitals in $[\{Ru(bpy)\}_2(biim)]^{2+}$. Interestingly, the Ru–N (biim) distance in the above dimer is longer than Ru–N (H_2biim) in $[Ru(pap)_2(H_2biim)]^{2+}$. It would be interesting to compare the above Ru–N lengths with Ru–N (biim) in a $Ru(pap)_2(biim)$ molecule. Unfortunately, we have not yet succeeded in growing X-ray-quality crystals of a compound containing a $M(pap)_2^{2+}$ unit and dianionic $biim^{2-}$ ligand. Electronic spectral data for the mono- and di-nuclear complexes are collected in Table 2.

Electrochemistry

The redox responses in both anodic and cathodic regions were determined for each mono- and di-nuclear species using cyclic voltammetry (CV). Electrochemical data are collected in Table 3 and representative voltammograms are shown in Fig. 4.

(*i*) Oxidation processes. The mononuclear complexes $[M(pap)_2(H_2biim)]^{2+}$ undergo oxidation irreversibly at 1.70 (M = Ru) and 1.52 V (M = Os) in acetonitrile. This response shifts cathodically for the deprotonated complexes, *viz.* $[M(pap)_2(Hbiim)]^+$ and $[M(pap)_2(biim)]$. The values of p*K* for the above protonated complexes are small which is believed to be responsible for the irreversible nature in an aprotic solvent. For the homobinuclear complexes $[(pap)_2Ru(biim)Ru(pap)_2]^{2+}$ and $[(pap)_2Os(biim)Os(pap)_2]^{2+}$ two successive electrode oxidation couples are observed and the separations between the two are 0.26 (Ru) and 0.24 V (Os). The first oxidation potentials of the binuclear complexes are systematically much lower (*ca.* 0.5 V) than the anodic responses for the mononuclear complex. This is due[24] to the stronger π-donor ability of the dianion bridge $biim^{2-}$ than the neutral terminal H_2biim. The separation between two successive anodic responses for the unsymmetrical $[(bpy)_2Ru(biim)Ru(pap)_2]^{2+}$ is 0.26 V. The first oxidation process, in this case, is assigned to the $(bpy)_2Ru^{III}(biim)$–$(bpy)_2Ru^{II}(biim)$ couple. The two oxidative waves for the most unsymmetrical complex $[(bpy)_2Ru(biim)Os(pap)_2]^{2+}$ occur at 0.79 and 1.00 V, the former being attributed to the oxidation of the ruthenium centre in the above complex.

In order to study the properties of the mixed-valence species, controlled-potential coulometry of $[(pap)_2Ru(biim)Ru(pap)_2]^{2+}$

Table 3 Cyclic voltammetric data[a]

Compound	Oxidation $E_{\frac{1}{2}}$/V	Reduction $-E_{\frac{1}{2}}$/V
$[Ru(pap)_2(H_2biim)][ClO_4]_2$	1.70[b]	0.18, 0.30, 0.65, 1.08,[c] 1.54,[c] 2.0[c]
$[Ru(pap)_2(Hbiim)]ClO_4{\cdot}H_2O$	0.96[b]	0.33, 0.45, 1.0, 1.78, 1.88[c]
$[Ru(pap)_2(biim)]{\cdot}2H_2O$	0.38[b]	0.28, 0.42, 0.85, 1.01, 1.78[c]
$[Os(pap)_2(H_2biim)][ClO_4]_2{\cdot}2H_2O$	1.52[b]	0.16, 0.43, 1.34,[c] 1.56,[c] 2.10[c]
$[Os(pap)_2(Hbiim)]ClO_4{\cdot}H_2O$	0.94[b]	0.30, 0.85, 1.36[c]
$[Os(pap)_2(biim)]{\cdot}2H_2O$	0.34[b]	0.25, 0.68, 1.16[c]
$[(pap)_2Ru(biim)Ru(pap)_2][ClO_4]_2{\cdot}3H_2O$	1.13, 1.39	0.33, 0.47, 0.88, 0.97, 1.84
$[(pap)_2Ru(biim)Os(pap)_2][ClO_4]_2{\cdot}2H_2O$	1.10, 1.28	0.31, 0.46, 0.84, 0.95, 1.65,[c] 1.87,[c] 2.12[c]
$[(pap)_2Ru(biim)Ru(bpy)_2][ClO_4]_2{\cdot}3H_2O$	0.76, 1.15	0.36, 0.93, 1.63, 1.80,[c] 1.93,[c] 2.60[c]
$[(pap)_2Os(biim)Os(pap)_2][ClO_4]_2{\cdot}2H_2O$	1.05, 1.29	0.28, 0.50, 0.80, 0.92, 2.10[c]
$[(pap)_2Os(biim)Ru(bpy)_2][ClO_4]_2{\cdot}3H_2O$	0.79, 1.0	0.41, 0.88, 1.61,[c] 1.86,[c] 2.08[c]

[a] Experiments were carried out in CH_3CN at 298 K using 0.1 M NEt_4ClO_4 as supporting electrolyte. The reported data correspond to a scan rate of 50 mV s^{-1}. [b] Irreversible response; the potential corresponds to E_{pa}. [c] Irreversible response; the potential corresponds to E_{pc}.

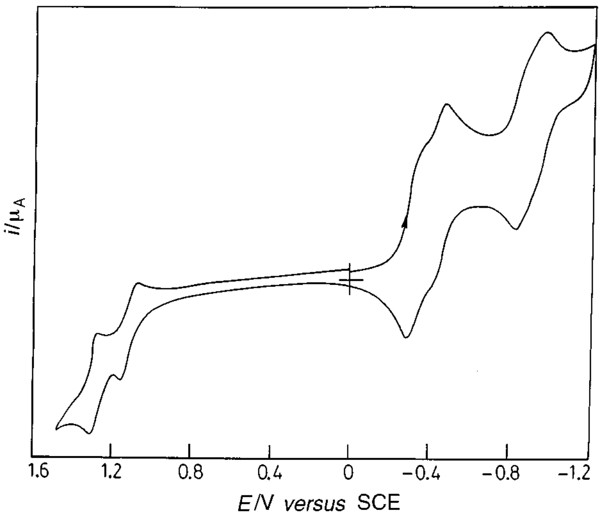


Fig. 4 Cyclic voltammogram of $[(pap)_2Ru(biim)Os(pap)_2]^{2+}$ in CH_3CN: working electrode, platinum; scan rate 50 mV s^{-1}; supporting electrolyte, NEt_4ClO_4

was performed at 1.3 V in CH_3CN. The spectrum of the electrolysed solution did not show any characteristic intervalence transition. However, cyclic voltammetry of the oxidised solution showed responses due to the complexes $[Ru(pap)_2(CH_3CN)_2]^{3+/2+}$, $[Ru(pap)_2(biim)]^{+/0}$ and $[Ru(pap)_2(Hbiim)]^{2+/+}$. These results suggest that the mixed-valence $[(pap)_2Ru^{III}(biim)Ru^{II}(pap)_2]^{3+}$ dimer is stable only on the cyclic voltammetry timescale, but is unstable on a longer timescale and undergoes unsymmetrical bridge cleavage to form monomeric species as shown in equations (5) and (6). A similar result was obtained

$$[(pap)_2Ru(biim)Ru(pap)_2]^{2+} \rightleftharpoons [(pap)_2Ru(biim)Ru(pap)_2]^{3+} + e^- \quad (5)$$

$$[(pap)_2Ru(biim)Ru(pap)_2]^{3+} + 2CH_3CN \rightleftharpoons [Ru(pap)_2(CH_3CN)_2]^{2+} + [Ru(pap)_2(biim)]^+ \quad (6)$$

from the spectral analysis of the partially oxidised dimer with Ce^{4+}. The appearance of the monomeric protonated complex is consistent with the basicity of the co-ordinated biim. This situation is similar[26] to the dipyrazolyl-bridged dimer $[(bpy)_2Ru(pz)_2Ru(bpy)_2]^{2+}$ where it has been concluded that the difference between the formal electrode potentials for the two anodic responses is due to electrostatic effects and the mixed-valence complexes in these cases may be described as localised.

(*ii*) Reduction processes. Free pap displays two quasi-reversible cyclic voltammetric responses[8a] at −1.31 and −1.57 V. Therefore, multiple reduction waves were anticipated in both mono- and di-nuclear complexes. The monomeric complexes $[M(pap)_2(H_2biim)]^{2+}$ display four reduction waves in the range −0.15 to −2.5 V. The symmetrical dimeric complexes $[(pap)_2Ru(biim)Ru(pap)_2]^{2+}$ and $[(pap)_2Os(biim)Os(pap)_2]^{2+}$ show almost identical voltammetric responses in the range 0 to −2.5 V at a glassy-carbon working electrode. The first four waves appear as two pairs[10,27] (two closely spaced responses) and the fifth is a two electron-transfer process. The first reduction of the ruthenium dimer occurs at −0.33 V and that for the osmium congener at −0.28 V. Theoretically, eight-electron reduction is expected in a complex containing four pap ligands. However, in practice, six ligand reductions are observed. We believe that two more lie beyond the accessible potential range. The heterodinuclear complex $[(pap)_2Ru(biim)Os(pap)_2]^{2+}$ shows a similar pattern of reductive waves. This indicates that the ligand-based reductions are very little affected by the change of metal from ruthenium to osmium. The situation was completely different in the two asymmetric complexes containing two different terminal ligands, $[(pap)_2Ru(biim)Ru(bpy)_2]^{2+}$ and $[(pap)_2Os(biim)Ru(bpy)_2]^{2+}$ where well separated responses were observed. The azo ligand, pap, being a better π acceptor, is reduced first before the reduction of bpy starts.

Experimental

Materials

The starting complexes $M(pap)_2X_2$ (M = Ru or Os, X = Cl or Br), $[Ru(bpy)_2Cl_2]$,[28] $[Ru(pap)_2(OH_2)_2][ClO_4]_2{\cdot}H_2O$[9] and $[Ru(pap)_2(CH_3CN)_2][ClO_4]_2$[9] were prepared by the literature methods. The synthesis of biimidazole[29] and its reaction with silver were reported earlier.[30] Solvents and chemicals used for syntheses were of analytical grade. The supporting electrolyte tetraethylammonium perchlorate and solvents for electrochemical work were obtained as before.[8] **CAUTION**: perchlorate salts of metal complexes are generally explosive. Although no detonation tendencies have been observed, care is advised and handling of only small quantities recommended.

Physical measurements

A Shimadzu UV 2100 UV/VIS spectrophotometer was used to record electronic spectra. The IR spectra was recorded with a Perkin-Elmer 783 spectrophotometer, ^1H NMR spectra in CD_3CN with a Bruker Avance DPX 300 spectrophotometer; $SiMe_4$ was used as internal standard. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C, H, N). Electrochemical measurements were performed under a dry nitrogen atmosphere on a PAR model 370-4 electrochemistry system as described earlier.[31] All potentials reported in this work are referenced to the saturated calomel electrode (SCE) and are uncorrected for junction contribution. The pH measurements were made with a μ-pH System 361 Systronics pH meter, standardised with buffers 7.0 and 9.2. A 50% water–1,4-dioxane buffer mixture was employed because of the limited solubility of the complexes in pure aqueous solution. Electrical conductivities were measured by using a Systronics Direct Reading Conductivity meter 304. The p*K* values were determined by pH-metric titration as described before.[11,32,33]

Syntheses of complexes

[Ag(H$_2$biim)]NO$_3$. To a boiling ethanolic suspension of H$_2$biim (0.197 g, 1.47 mmol) was added AgNO$_3$ (0.25 g, 1.47 mmol) and refluxed for 1 h during which the solution became straw yellow. It was then concentrated to one-third of its initial volume and kept in a refrigerator overnight. Off-white crystals were filtered off and washed with a small volume of cold water. Yield: 95% (Found: C, 23.38; H, 2.10; N, 23.29. Calc. for $C_6H_6AgN_5O_3$: C, 23.68; H, 1.97; N, 23.02%).

The monomeric complexes were synthesized by following the silver(I)-assisted transmetallation route. Details are given for one representative case.

[Ru(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$. The complex [RuCl$_2$(pap)$_2$] (0.142 g, 0.263 mmol) and [Ag(H$_2$biim)]NO$_3$ (0.160 g, 0.536 mmol) were refluxed for 1 h in methanol–water (3 : 1 v/v, 70 cm^3). The solution changed from blue to pink. The cooled mixture was filtered to remove precipitated AgCl. The pink filtrate was then evaporated under reduced pressure to remove methanol, filtered and further concentrated to 15 cm^3, to which was added a saturated aqueous solution (2 cm^3) of sodium perchlorate containing 0.1 M perchloric acid. The reddish pink precipitate of [Ru(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$, thus obtained, was filtered off and recrystallised from dichloromethane–diethyl ether. Yield: 92% (Found: C, 41.60; H, 3.12; N, 17.11. Calc. for $C_{28}H_{24}Cl_2N_{10}O_8Ru$: C, 42.00; H, 3.00; N, 17.49%). $\Lambda_M = 260\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in CH$_3$CN).

[Os(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$·2H$_2$O. This brownish red complex was synthesized by an analogous procedure, starting from [OsBr$_2$(pap)$_2$] instead of [RuCl$_2$(pap)$_2$]. Yield: 75% (Found: C, 36.00; H, 2.90; N, 15.00. Calc. for $C_{28}H_{28}Cl_2N_{10}O_{10}Os$: C, 36.31; H, 3.02; N, 15.13%). $\Lambda_M = 270\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in CH$_3$CN).

[Ru(bpy)$_2$(H$_2$biim)][ClO$_4$]$_2$·H$_2$O. Synthesized by following a similar procedure to that described for its pap analogue. Yield: 90%.

[M(pap)$_2$(Hbiim)]ClO$_4$·H$_2$O (M = Ru or Os). The compound, [Ru(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$ (0.1 g, 0.125 mmol) was dissolved in aqueous acetonitrile (10 cm^3). The solution was raised to pH 5.5 by addition of dilute aqueous NaOH. It became violet. On addition of a saturated aqueous solution (0.5 cm^3) of sodium perchlorate the desired crystalline compound was deposited. It was filtered off and dried in vacuum over P$_4$O$_{10}$. Yield: 90% (Found: C, 46.27; H, 3.41; N, 19.27. Calc. for $C_{28}H_{25}ClN_{10}O_5Ru$: C, 46.82; H, 3.48; N, 19.50%). $\Lambda_M = 120\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in CH$_3$CN). The osmium analogue was obtained similarly in 82% yield (Found: C, 41.40; H, 3.02; N, 17.48. Calc. for $C_{28}H_{25}ClN_{10}O_5Os$: C, 41.65; H, 3.09; N, 17.35%). $\Lambda_M = 160\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in CH$_3$CN).

[M(pap)$_2$(biim)]·2H$_2$O (M = Ru or Os). These complexes were prepared using a similar procedure. For example, in the synthesis of [Ru(pap)$_2$(biim)]·2H$_2$O, triethylamine (0.05 g, 0.495 mmol) was added to a methanolic solution (25 cm^3) of [Ru(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$ (0.1 g, 0.125 mmol). The reddish pink solution immediately became intense blue-violet. After being refluxed for 30 min, the solution was concentrated to one-third of its initial volume and diethyl ether added. The precipitate was immediately filtered off and dried in vacuum. Yield 85% (Found: C, 52.16; H, 3.98; N, 21.65. Calc. for $C_{28}H_{26}N_{10}O_2Ru$: C, 52.90; H, 4.09; N, 22.04%). The osmium analogue [Os(pap)$_2$(biim)]·2H$_2$O was obtained similarly in 80% yield (Found: C, 46.25; H, 3.48; N, 19.76. Calc. for $C_{28}H_{26}N_{10}O_2Os$: C, 46.39; H, 3.59; N, 19.33%).

[{Ru(pap)$_2$}$_2$(biim)][ClO$_4$]$_2$·3H$_2$O. The complex [Ru(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$ (0.1 g, 0.125 mmol) was dissolved in acetonitrile (30 cm^3) and triethylamine (0.03 g, 0.297 mmol) was added which produced an intense blue-violet solution. To it [Ru(pap)$_2$(CH$_3$CN)$_2$][ClO$_4$]$_2$ (0.093 g, 0.124 mmol) was added and the mixture heated to reflux under N$_2$ for 6 h. The solution changed to brown-violet. It was concentrated to one-third of its initial volume and a solid mass was precipitated on addition of diethyl ether. The precipitate was redissolved in the minimum volume of dichloromethane and subjected to column chromatography on neutral alumina (1 × 10 cm). A red-violet band was eluted with dichloromethane–acetonitrile (3 : 1). The solvent was evaporated to dryness under vacuum and recrystallised from dichloromethane–diethyl ether. Yield: 58% (Found: C, 45.72; H, 3.55; N, 16.54. Calc. for $C_{50}H_{46}Cl_2N_{16}O_{11}Ru_2$: C, 45.48; H, 3.48; N, 16.97%). $\Lambda_M = 260\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in CH$_3$CN).

[(pap)$_2$Ru(biim)Os(pap)$_2$][ClO$_4$]$_2$·2H$_2$O. Using [OsBr$_2$(pap)$_2$] in place of [Ru(pap)$_2$(CH$_3$CN)$_2$][ClO$_4$]$_2$ and following the above-mentioned procedure a pink compound was isolated. Yield: 45% (Found: C, 43.23; H, 3.53; N, 16.02. Calc. for $C_{50}H_{44}Cl_2N_{16}O_{10}OsRu$: C, 43.15; H, 3.16; N, 16.11%). $\Lambda_M = 240\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in CH$_3$CN).

[(pap)$_2$Ru(biim)Ru(bpy)$_2$][ClO$_4$]$_2$·3H$_2$O. Following the same procedure and using [Ru(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$ and [Ru(bpy)$_2$(CH$_3$CN)$_2$]$^{2+}$ in 1 : 1 molar proportion, a brownish red compound was isolated. Yield: 60% (Found: C, 45.76; H, 3.63; N, 15.45. Calc. for $C_{48}H_{44}Cl_2N_{14}O_{11}Ru_2$: C, 45.52; H, 3.47; N, 15.49%). $\Lambda_M = 270\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in CH$_3$CN).

[{Os(pap)$_2$}$_2$(biim)][ClO$_4$]$_2$·2H$_2$O. The complex [Os(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$·2H$_2$O (0.1 g, 0.108 mmol) was dissolved in acetonitrile (30 cm^3) and triethylamine (0.025 g, 0.247 mmol) was added which produced a pinkish brown colour. To it [OsBr$_2$(pap)$_2$] (0.077 g, 0.107 mmol) was added and the mixture heated to reflux for 8 h under N$_2$. The solution became brown. It was concentrated to one-third of its initial volume and diethyl ether added. The precipitate was dissolved in the minimum volume of dichloromethane and subjected to column chromatography on neutral alumina (1 × 10 cm). A brown band was eluted with dichloromethane–acetonitrile (2 : 1). The compound was obtained on evaporation to dryness under vacuum and recrystallised from acetonitrile–water. Yield: 40% (Found: C, 40.79; H, 3.05; N, 15.45. Calc. for $C_{50}H_{44}Cl_2N_{16}O_{10}Os_2$: C, 40.55; H, 2.97; N, 15.14%). $\Lambda_M = 230\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in CH$_3$CN).

[(pap)$_2$Os(biim)Ru(bpy)$_2$][ClO$_4$]$_2$·3H$_2$O. This brown compound was synthesized following a similar procedure using [Os(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$·2H$_2$O and [Ru(bpy)$_2$(CH$_3$CN)$_2$]$^{2+}$ in 1 : 1 molar proportions. Yield: 52%. (Found: C, 42.75; H, 3.10; N, 14.73. Calc. for $C_{48}H_{44}Cl_2N_{14}O_{11}OsRu$: C, 42.53; H, 3.24; N, 14.47%). $\Lambda_M = 260\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in CH$_3$CN).

Crystallography

Diffraction measurements were carried out at 25 °C on a Nonius CAD-4 fully automated four-circle diffractometer. The unit-cell dimensions are listed in Table 4. All data reduction and structure refinements were performed using the NRCVAX package.[34] The structures were solved by the Patterson method. Absorption corrections were made with the NRCVAX package of programs. Hydrogen atoms were placed at calculated positions.

Single crystals of [Ru(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$·3CH$_2$Cl$_2$ were grown at room temperature by slow diffusion of toluene into

Table 4 Crystallographic data and refinement results for [Ru(pap)$_2$(H$_2$biim)][ClO$_4$]$_2$·3CH$_2$Cl$_2$ **1** and [{Ru(bpy)$_2$}$_2$(biim)][ClO$_4$]$_2$ **2**

	1	**2**
Formula	$C_{31}H_{30}Cl_8N_{10}O_8Ru$	$C_{46}H_{36}Cl_2N_{12}O_8Ru_2$
M	1055.75	1157.90
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnna*	*C*2/*c*
a/Å	15.3913(19)	22.300(5)
b/Å	12.611(6)	14.6141(18)
c/Å	21.571(4)	17.028(3)
β/°		121.177(17)
U/Å^3	4186.9(22)	4747.8(15)
D_c/g cm^{-3}	1.665	1.620
Measured reflections	3682	4178
Observed reflections [$I > 2\sigma(I)$]	1565	1874
Transmission factors (maximum, minimum)	0.975, 1.000	0.958, 1.000
μ/cm^{-1}	5.438	9.552
Crystal size/mm	0.40 × 0.45 × 0.75	0.13 × 0.13 × 0.13
R, *R′*	0.083, 0.089	0.044, 0.040
Goodness of fit	1.70	1.23

Details in common: $Z = 4$; λ(Mo-Kα) 0.7107 Å.

a dichloromethane solution of the compound. The crystals contain three molecules of CH$_2$Cl$_2$ as solvent of crystallisation. The cation is located at the crystallographic two-fold axis; only half of the cation occupies the asymmetric unit. The perchlorate is located at a general position; there is no crystallographic symmetry present in the anion. All three CH$_2$Cl$_2$ are located at two-fold axes, two being disordered. The unit cell was determined and refined using setting angles of 25 reflections, with 2θ angles in the range 15.44 to 24.0°. Data were collected by θ–2θ scans with $2\theta_{max} = 50°$.

Single crystals of [(bpy)$_2$Ru(biim)Ru(bpy)$_2$][ClO$_4$]$_2$ were obtained similarly. The asymmetric unit consists of half the molecule which generates the dinuclear complex through a crystallographic inversion centre located at the midpoint of the C1–C1 bond. The unit cell was determined and refined using setting angles of 25 reflections, with 2θ angles in the range 15.16 to 22.46°. Data were collected as above.

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