Chemistry of Ruthenium. Part 10.† Triazene 1-Oxide Complexes of Bis(2,2′-bipyridine)ruthenium-(II) and -(III). Synthesis, Spectra, and Electrochemistry

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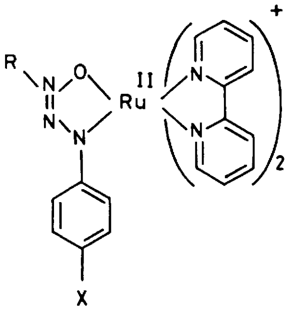
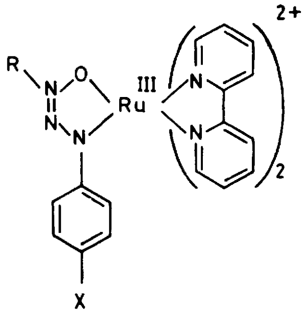
Mixed ruthenium complexes of type $[Ru(bipy)_2L]ClO_4\cdot H_2O$ derived from 2,2′-bipyridine (bipy) and triazene 1-oxides, $RN(O)=N-NH-C_6H_4X$-*p* (HL: R = Et or Ph; X = Me, H, Cl, CO_2Et, or NO_2) are described. In solution they display two quasi-reversible reductions due to electron transfer to co-ordinated bipy units. The $Ru^{III}-Ru^{II}$ couple occurs in the range 0.16—0.44 V *versus* s.c.e. The formal potential of this couple is linearly related to the Hammett constant of substituent X. The low-spin ruthenium(III) analogue, $[Ru(bipy)_2L]^{2+}$, is furnished by both coulometric and chemical oxidations. The energy of the ligand-to-metal charge-transfer band of $[Ru(bipy)_2L]^{2+}$ correlates linearly with the $Ru^{III}-Ru^{II}$ formal potential.

In an earlier paper[1] we demonstrated that the triazene 1-oxide ligand system, $RN(O)=N-NH-C_6H_4X$-*p* (HL: R = Et or Ph; X = Me, H, Cl, CO_2Et, or NO_2), binds to trivalent ruthenium affording the crystalline low-spin tris-chelates, $[RuL_3]$. These undergo electrochemical reduction to the ruthenium(II) analogues, $[RuL_3]^-$. The latter complexes are however unstable even on the cyclic voltammetric time-scale and no proper characterisation has therefore been possible. The HL system appears to be particularly suited for stabilising the higher oxidation states of ruthenium. In contrast to $[RuL_3]^-$ the ruthenium(IV) cation, $[RuL_3]^+$ is readily formed both chemically and electrochemically and is stable enough to be isolated[2] as salts. The present work originated from our search for stable Ru^{II}-L species. One strategy has been to bind both L and a coligand which is a recognised stabiliser of ruthenium(II). An obvious coligand of this type is 2,2′-bipyridine (bipy). We now describe a group of stable cations of type $[Ru^{II}(bipy)_2L]^+$ (1), isolated as perchlorates. Their redox stability is examined electrochemically and chemically. The ruthenium(III) counterpart $[Ru^{III}(bipy)_2L]^{2+}$ (2), has also been found to be stable enough for isolation and characterisation. Two types of $E_{298}^0(Ru^{III}-Ru^{II})$ correlations are investigated: the correlation with Hammett constants of substituent X and the correlation with ligand ⟶ metal charge-transfer transition energies of $[Ru^{III}(bipy)_2L]^{2+}$. The various ligands used (L^1—L^{10}) and the ruthenium complexes [(1a)—(1j); (2a)—(2j)] studied are shown opposite. The co-ordination sphere in all complexes is of type RuN_5O.



(1)



(2)

R	X	L	Complex
Et	Me	L^1	(1a), (2a)
Et	H	L^2	(1b), (2b)
Et	Cl	L^3	(1c), (2c)
Et	CO_2Et	L^4	(1d), (2d)
Et	NO_2	L^5	(1e), (2e)
Ph	Me	L^6	(1f), (2f)
Ph	H	L^7	(1g), (2g)
Ph	Cl	L^8	(1h), (2h)
Ph	CO_2Et	L^9	(1i), (2i)
Ph	NO_2	L^{10}	(1j), (2j)

Results and Discussion

Synthesis and Spectra of (1).—The synthesis of $[Ru^{II}(bipy)_2L]^+$ was achieved by two different routes: (*a*) the decarbonation[3] of *cis*-$[Ru(bipy)_2(CO_3)]$ with two equivalents of HL in ethanol [reaction (i)] and (*b*) the Ag^+-assisted halide displacement[4] from *cis*-$[Ru(bipy)_2Cl_2]$ in ethanol and subsequent reaction of the bis(ethanol) complex[5,6] with the conjugate base (HL + NaOH or K_2CO_3) of HL [reaction (ii)]. The syntheses were carried out at room temperature (*ca.* 300 K) in air. The complexes were recovered as brown diamagnetic crystalline perchlorate monohydrate salts, $[Ru(bipy)_2L]ClO_4\cdot H_2O$. These are highly soluble in polar organic solvents but only partly so in water. In solution they show the expected 1 : 1 electrolytic behaviour (Table 1). Analytical data are given in Table 1.

$$[Ru(bipy)_2(CO_3)] + HL \longrightarrow [Ru(bipy)_2L]^+ + HCO_3^- \quad \text{(i)}$$

$$[Ru(bipy)_2(EtOH)_2]^{2+} + L^- \longrightarrow [Ru(bipy)_2L]^+ \quad \text{(ii)}$$

The i.r. spectra display the stretching (3 400—3 500 cm^{-1}, broad and strong) and bending (1 620—1 630 cm^{-1}, broad and weak) vibrations of H_2O and ionic perchlorate (1 060—1 090 cm^{-1}, broad and strong; 610—615 cm^{-1}, sharp and strong). A strong and sharp band in the region 1 580—1 600 cm^{-1} is assigned to ν(C=C) + ν(C=N). The complexes (1d) and (1i) show strong unco-ordinated carbonyl stretches at 1 690 and 1 710 cm^{-1} respectively. The expected vibrations due to 2,2′-bipyridine[7] and triazine 1-oxides[1,8] [$\nu(N_3)$ in the region 1 390—1 495 cm^{-1} and ν(NO) in the region 1 180—1 210 cm^{-1}] are systematically present in all the complexes and are therefore not specifically reported here.

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† Part 9, A. R. Chakravarty and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1983, 961.

Table 1. Microanalytical, molar conductivity, and spectroscopic data of $[Ru^{II}(bipy)_2L]ClO_4{\cdot}H_2O$

Complex	Analysis [a] (%) C	H	N	Conductivity data [b,c] Λ_M/Ω^{-1} cm^2 mol^{-1}	Electronic spectral data [b,d] λ/nm (ε/dm^3 mol^{-1} cm^{-1})
(1a)	49.3 (49.1)	4.2 (4.2)	13.6 (13.8)	169	606 (2 400), 506 (6 000), 448 (sh) (6 400), 408 (sh) (8 100), 380 (sh) (8 700), 342 (11 200), 293 (45 300), 242 (37 800), 218 (37 700)
(1b)	48.7 (48.4)	4.1 (4.0)	14.0 (14.1)	155	600 (2 500), 506 (6 100), 440 (sh) (6 500), 404 (sh) (7 900), 380 (8 300), 344 (9 000), 295 (45 100), 246 (23 700), 214 (23 800)
(1c)	46.4 (46.1)	3.7 (3.7)	13.7 (13.4)	152	600 (3 000), 500 (7 000), 440 (sh) (8 600), 406 (10 000), 380 (sh) (9 600), 346 (10 300), 294 (50 500), 246 (25 200), 214 (26 800)
(1d)	49.1 (48.5)	4.2 (4.2)	12.9 (12.8)	160	600 (sh) (2 900), 500 (sh) (8 200), 444 (13 200), 416 (sh) (11 100), 342 (9 900), 294 (56 500), 244 (22 300), 212 (23 700)
(1e)	45.6 (45.4)	3.7 (3.7)	15.3 (15.1)	163	560 (sh) (10 800), 502 (16 700), 334 (16 700), 294 (51 000), 244 (25 000), 214 (25 300)
(1f)	52.6 (52.3)	3.9 (4.0)	13.1 (13.0)	156	640 (sh) (2 400), 480 (12 800), 452 (sh) (11 900), 380 (sh) (9 300), 322 (sh) (15 600), 294 (52 500), 244 (27 200), 212 (27 700)
(1g)	52.0 (51.7)	3.8 (3.8)	13.5 (13.2)	134	616 (sh) (2 200), 480 (10 300), 448 (sh) (9 500), 322 (sh) (14 400), 294 (57 000), 244 (24 600), 214 (24 900)
(1h)	49.0 (49.4)	3.7 (3.5)	12.3 (12.6)	153	618 (sh) (2 700), 480 (13 900), 446 (sh) (12 300), 320 (sh) (17 800), 294 (58 400), 242 (29 500), 212 (29 900)
(1i)	51.5 (51.6)	4.1 (3.9)	11.7 (12.0)	155	640 (sh) (2 400), 490 (15 400), 444 (sh) (12 200), 326 (23 000), 296 (57 200), 242 (30 000), 210 (28 300)
(1j)	48.6 (48.8)	3.5 (3.4)	14.3 (14.2)	142	548 (7 600), 490 (7 900), 354 (16 000), 294 (33 200), 240 (20 200), 214 (21 800)

[a] Calculated values are in parentheses. [b] In acetonitrile. [c] Molar conductivity at 298 K. [d] (sh) = shoulder.

Electronic spectral data for (1) in acetonitrile solution are shown in Table 1 and Figure 1. For the majority of complexes three allowed bands occur in the visible region (*ca.* 450, *ca.* 500, and *ca.* 600 nm) (Table 1). These are believed to represent metal-to-ligand charge-transfer (m.l.c.t.) transitions as is common [9,10] in ruthenium complexes of unsaturated ligands.

Electrochemistry.—The redox activity of the complexes was studied in all cases by cyclic voltammetry on the positive (up to +2.0 V) side of a saturated calomel electrode (s.c.e.) in acetonitrile solution (0.1 mol dm^{-3} $[NEt_4][ClO_4]$, 298 K) using a platinum working electrode. Two representative chelates were also examined on the negative (down to −2.4 V) side using a glassy carbon electrode. The results are collected in Table 2. All potentials are referred to s.c.e.

Table 2. Cyclic voltammetric data [a] of $[Ru(bipy)_2L]ClO_4{\cdot}H_2O$ in acetonitrile at 298 K

Complex	Ru^{III}–Ru^{II} couple [b] E_{298}^0/V	ΔE_p/mV	Ru^{III} or L oxidation [b] E_{pa}/V	Ligand reduction [c] $-E_{298}^0$/V (ΔE_p/mV)
(1a)	0.16	68	1.40	1.57 (100); 1.83 (120)
(1b)	0.22	70	1.63	*d*
(1c)	0.25	80	1.54	*d*
(1d)	0.28	65	1.58	*d*
(1e)	0.36	70	1.62	*d*
(1f)	0.25	80	1.42	*d*
(1g)	0.29	70	1.54	1.56 (140); 1.79 (90)
(1h)	0.32	60	1.48	*d*
(1i)	0.41	75	1.56	*d*
(1j)	0.44	80	*d*	*d*

[a] Supporting electrolyte $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}); all potentials are referenced to s.c.e.; $E_{298}^0 = 0.5(E_{pc} + E_{pa})$; E_{pc} and E_{pa} are cathodic and anodic peak potentials respectively; scan rate is 50 mV s^{-1}. [b] Platinum electrode. [c] Glassy carbon electrode. [d] Not examined.

The Ruthenium(III)-*Ruthenium*(II) *Couple.*—All the complexes display a cyclic response with characteristic anodic (E_{pa}) and cathodic (E_{pc}) peak potentials in the range 0.16—0.44 V due to the Ru^{III}–Ru^{II} couple [equation (iii)]. Figure 2 shows the cyclic voltammogram of complex (1a). The E_{298}^0

$$[Ru^{III}(bipy)_2L]^{2+} + e^- \rightleftharpoons [Ru^{II}(bipy)_2L]^+ \quad \text{(iii)}$$

values calculated from the average of the peak potentials for the oxidation and reduction waves are recorded in Table 2.

The peak-to-peak separation (ΔE_p) ranges between 70 and 80 mV at a scan rate of 50 mV s^{-1}. The anodic and cathodic peak heights are equal and vary as the square root of the scan rate. The Ru^{III}–Ru^{II} couple is evidently reversible to quasi-reversible in nature. Constant potential coulometric experiments (see below) confirmed the one-electron character of the electrode in reaction (iii).

Search for Ruthenium(IV)-*Ruthenium*(III) *Couple.*—In $[RuL_3]$ the Ru^{III}–Ru^{II} and Ru^{IV}–Ru^{III} couples are separated by *ca.* 1.4 V.[1] We therefore considered the possibility of observing the Ru^{IV}–Ru^{III} couple for the present complexes near 1.6 V. An irreversible (no significant response on scan reversal in cyclic voltammetry) anodic response is indeed observed for the complexes in this region (Figure 2, Table 2). This response

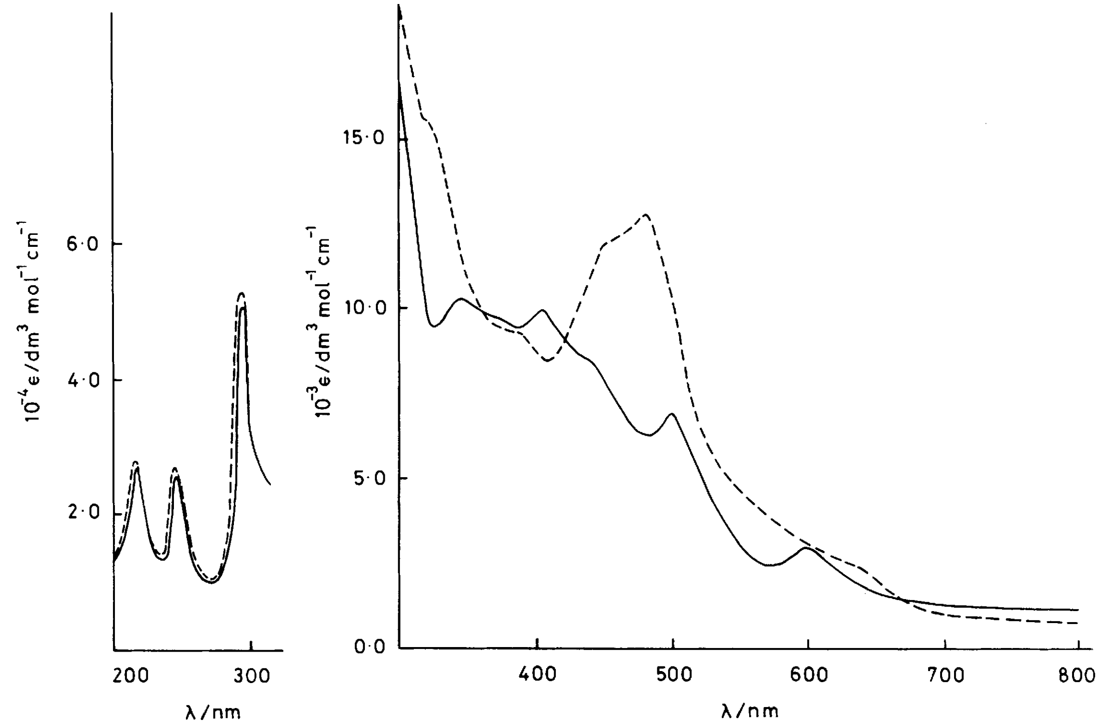

Figure 1. Electronic spectra of $[Ru(bipy)_2L^3]ClO_4{\cdot}H_2O$ (——) and $[Ru(bipy)_2L^6]ClO_4{\cdot}H_2O$ (— — —) in acetonitrile

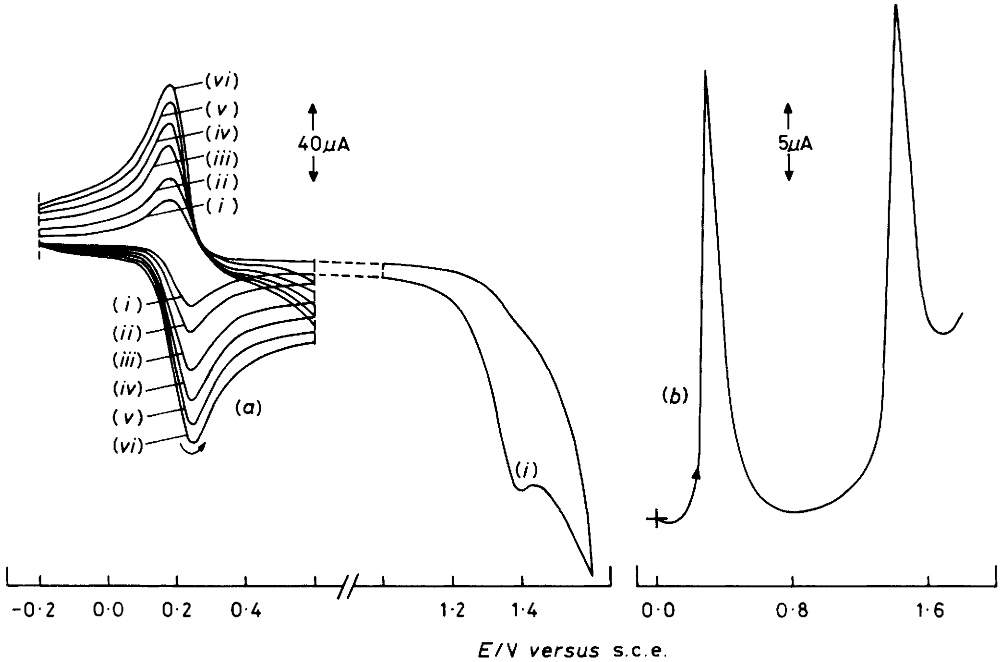

Figure 2. (a) Cyclic voltammograms of $[Ru(bipy)_2L^1]ClO_4{\cdot}H_2O$ (0.76 mol dm^{-3}) at different scan rates of (i) 50, (ii) 100, (iii) 200, (iv) 300, (v) 400, and (vi) 500 mV s^{-1}; the region above 1.0 V is shown only in the case (i). (b) Differential pulse voltammogram of $[Ru(bipy)_2L^8]ClO_4{\cdot}H_2O$ (1.40 mol dm^{-3}) at scan rate 20 mV s^{-1} and modulation amplitude 25 mV. In both (a) and (b) acetonitrile (0.1 mol dm^{-3} $[NEt_4][ClO_4]$) is the solvent and platinum is the working electrode

overlies the sharp rise in current due to solvent cut-off. However, its one-electron stoicheiometry is identifiable by comparison with the Ru^{III}–Ru^{II} couple with the help of differential pulse voltammetry (Figure 2). While the response [equation (iv)] could be due to $Ru^{III} \longrightarrow Ru^{IV}$ oxidation, the possibility that it is due to ligand (L) oxidation cannot be excluded. This complication arises since $[RuL_3]$ also displays [11] one or more similar response(s) in the same region.

$$[Ru(bipy)_2L]^{2+} \longrightarrow [Ru(bipy)_2L]^{3+} + e^- \qquad (iv)$$

Reduction of Co-ordinated bipy.—The electron transfer behaviour of (1a) and (1g) was also studied on the negative side of s.c.e. Both display two successive quasi-reversible couples at *ca.* −1.6 and *ca.* −1.8 V (Table 2, Figure 3). The $[RuL_3]$ complexes *do not* show [1,11] this type of behaviour in this potential region. We assign the couples to bipy reduction. It is well documented [12-15] that bipy is a potential carrier of electron transfer, each bipy successively accepting two electrons in one electrochemically accessible lowest unoccupied molecular orbital. Hence in $[Ru(bipy)_2L]^+$ four successive reductions are expected. The observed two reductions can be represented by equations (v) and (vi). The remaining two reductions are not observed due to solvent cut-off (Figure 3).

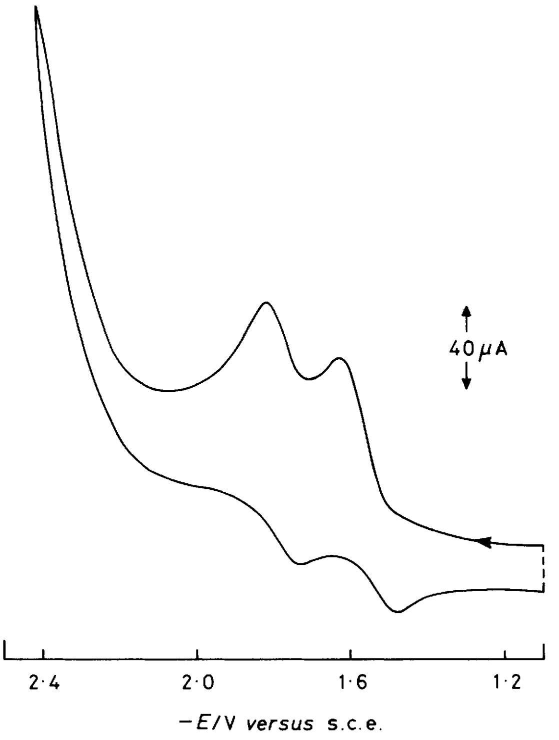

Figure 3. Cyclic voltammogram of $[Ru(bipy)_2L^7]ClO_4{\cdot}H_2O$ (0.65 mol dm^{-3}) in acetonitrile (0.1 mol dm^{-3} $[NEt_4][ClO_4]$) at a glassy carbon electrode (scan rate 50 mV s^{-1}) at negative potentials

$$[Ru^{II}(bipy)_2L]^+ + e^- \rightleftharpoons [Ru^{II}(bipy)(bipy^{\cdot -})L] \tag{v}$$

$$[Ru^{II}(bipy)(bipy^{\cdot -})L] + e^- \rightleftharpoons [Ru^{II}(bipy^{\cdot -})_2L]^- \tag{vi}$$

Due to the presence of positive charge on the metal ion the formal potential for the first reduction of bipy in equation (v) is uniformly more positive than that of free [13] bipy (−2.17 V). The present results can be compared with [14] the first two ligand reduction couples of $[Ru(bipy)_3]^{2+}$ (E_{298}^0, −1.31 and −1.47 V).

Characterisation of $[Ru^{III}(bipy)_2L]^{2+}$ (2).—On coulometric oxidation (0.50—0.75 V) (Table 3) of $[Ru^{II}(bipy)_2L]^+$, the colour of the solution changes from brown to green and the resulting solution displays a cyclic voltammetric response identical to that of (1). The green solution can be reconverted quantitatively to the brown solution by coulometry at −0.1 V (Table 3). The green solutions are thus quite stable.

Two representative species, *viz.* (2a) and (2g), were also synthesised by chemical oxidation of the corresponding ruthenium(II) complex with Ce^{4+}. These were isolated as crystalline perchlorate salts of composition $[Ru^{III}(bipy)_2L][ClO_4]_2{\cdot}H_2O$. Their characterisation data are given in Table 4. The magnetic moments correspond to low-spin ($S = \frac{1}{2}$) character (Table 4). They are uniformly 1 : 2 electrolytic in acetonitrile solution (Table 4).

The electronic spectra of oxidised species, (2), produced

Table 3. Coulometric oxidation of $[Ru^{II}(bipy)_2L]^+$ and electronic spectra of $[Ru^{III}(bipy)_2L]^{2+}$ in acetonitrile [a]

	Coulometric data [b]			
Complex	Applied potential/V	Q	n	Electronic spectral data [c] λ/nm (ε/dm^3 mol^{-1} cm^{-1})
(1a) [d]	0.55	0.91	0.95	680 (4 300), 372 (8 200), 318 (sh) (16 800), 280 (37 800), 246 (30 300), 214 (37 000)
(1b)	0.55	0.91 [e]	0.93	652 (4 500), 480 (sh) (1 300), 364 (8 200), 316 (sh) (16 300), 274 (36 600), 246 (33 000), 210 (27 400)
(1c)	0.50	0.86	0.90	662 (3 750), 364 (7 100), 316 (sh) (16 000), 278 (29 100), 252 (sh) (21 200), 214 (26 500)
(1d)	0.55	0.83	1.03	652 (4 200), 360 (8 600), 316 (sh) (19 400), 280 (39 200), 248 (sh) (31 300), 212 (38 000)
(1e)	0.70	1.02	1.07	640 (5 200), 550 (sh) (2 100), 358 (14 700), 316 (sh) (30 900), 284 (41 200), 250 (36 300), 212 (40 000)
(1f)	0.55	0.99	1.02	734 (5 000), 452 (sh) (7 100), 380 (11 900), 316 (sh) (25 000), 284 (37 400), 246 (32 400), 214 (43 000)
(1g) [d]	0.55	0.89	0.92	716 (3 840), 500 (3 000), 384 (9 950), 316 (sh) (22 100), 286 (34 750), 246 (28 900), 216 (30 000)
(1h)	0.60	1.00	1.04	726 (4 800), 448 (sh) (6 700), 376 (sh) (12 300), 316 (sh) (26 100), 286 (40 500), 244 (35 700), 214 (47 600)
(1i)	0.75	0.93	0.96	716 (4 100), 570 (sh) (2 000), 358 (11 850), 314 (sh) (30 400), 284 (43 200), 242 (32 000), 214 (46 000)
(1j)	0.75	1.04	1.08	704 (5 900), 564 (sh) (3 400), 392 (sh) (8 050), 336 (10 300), 316 (16 400), 290 (19 700), 246 (18 750), 216 (19 700)

[a] Supporting electrolyte, $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}). [b] 0.01 mmol. solute in MeCN (30 cm^3) containing $[NEt_4][ClO_4]$ (300 mg). Coulometric data are averages of at least three independent measurements; Q is the coulomb count at the end of electrolysis; $n = Q/Q'$ where Q' is the calculated coulomb count for $1e^-$ transfer. [c] Spectral data are taken immediately after electrolysis. [d] The corresponding oxidised species are isolated chemically (see text). [e] On reduction at −0.1 V, Q is 0.90.

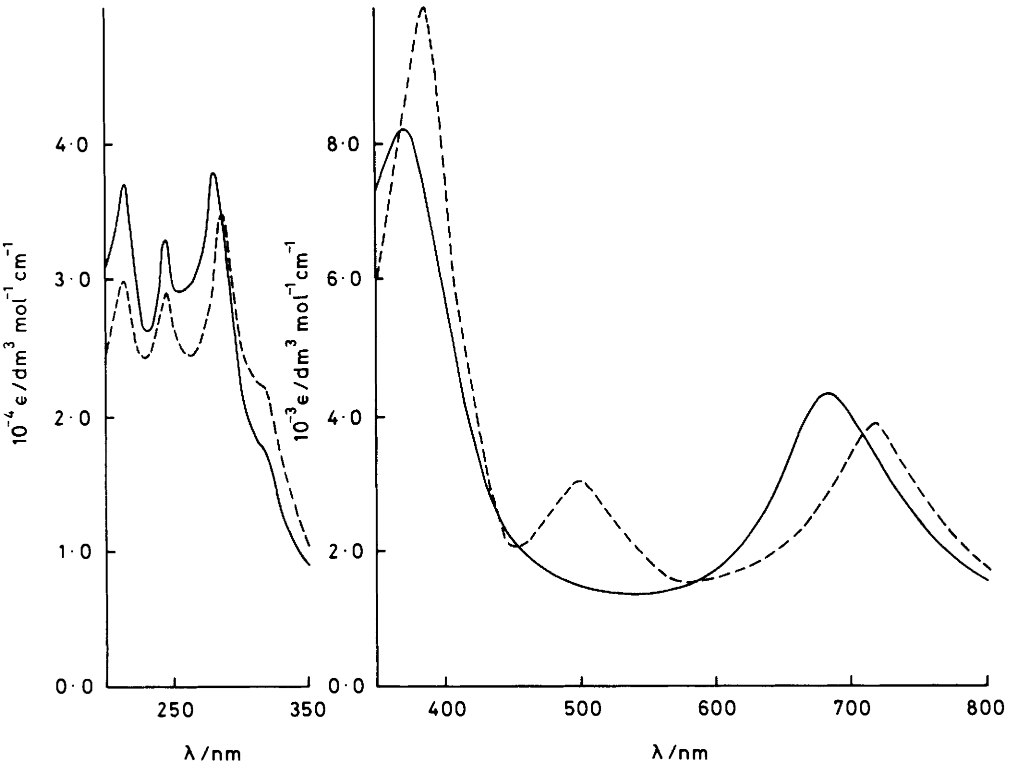

Figure 4. Electronic spectra of $[Ru(bipy)_2L^1][ClO_4]_2·H_2O$ (——) and $[Ru(bipy)_2L^7][ClO_4]_2·H_2O$ (— — —) in acetonitrile

Table 4. Microanalytical, molar conductivity, and magnetic data for $[Ru^{III}(bipy)_2L][ClO_4]_2·H_2O$

Complex	Analysis [a] (%) C	H	N	Λ_M [b]/ Ω^{-1} cm^2 mol^{-1}	$\mu_{eff.}$[c]/B.M.
(2a)	42.9 (43.1)	3.5 (3.7)	11.9 (12.1)	222	2.23
(2g)	45.2 (45.6)	3.0 (3.3)	11.2 (11.6)	212	1.87

[a] Calculated values are in parentheses. [b] Molar conductivity in acetonitrile at 298 K. [c] B.M. = 0.927 × 10^{-23} A m^2.

coulometrically as well as those isolated chemically were recorded in the range 200—800 nm (Table 3, Figure 4). An allowed band in the region 600—750 nm (Table 3) is the most characteristic feature. Significantly, $[RuL_3]$ is also green due to a band of similar intensity in the same region. The band is assigned L(π) ⟶ Ru(t_2) as in the case [1] of $[RuL_3]$.

The possibility that the band is actually a bipy(π) ⟶ Ru(t_2) transition is excluded from intensity and energy considerations. Such transitions are usually weak [5,16] (ε *ca.* 100—400 dm^3 mol^{-1} cm^{-1}). Also, the energy of such a transition increases with decrease in the *Dq* value of ligands associated with bipy: $[Ru(bipy)_2Cl_2]^+$, 520; [16] $[Ru(bipy)_3]^{3+}$, 676; [16] and $[Ru(bipy)_2\{Ph_2P(CH_2)_3PPh_2\}]^{3+}$, 779 nm.[5] Since the *Dq* value of L is relatively low,[17] the bipy ⟶ Ru band should occur at energies considerably higher than those of the bands under consideration.

Correlations.—There is a remarkable shift of the Ru^{III}–Ru^{II} couple to higher potential in going from $[RuL_3]$ (−0.6 to −1.2 V) [1] to $[Ru(bipy)_2L]^+$ (0.16 to 0.44 V). Even then the potentials of $[Ru^{II}(bipy)_2L]^+$ are quite low among complexes of $[Ru^{II}(bipy)_2]^{2+}$. In acetylacetonatobis(2,2′-bipyridine)ruthenium(II) the potential is 0.51 V [11] and in bis(2,2′-bipyridine)(isonitrosoketonato)ruthenium(II) complexes, which like (1) have the RuN_5O co-ordination sphere, $E_{298}{}^0$ is near 0.9 V.[18] The lowest potential reported to date is that of *cis*-$[Ru(bipy)_2Cl_2]$ (0.30 V).[3] The potentials of complexes (1a)—(1d), (1f), and (1g) are *lower* than this. Clearly, the triazene 1-oxides have a special stabilising effect on the ruthenium(III) state.

Within the group of complexes (1), the $E_{298}{}^0$ values of the Ru^{III}–Ru^{II} couple are sensitive to R and X. The values increase with decreasing electron-releasing power of the substituents. The Hammett equation (vii) is applicable (Figure 5). Here $\Delta E_{298}{}^0$ is the shift in potential from the standard

$$\Delta E_{298}{}^0 = \sigma\rho \qquad \text{(vii)}$$

(X = H), σ is the Hammett substituent constant, and ρ is the reaction constant. The R = Et complexes have lower $E_{298}{}^0$ values than those of R = Ph complexes (Figure 5) reflecting the higher electron-releasing power of the Et group. The observed ρ values (Figure 5) compare well with those for the M^{III}–M^{II} couple in $[ML_3]$ (M = Fe^{III}, Co^{III}, or Ru^{III}) systems.[1,19] In this connection we note that a linear $E_{298}{}^0$ *versus* σ correlation among complexes of the $[Ru(bipy)_2]^{2+}$ moiety is so far reported only in the case of $[Ru(bipy)_2Cl\{N(O)C_6H_4X\text{-}p\}]PF_6$.[20]

Interestingly, $E_{298}{}^0$ values of the Ru^{III}–Ru^{II} couple also correlate linearly with the ν(l.m.c.t.) value of the corresponding $[Ru^{III}(bipy)_2L]^{2+}$ complex in most cases (Figure 6). This correlation, which is also a correlation of ν(l.m.c.t.) with σ, reflects that the presence of an electron-withdrawing group destabilises the ligand cation level while stabilising the reduced metal level.

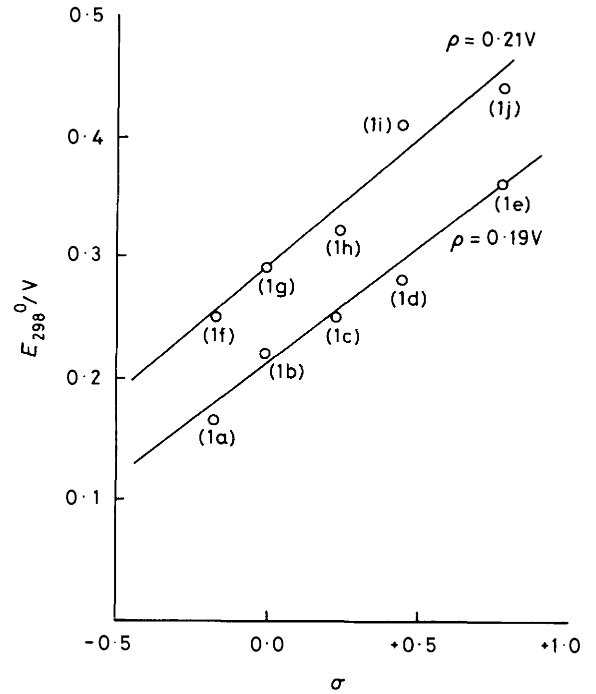

Figure 5. Least-squares plots of $E_{298}{}^0$ *versus* σ for two groups of $[Ru(bipy)_2L]ClO_4{\cdot}H_2O$ [R = Et, (1a)—(1e); R = Ph, (1f)—(1j)]

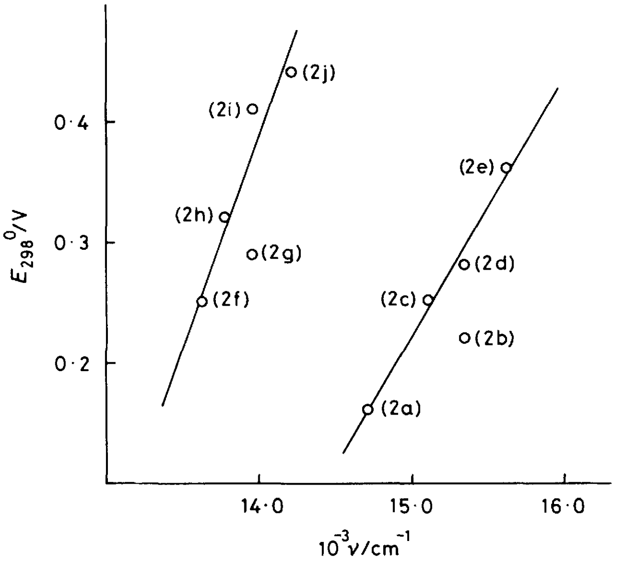

Figure 6. Correlation of $E_{298}{}^0$ (Ru^{III}–Ru^{II}) with l.m.c.t. band energy in $[Ru^{III}(bipy)_2L]^{2+}$. The data points for (2b) and (2g) are not utilised in the least-squares lines

Conclusions

Our goal of obtaining stable triazene 1-oxide complexes of ruthenium(II) is achieved. The complexes (1) display the Ru^{III}–Ru^{II} couple subject to the systematic shift of formal potentials under the influence of substituent X. There is a parallel shift of the energy of the l.m.c.t. band of (2). The Ru^{III}–Ru^{II} potentials of several complexes are lower than the lowest values so far known for $[Ru(bipy)_2]^{3+}$ complexes. The redox potentials of the present complexes as well as those of[1,19] $[RuL_3]$, $[FeL_3]$, $[CoL_3]$, and $[CuL_2]$ show that the triazene 1-oxides are ideally suited for binding metal ions in higher oxidation states.

Experimental

Starting Materials.—*cis*-$[Ru(bipy)_2Cl_2]{\cdot}2H_2O$ and *cis*-$[Ru(bipy)_2(CO_3)]{\cdot}2H_2O$ were prepared by using published[3,4] procedures. The triazene 1-oxides (HL^1—HL^{10}) were prepared according to the literature.[1,19] Electrochemically pure acetonitrile and tetraethylammonium perchlorate were obtained as before.[1,19]

Physical Measurements.—Solution electrical conductivity, u.v.-visible, and i.r. spectra were recorded using a Philips PR 9500 bridge, Pye Unicam SP8-150, and Beckman IR 20A spectrometers respectively. Magnetic susceptibility was measured in a Princeton Applied Research (PAR) 155 vibrating sample magnetometer. In general electrochemical measurements were made using a PAR 370-4 electrochemistry system, Precision X-Y recorder, and PAR 377A cell system as before.[1,19] Differential pulse voltammetric measurements required the PAR 174A polarographic analyser. Measurements were carried out under a dry and purified nitrogen atmosphere. Planar Beckman model 39273 platinum inlay or PAR G0021 glassy carbon working electrode, platinum wire auxiliary electrode, and a saturated aqueous calomel reference electrode (s.c.e.) were used in the three-electrode measurements. A platinum wire-gauge working electrode was used in coulometric experiments. All electrochemical data were obtained at 298 K and are uncorrected for junction potentials.

The following σ values for the *para* substituent were used:[1,19] Me, −0.17; H, 0.00; Cl, +0.23; CO_2Et, +0.45; NO_2, +0.78.

Syntheses of Compounds.—Bis(2,2′-bipyridine)(triazene 1-oxidato)ruthenium(II) perchlorate monohydrate, $[Ru^{II}(bipy)_2L]ClO_4{\cdot}H_2O$ complexes were prepared by using either of the two general procedures.

Bis(2,2′-*bipyridine*)(1-*ethyl*-3-p-*tolyltriazene* 1-*oxidato*)-*ruthenium*(II) *perchlorate monohydrate*, $[Ru(bipy)_2L^1]ClO_4{\cdot}H_2O$. To a solution of *cis*-$[Ru(bipy)_2(CO_3)]{\cdot}2H_2O$ (120 mg, 0.24 mmol) in ethanol (20 cm^3), HL^1 (0.56 mmol) was added. The mixture was stirred at 298 K over a period of 2.5 h under magnetic stirring. The initial violet solution gradually turned brown. To the reaction mixture *ca.* 5 cm^3 of a saturated aqueous solution of $NaClO_4$ were added. It was then kept in air for slow evaporation. The brown precipitate was collected by filtration and washed with ice-cold water and then with diethyl ether. The compound thus obtained was dried *in vacuo* over P_4O_{10}. The dried precipitate was dissolved in a small volume of acetonitrile and was subjected to chromatography on a silica gel (60—120 mesh) column (30 × 1 cm). A brown band was eluted with a 1 : 1 benzene–acetonitrile mixture. Crystals were obtained by complete evaporation of the brown eluate at room temperature (yield *ca.* 60%).

Bis(2,2′-*bipyridine*)(1-*ethyl*-3-*phenyltriazene* 1-*oxidato*)-*ruthenium*(II) *perchlorate monohydrate*, $[Ru(bipy)_2L^2]ClO_4{\cdot}H_2O$. A mixture of *cis*-$[Ru(bipy)_2Cl_2]{\cdot}2H_2O$ (100 mg, 0.19 mmol) and $AgClO_4{\cdot}H_2O$ (100 mg, 0.44 mmol) in ethanol was heated to reflux for 1 h. The initial violet solution turned orange-red. It was then cooled and filtered through a G-4 Gooch sintered-glass funnel. To the filtrate [bis(ethanol) species] HL^2 (50 mg, 0.30 mmol) and 2 cm^3 of 0.01 mol dm^{-3} NaOH solution were added dropwise. The mixture was stirred for 2 h at 298 K magnetically. The precipitated complex was filtered off, washed with ice-cold water, and then with diethyl ether. The compound thus obtained was dried *in vacuo* over P_4O_{10}. Purification of the product was achieved as described in the above method (yield *ca.* 65%).

Bis(2,2′-*bipyridine*)(1-*phenyl*-3-*phenyltriazene* 1-*oxidato*)-*ruthenium*(III) *diperchlorate monohydrate*, $[Ru^{III}(bipy)_2L^7][ClO_4]_2\cdot H_2O$. $[Ru^{II}(bipy)_2L^7]ClO_4\cdot H_2O$ (150 mg, 0.2 mmol) was dissolved in acetonitrile (20 cm^3). To this, $[NH_4]_4[Ce(SO_4)_4]\cdot 2H_2O$ (150 mg, 0.24 mmol) solution (20 cm^3 water +0.2 cm^3 concentrated sulphuric acid) was added. The mixture was stirred magnetically for 2 h. A saturated aqueous solution of $NaClO_4$ (*ca.* 5 cm^3) was then added. On slow evaporation shiny green crystals resulted. These were collected by filtration and washed thoroughly with ice-cold water. The product was dried *in vacuo* over P_4O_{10} (yield *ca.* 60%).

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