Chemistry of Ruthenium. Part 6.† Bis(2,2′-bipyridine)(isonitrosoketonato)ruthenium(II) Perchlorate Monohydrate. Synthesis, Spectra, and Electrochemistry

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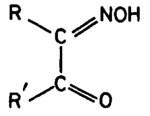
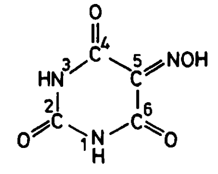
New ruthenium(II) complexes of type $[Ru(bipy)_2(L)](ClO_4)\cdot H_2O$ are formed by the reaction of $[Ru(bipy)_2Cl_2]$ with HL and in one case by chelative nitrosation of ketones with $[Ru(bipy)_2(NO)Cl]^{2+}$ [HL = RC(=NOH)C(=O)R′, bipy = 2,2′-bipyridine]. These display metal-to-ligand charge-transfer transitions in the visible region (450—490 nm), a reversible Ru^{III}–Ru^{II} couple near 0.9 V *versus* s.c.e., and one or more ligand reduction couples below −1 V. Trends of $E_{298}°$ values for a group of related complexes are rationalised. The oxidised complex $[Ru(bipy)_2(L)]^{2+}$ is unstable and has a ligand-to-metal charge-transfer transition near 600 nm. Its energy correlates linearly with $E_{298}°$ of the Ru^{III}–Ru^{II} couple. In acetonitrile, $[Ru(bipy)_2(L)]^+$ can be protonated to $[Ru(bipy)_2(HL)]^{2+}$. The Ru^{III}–Ru^{II} couple of the protonated complex is at a higher (~1.0 V) potential than that of $[Ru(bipy)_2(L)]^+$. The chemistries of $[Ru(bipy)_2(L)]^+$ and $[RuX_2(HL)(L)]$ are compared.

In Part 4 of this series, it was shown [1] that isonitrosoketones (HL) (hydroxyiminoketone) chelate the *trans*-dihalogenoruthenium(III) moiety furnishing low-spin species of type $[Ru^{III}X_2(HL)(L)]$ (X = Cl or Br), in which the internally hydrogen bonded (HL)(L) fragment spans grossly planar four-co-ordination. These complexes act as oxidising agents of moderate strengths. In the present work we examine [2] the chelation of isonitrosoketones to the *cis*-bis(2,2′-bipyridine)-ruthenium(II) moiety, $[Ru(bipy)_2]^{2+}$. The pertinent isonitrosoketones are HL^1–HL^8 (see below). The complexes synthesised are of the type $[Ru^{II}(bipy)_2(L)](ClO_4)\cdot H_2O$. The two synthetic approaches used are: (*i*) the direct reaction of HL with *cis*-$[Ru(bipy)_2Cl_2]$ and (*ii*) the addition of the co-ordinated nitrosyl of *cis*-$[Ru(bipy)_2(NO)Cl]^{2+}$ to a ketone. The spectra, electron transfer behaviour, and proton transfer character of the complexes are compared with those of $[RuX_2(HL)(L)]$.



R	R′	
H	Ph	HL^1
Me	Ph	HL^2
Ph	Ph	HL^3
Me	Me	HL^4
Et	Me	HL^5
Ph	Me	HL^6
$CONH_2$	NH_2	HL^7



HL^8 (1)

Experimental

Starting Materials.—Hydroxyiminopropiophenone (HL^2), α-benzil oxime (HL^3), biacetyl oxime (HL^4), hydroxyiminopropyl methyl ketone (HL^5), and α-hydroxyimino-α-phenylacetone (HL^6) were obtained as before.[3] Hydroxyiminoacetophenone (HL^1) was prepared in the same way as HL^2. The synthesis of hydroxyiminomalonamide (HL^7) and violuric acid (HL^8) were as reported.[4] Published procedures [5] were used to make *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ and $[Ru(bipy)_2(NO)Cl](ClO_4)_2$. Electrochemically pure acetonitrile and tetraethylammonium perchlorate were prepared as before.[3] For protonation experiments, standard perchloric acid solution (~0.01 mol dm^{-3} in CH_3CN) was used.[1]

Physical Measurements.—Solution electrical conductivity in MeCN, u.v.–visible, and i.r. spectra were recorded using Philips PR 9500 bridge, Pye Unicam SP8-150, and Beckman IR 20A spectrometers respectively. Electrochemical measurements were made using a Princeton Applied Research (PAR) 370-4 electrochemistry system, Precision X-Y recorder, and PAR 377A cell system as before.[1] Differential pulse polarographic measurements required the PAR 174A polarographic analyser. Planar Beckman model 39273 platinum inlay working electrode, platinum wire auxiliary electrode, and a saturated calomel reference electrode (s.c.e.) were used in three-electrode measurements and 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.

Determination of Electrode Area, Diffusion Coefficients, and Heterogeneous Rate Constants.—The area of the electrode (0.184 ± 0.001 cm^2) was determined chronoamperometrically.[6] The diffusion coefficient (*D*) was calculated using the Cottrell equation.[7] The heterogeneous rate constant, $k_{s,h}$, was obtained from equation (i) taken in conjunction with the

$$\psi = (D_{ox.}/D_{red.})^{\alpha}\, k_{s,h}/(\pi n F v D_{ox.}/RT)^{\frac{1}{2}} \qquad \text{(i)}$$

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† Part 5 is ref. 35.

Table 1. Heterogeneous electron-transfer rate constants [a] of $[Ru(bipy)_2(L^3)](ClO_4)\cdot H_2O$ in acetonitrile [b,c]

$10^5 D$/cm^2 s^{-1}	v/V s^{-1}	ΔE_p/mV	ψ	$\psi v^{\frac{1}{2}}$	$10^2 k_{s,h}$/cm s^{-1}
1.19	0.10	87	0.855	0.270	1.03
	0.20	100	0.570	0.255	0.97
	0.30	112	0.420	0.266	1.01
	0.40	120	0.360	0.279	1.06

[a] At 298 K. [b] Electrolyte 0.1 mol dm^{-3} $NEt_4^+ClO_4^-$. [c] Concentration of the complex ~1 × 10^{-3} mol dm^{-3}.

Table 2. Analytical data for the complexes [a]

Compound	Formula	Found (%)			Required (%)		
		C	H	N	C	H	N
(2a) $[Ru(bipy)_2(L^1)](ClO_4)\cdot H_2O$ [b]	$C_{28}H_{24}ClN_5O_7Ru$	50.2	3.3	10.5	49.5	3.5	10.3
(2b) $[Ru(bipy)_2(L^2)](ClO_4)\cdot H_2O$	$C_{29}H_{26}ClN_5O_7Ru$	50.4	4.0	9.8	50.3	3.8	10.1
(2c) $[Ru(bipy)_2(L^3)](ClO_4)\cdot H_2O$	$C_{34}H_{28}ClN_5O_7Ru$	54.4	3.5	9.2	54.1	3.7	9.3
(2d) $[Ru(bipy)_2(L^4)](ClO_4)\cdot H_2O$	$C_{24}H_{24}ClN_5O_7Ru$	45.8	3.8	11.2	45.7	3.8	11.1
(2e) $[Ru(bipy)_2(L^5)](ClO_4)\cdot H_2O$	$C_{25}H_{26}ClN_5O_7Ru$	46.1	3.9	10.5	45.8	3.8	10.7
(2f) $[Ru(bipy)_2(L^6)](ClO_4)\cdot H_2O$ [c]	$C_{29}H_{26}ClN_5O_7Ru$	50.0	3.4	10.0	50.3	3.8	10.1
(2g) $[Ru(bipy)_2(L^7)](ClO_4)\cdot H_2O$ [d]	$C_{23}H_{22}ClN_7O_8Ru$	41.6	3.3	14.4	41.8	3.2	14.8
(2h) $[Ru(bipy)_2(L^8)](ClO_4)\cdot H_2O$	$C_{24}H_{20}ClN_7O_9Ru$	41.6	2.7	14.0	42.0	2.9	14.3

[a] All results refer to the complexes prepared by reacting *cis*-$[Ru(bipy)_2Cl_2]$ with HL. [b] Analytical data found for (2a) prepared by the NO transfer reaction are: C, 50.1; H, 3.4; N, 10.0%. [c] Chlorine: found, 5.4; calc. 5.1%. [d] Chlorine: found, 5.6; calc. 5.4%.

working curve of Nicholson.[8] The transmission coefficient, α, was set at 0.5. The diffusion coefficient of the oxidised species ($D_{ox.}$) is assumed to be equal to that of the reduced species ($D_{red.}$) *i.e.* $D_{ox.} = D_{red.} = D$. Definitions of other symbols in equation (i) are: Ψ, a kinetic variable n, number of electrons transferred; F, Faraday; v, scan rate; R, gas constant; and T, temperature in K. Representative data are in Table 1.

Coulometric Oxidation of $[Ru(bipy)_2(L)](ClO_4)\cdot H_2O$.—A solution of the sample (*ca.* 10 mg) in 25 cm^3 acetonitrile (0.2 mol dm^{-3} in $NEt_4^+ClO_4^-$) was electrolysed at 1.2 V *versus* s.c.e. using a platinum gauge working electrode to constant coulomb count. The ratio of this count to the calculated count is equal to n (see Table 6). The oxidised solution was suitably diluted for spectrophotometric measurements.

Synthesis of Compounds.—Bis(2,2′-bipyridine)(isonitrosoketonato)ruthenium(II) perchlorate monohydrate, $[Ru(bipy)_2(L)](ClO_4)\cdot H_2O$, complexes were prepared by using the following general procedure.

To a solution of $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (0.25 mmol) in a 1 : 1 methanol–water mixture (20 cm^3), HL (0.25 mmol) (in the particular case of HL^7, the ammonium salt) was added. The mixture was heated to reflux for 2 h. The initial violet solution gradually turned orange-red. It was then cooled and filtered. To the filtrate concentrated sodium perchlorate solution (*ca.* 5 cm^3) (in water) was added dropwise. Crystals usually started depositing immediately. The mass was cooled in a refrigerator to 273 K for 6 h. The 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}. Recrystallisation was achieved from a 2 : 1 methanol-water mixture containing a few drops of concentrated aqueous sodium perchlorate solution (yield, 40—60%). Crystals were orange-red to brownish black in colour. Analytical data of $[Ru(bipy)_2(L)](ClO_4)\cdot H_2O$ complexes are given in Table 2.

Preparation of $[Ru(bipy)_2(L^1)](ClO_4)\cdot H_2O$ ***by*** **NO** ***transfer reaction.*** The compound $[Ru(bipy)_2(NO)Cl](ClO_4)_2$ (100 mg, 0.13 mmol) was added to acetophenone (40 mg, 0.33 mmol) and sodium methoxide (20 mg, 0.37 mmol) in methanol (10 cm^3). The solution was heated to reflux for 8 h, cooled to room temperature (*ca.* 298 K), and filtered. To the filtrate concentrated aqueous sodium perchlorate (*ca.* 5 cm^3) was added followed by addition of water (20 cm^3). The solution was kept in air for slow evaporation and the precipitate thus obtained was washed with water and finally with diethyl ether. The compound was dried under vacuum over P_4O_{10}. The crude product was chromatographed on an alumina column (20 × 1 cm) in benzene solvent. The orange-red band of $[Ru(bipy)_2(L^1)](ClO_4)\cdot H_2O$ was eluted out using benzene–acetonitrile (1 : 1 v/v) as eluant. Yield *ca.* 20%.

Results and Discussion

Reaction of cis-$[Ru(bipy)_2Cl_2]$ *with* HL.—The nucleophilic displacement of halide ions from *cis*-$[Ru(bipy)_2Cl_2]$ by HL in hot aqueous methanol is of general applicability. It is very likely that the actual reaction [equation (ii)] is between $[Ru(bipy)_2(MeOH)Cl]^+$ and HL; the former being formed by the solvolysis[9] of $[Ru(bipy)_2Cl_2]$. The complex cation is

$$[Ru(bipy)_2(MeOH)Cl]^+ + HL \longrightarrow \underset{(2)}{[Ru(bipy)_2(L)]^+} \quad (ii)$$

isolated as a crystalline perchlorate, $[Ru(bipy)_2(L)](ClO_4)\cdot H_2O$. In course of the reaction (ii), HL is deprotonated. The acidity of HL is evidently much augmented *via* co-ordination to ruthenium(II). The complexes are uniformly diamagnetic and behave as 1 : 1 electrolytes[10] in acetonitrile solution (Table 3). All observations are in agreement with the tris chelate formulation (2).

Chelative Nitrosation by Co-ordinated Nitrosyl.—The synthesis of (2) has also been achieved in a limited way *via* electrophilic addition of co-ordinated nitrosyl to the activated α-methylene carbon of a ketone [equation (iii)]. Thus acetophenone furnishes $[Ru(bipy)_2(L^1)](ClO_4)\cdot H_2O$. A few cases of the nitrosation of activated organic compounds by ruthenium

Table 3. Spectral and conductivity data of $[Ru(bipy)_2(L)](ClO_4)\cdot H_2O$

Complex	I.r. data [a,b]/cm^{-1}		Λ_M [c]/Ω^{-1} cm^2 mol^{-1}	Electronic spectral data [d,e] λ/nm (ε/dm^3 mol^{-1} cm^{-1})
	ν(CO)	ν(NO)		
(2a) $[Ru(bipy)_2(L^1)](ClO_4)\cdot H_2O$	1 505	1 215	154	485 (17 200), 336 (16 200), 288 (59 400), 252 (sh), 244 (27 200), 216 (26 300)
(2b) $[Ru(bipy)_2(L^2)](ClO_4)\cdot H_2O$	1 500	1 235	135	482 (14 700), 332 (16 800), 289 (61 400), 252 (sh), 243 (38 100), 216 (33 100)
(2c) $[Ru(bipy)_2(L^3)](ClO_4)\cdot H_2O$	1 515	1 270	140	489 (17 700), 338 (sh) (13 000), 289 (46 000), 252 (sh), 242 (26 000), 218 (26 000)
(2d) $[Ru(bipy)_2(L^4)](ClO_4)\cdot H_2O$	1 515	1 285	179	466 (11 700), 400 (sh) (6 300), 312 (sh) (13 500), 290 (62 400), 252 (sh), 242 (24 600), 218 (22 300)
(2e) $[Ru(bipy)_2(L^5)](ClO_4)\cdot H_2O$	1 505	1 240	204	465 (11 000), 400 (sh), 320 (sh) (66 800), 252 (sh), 242 (26 800), 218 (24 900)
(2f) $[Ru(bipy)_2(L^6)](ClO_4)\cdot H_2O$	1 518	1 270	182	465 (11 900), 400 (sh), 320 (sh), 290 (53 400), 252 (sh), 242 (27 700), 218 (25 700)
(2g) $[Ru(bipy)_2(L^7)](ClO_4)\cdot H_2O$	1 528 [f]	1 320	166	455 (14 500), 396 (sh) (8 000), 289 (56 900), 252 (sh), 242 (24 900), 216 (21 300)
(2h) $[Ru(bipy)_2(L^8)](ClO_4)\cdot H_2O$	1 459 [g]	1 365	161	458 (16 300), 320 (sh), 290 (56 200), 252 (sh), 242 (26 200), 218 (27 500)

[a] KBr disc, 4 400—400 cm^{-1}. [b] ν(CO), medium; ν(NO), very strong. [c] Molar conductivity at 298 K. [d] In acetonitrile at 298 K. [e] (sh) = shoulder. [f] Unco-ordinated ν(CO) at 1 650 cm^{-1}. [g] Unco-ordinated ν(CO) at 1 730 (C^2=O) and 1 670 (C^4=O) cm^{-1} [see structure (1) in text].

$$[Ru(bipy)_2(NO)Cl]^{2+} + RCH_2C(=O)R' \xrightarrow{NaOMe} [Ru(bipy)_2\{RC(=NO)C(=O)R'\}]^+ \quad (iii)$$

co-ordinated nitrosyl group are well documented.[11–13] Bearing these in mind, a rationalisation of reaction (iii) is given in the Scheme. Following the formation of the new C–N bond, deprotonation and electron redistribution occur resulting in the nitrogen co-ordinated isonitroso function. The keto group subsequently displaces the halide ion nucleophilically to complete chelation. The yield of $[Ru(bipy)_2(L^1)]^+$ in reaction (iii) is poor. This was also the case when we tried several other ketones. The poor yield arises from the formation of product(s) * other than $[Ru(bipy)_2(L)]^+$ in the course of reaction between $[Ru(bipy)_2(NO)Cl]^{2+}$ and the $-CH_2C(=O)-$ function.

Reaction with a Proton.—Except in the case of $[Ru(bipy)_2(L^7)]^+$ and $[Ru(bipy)_2(L^8)]^+$, addition of $HClO_4$ to $[Ru(bipy)_2(L)]^+$ in acetonitrile brings about a reaction [equation (iv)]. The species (3) has distinctive electrochemical and spectral responses that are considered in a later section. We have not

$$\underset{(2)}{[Ru(bipy)_2(L)]^+} + HClO_4 \longrightarrow \underset{(3)}{[Ru(bipy)_2(HL)]^{2+}} + ClO_4^- \quad (iv)$$

been able to isolate the salts of (3) in the pure form. However, crystals of a related substance *viz.* $[Ru(bipy)_2(HA)](ClO_4)_2\cdot H_2O$ [HA = RC(=NOH)N=NR′ (R′ = aryl)] have been isolated.[14] In (3), protonation is believed to occur at the oximato function. In the case of $[Ru(bipy)_2(L^7)]^+$ and $[Ru(bipy)_2(L^8)]^+$, protonation of the oximato oxygen did not occur possibly due to the strong electron withdrawing effect of the amide function.

Spectra.—In the i.r., stretching (3 400—3 440 cm^{-1}, broad and strong) and bending (1 620—1 635 cm^{-1}, sharp and medium) vibrations of H_2O and ionic perchlorate bands (1 100—1 180, broad and strong; 620—635 cm^{-1}, sharp and strong) are present. A strong and sharp band in the region 1 590—1 610 cm^{-1} is assigned to ν(C=C) + ν(C=N). The L^7 and L^8 complexes also show strong ν(NH) in the region 3 250—3 600 cm^{-1} and unco-ordinated carbonyl stretches in the expected region (Table 3). The vibrations due to co-ordinated 2,2′-bipyridine [15] are systematically present in all complexes and will not be considered here any further.

Upon the complex formation, ν(CO) and ν(NO) of the co-ordinated $-C(=O)C(=NO)-$ moiety is considerably shifted to lower and higher frequencies (Table 3) respectively compared to the free ligand values [*e.g.* in HL^3 ν(CO) is at 1 645 and ν(NO) is at 1 005 cm^{-1}]. Similar shifts occur [1] in $[RuX^2_2(HL)(L)]$ (X = Cl or Br). Metal assisted electron delocalisation and other factors which could be responsible for this effect have been considered elsewhere.[1,3,13]

Electronic spectral data for (2) in acetonitrile solution are displayed in Table 3 and Figure 1. Bands occurring below 300 nm are probably localised on the ligand. An intense band occurs in the region 450—490 nm associated with a higher energy shoulder (300—400 nm). This band is assigned to $t_{2g}(Ru) \longrightarrow \pi^*$(ligand) a metal-to-ligand charge-transfer (m.l.c.t.) transition.[16–18] The m.l.c.t. band of (3) in CH_3CN solution is red shifted with respect to that of (2) (Table 4; Figure 1). Such a red shift is understandable in terms of the effect of protonation on the π* orbital and is documented [19,20] in other ruthenium complexes.

In complexes of $[Ru(bipy)_2]^{2+}$, the $t_{2g}(Ru) \longrightarrow \pi^*$(bipy) transition usually occurs in the region 450—490 nm.[9,18,21–25] On the other hand, $[Ru(L^8)_3]^-$ and $[Ru^{II}X_2(HL)(L)]^-$ display [13,26] allowed bands at 495 and 640 nm respectively due to the transition $t_{2g}(Ru) \longrightarrow \pi^*(L)$. The m.l.c.t. transition in (2) and (3) in the visible region could thus arise from excitation to a π* level of bipy or L^- and a specific assignment is difficult. The complexes (2) can be divided into three groups on the basis of the m.l.c.t. band energy: R′ = Ph (485 ± 1); Me (465 ± 1); and HN- (456 ± 2 nm). This R′ sensitivity does suggest that L orbitals are in some way involved in the charge transfer state.

The complexes do not exhibit any emission spectra in

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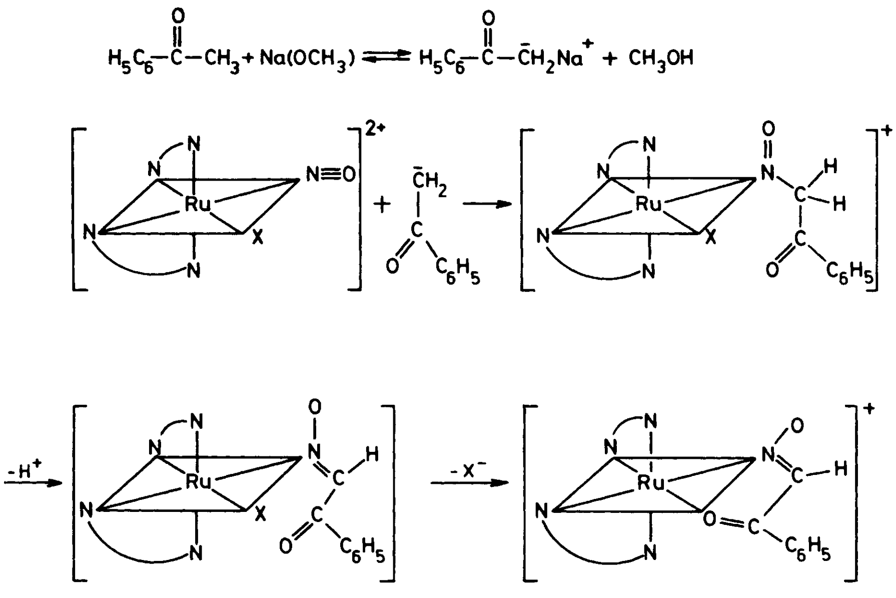
* Characterisation of these is in progress. I.r. data suggest that both co-ordinated bipy and isonitrosoketone are present in such product(s). We note that the poor yield of (2) is not due to oxidative C–C bond cleavage of the type observed in the reaction between $[Ru(NH_3)_5(NO)]^{3+}$ and the $-CH_2C(=O)-$ function (K. Schug and C. P. Guengerich, *J. Am. Chem. Soc.*, 1979, **101**, 235). The expected product of such cleavage is the nitrile adduct $[Ru(bipy)_2(NCR)Cl]^+$ or derivatives thereof (R. F. Jones and D. J. Cole-Hamilton, *Inorg. Chim. Acta Lett.*, 1981, **53**, L3). Such species could not be isolated from the reaction mixture.



(2)

Scheme.

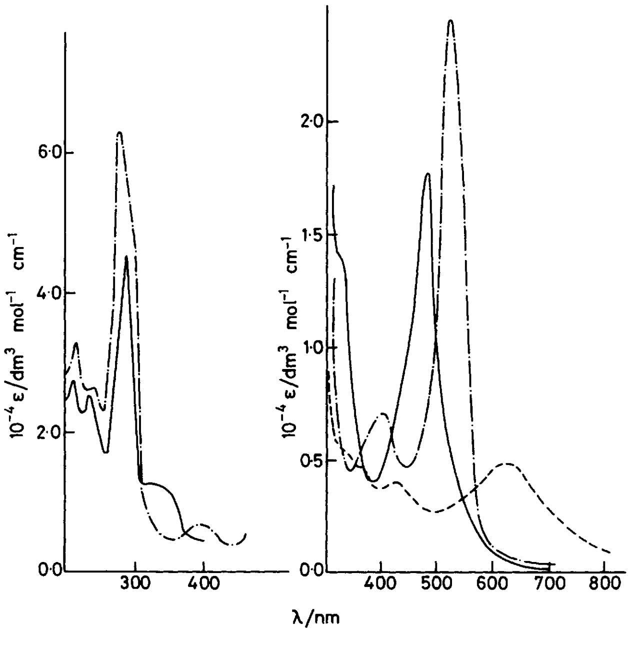


Figure 1. Electronic spectra of $[Ru(bipy)_2(L^3)]^+$ (——), $[Ru(bipy)_2(HL^3)]^{2+}$ (—.—), and $[Ru(bipy)_2(L^3)]^{2+}$ (- - -) in acetonitrile (conditions for generation of the protonated and the oxidised species are in Tables 3 and 5)

acetonitrile solution at room temperature. Low temperature work is in progress.

Metal Centred Redox Activity.—Variable scan cyclic voltammograms of the L^7 complex are shown in Figure 2, together with the differential pulse polarogram. Selected electrochemical data on (2) are in Table 5. All potentials are referenced to saturated calomel electrode (s.c.e.).

The cyclic response near 0.9 V in acetonitrile at platinum electrode has $i_{pa} = i_{pc}$, $iv^{\frac{1}{2}}$ = constant, while ΔE_p lies in the range 75—80 mV at $v \leqslant 50$ mV s^{-1} [*i*, current (μA); *E*,

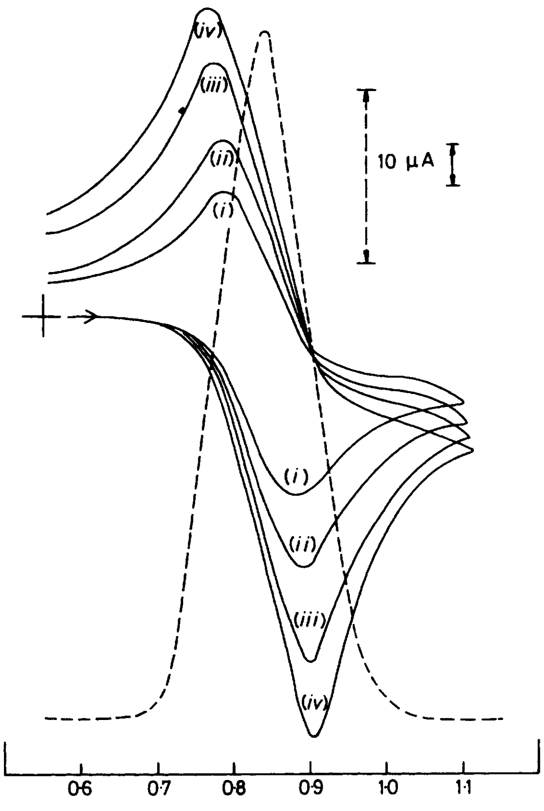


Figure 2. Cyclic voltammetric responses (——) of $[Ru(bipy)_2(L^7)]^+$ (1×10^{-3} mol dm^{-3}) in acetonitrile at scan rates (*v*) of 50 (*i*), 100 (*ii*), 200 (*iii*), and 300 mV s^{-1} (*iv*). Differential pulse polarographic response (- - -), of the same compound at *v* 1 mV s^{-1}; modulation amplitude, 25 mV (peak to peak); and pulse interval, 0.5 s

Table 4. Cyclic voltammetric and electronic spectral data [a] for $[Ru(bipy)_2(HL)]^{2+}$

Complex	Ru^{III}–Ru^{II} couple [b]		Electronic spectral data [c]
	$E_{298}°$/V	ΔE_p/mV	λ/nm (ε/dm³ mol⁻¹ cm⁻¹)
(3a) $[Ru(bipy)_2(HL^1)]^{2+}$	0.99	100	520 (16 400), 420 (4 950), 279 (44 100), 244 br
(3b) $[Ru(bipy)_2(HL^2)]^{2+}$	0.96	100	512 (18 350), 408 (6 400), 279 (56 400), 250 (3 100), 218 (25 300)
(3c) $[Ru(bipy)_2(HL^3)]^{2+}$	0.98	80	522 (24 300), 404 (7 050), 280 (63 300), 246 (sh), 218 (35 100)
(3d) $[Ru(bipy)_2(HL^4)]^{2+}$	1.03	100	474 (12 600), 416 (sh) (7 050), 280 (54 900), 244 (21 200), 219 (23 000)
(3e) $[Ru(bipy)_2(HL^5)]^{2+}$	1.01	100	477 (10 650), 416 (sh) (7 100), 280 (45 000), 246 (sh), 219 (18 300)
(3f) $[Ru(bipy)_2(HL^6)]^{2+}$	0.96	100	488 (12 650), 408 (sh) (6 700), 280 (47 300), 244 (22 700), 218 (25 300)

[a] $[Ru(bipy)_2(HL)]^{2+}$ species were obtained by protonation (with $HClO_4$) of $[Ru(bipy)_2(L)]^+$ in acetonitrile solution (0.1 mol dm⁻³ $NEt_4^+ClO_4^-$). [b] Scan rate = 50 mV s⁻¹. [c] br = broad; (sh) = shoulder.

Table 5. Electrochemical data [a] of $[Ru(bipy)_2(L)](ClO_4)\cdot H_2O$ at platinum electrode in acetonitrile at 298 K

Complex	$Ru^{III}Ru^{II}$ couple				Ligand reduction
	Formal potential		Rate data		
	E_{298}^0/V	ΔE_p/mV	$10^5 D$/cm² s⁻¹	$10^2 k_{s,h}$/cm s⁻¹	E_{298}^0/V (ΔE_p/mV)
(2a)	0.90	70	0.77	0.86	−1.44(75), −1.73 [b]
(2b)	0.83	70	1.14	0.91	−1.44,[b] −1.51(85), −1.75 [b]
(2c)	0.93	75	1.19	1.03	−1.64 [b]
(2d)	0.82	80	1.40	0.82	−1.54(80)
(2e)	0.85	70	1.38	1.07	−1.57 [b]
(2f)	0.84	75	1.08	0.74	−1.60 [b]
(2g)	0.83	80	1.28	0.56	−1.58 [b]
(2h)	1.05	85	0.96	0.44	

[a] Supporting electrolyte $NEt_4^+ClO_4^-$ (0.1 mol dm⁻³). [b] Cathodic peak potential (anodic response ill defined).

Table 6. Coulometric data [a] of $[Ru(bipy)_2(L)](ClO_4)\cdot H_2O$ (2) in acetonitrile and electronic spectral data of the oxidised solution containing $[Ru(bipy)_2(L)]^{2+}$ (4)

Complex	n [b]	Oxidized complex	Electronic spectral data [c] λ/nm (ε/dm³ mol⁻¹ cm⁻¹)
(2c)	0.95	(4c) [d]	625 (4 650), 435 (4 070), 390 (sh), 360 (sh), 292 (20 100)
(2d)	1.04	(4d)	550 (3 500), 365 (4 700), 291 (23 900)
(2e)	0.97	(4e)	555 (3 150), 375 (4 300)
(2f)	0.98	(4f)	568 (3 100), 390 (5 000), 364 (sh), 314 (sh), 280 (27 200)

[a] Potential set at 1.2 V in presence of supporting electrolyte $NEt_4^+ClO_4^-$ (0.1 mol dm⁻³). [b] n = Total number of electrons transferred in the oxidative electrolysis at constant potential = Q(found)/Q(calc.), where Q = coulomb. [c] (sh) = shoulder. [d] (4c) was obtained by coulometric oxidation of (2c). Similarly (4d), (4e), and (4f) were obtained from (2d), (2e), and (2f) respectively.

potential (V *versus* s.c.e.); v, scan rate (mV s⁻¹); ΔE_p, peak to peak separation (mV); subscripts p, c, and a, stand for peak, cathodic, and anodic respectively]. A nearly reversible one-electron process is indicated. In constant potential experiments (stirred solutions), substantial electrolysis occurred at potentials higher than E_{pa} while little current flowed below E_{pc}. Thus $[Ru(bipy)_2(L)]^+$ undergoes oxidation and not reduction. Constant potential coulometry performed in several cases (Table 6) confirmed the one-electron character of the electrode reaction [equation (v)]. The formal potential E_{298}^0 was calculated from equation (vi). At $v > 50$ mV s⁻¹, ΔE_p rapidly increased with scan rates and this made possible the calculation of the heterogeneous rate constant $k_{s,h}$ for the electron transfer process (v) (Tables 1 and 5).

$$\underset{(4)}{[Ru(bipy)_2(L)]^{2+}} + e^- \rightleftharpoons \underset{(2)}{[Ru(bipy)_2(L)]^+} \qquad (v)$$

$$E_{298}^0 = 0.5\,(E_{pa} + E_{pc}) \qquad (vi)$$

Effect of protonation. Addition of $HClO_4$ to $[Ru(bipy)_2(L)]^+$ in acetonitrile progressively diminishes the response due to couple (v). Simultaneously a new response appears at a potential higher than that of couple (v). The current due to couple (v) decreases in proportion to the mol ratio of $HClO_4$ to $[Ru(bipy)_2(L)]^+$ (Figure 3). When this ratio reaches 1 : 1, the original response is completely replaced by a new response of equal height. The new response is ascribed to the couple (vii).

$$[Ru(bipy)_2(HL)]^{3+} + e^- \rightleftharpoons \underset{(3)}{[Ru(bipy)_2(HL)]^{2+}} \qquad (vii)$$

At slow scan rates ($v \leqslant 50$), ΔE_p for the couple (vii) is ~100 mV. Formal potentials calculated from equation (vi) are

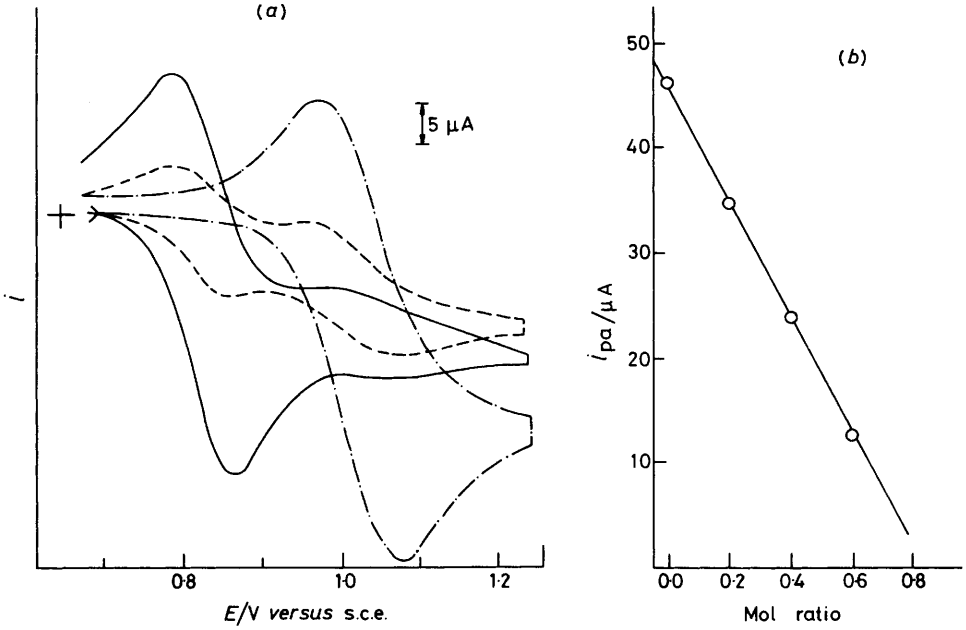


Figure 3. Effect of protonation on voltammetric response of $[Ru(bipy)_2(L^4)]^+$ in acetonitrile. (*a*) Cyclics at different $HClO_4$: complex mol ratios: 0.25 (——); 0.65 (- - -); and 1.00 (— . —). (*b*) Linear plot of anodic current with $HClO_4$: complex mol ratio

in Table 4. At higher scan rates $k_{s,h}$ could be determined. Representative results are: (3d; L = L^4) $D = 1.36 \times 10^{-5}$, $k_{s,h} = 0.32 \times 10^{-2}$ and (3e; L = L^5) $D = 1.26 \times 10^{-5}$ cm^2 s^{-1}, $k_{s,h} = 0.44 \times 10^{-2}$ cm s^{-1}. The reversibility quality of couple (vii) is poorer than the couple (v). The shift of $E_{298}{}^0$ towards higher potential in going from couple (v) to couple (vii) means that addition of a proton makes electron removal more difficult, as expected.[1,27]

Our attempt to study the redox chemistry of (3) in aqueous solution was vitiated by solvent interference (in H_2O, Pt electrodes can go [28] only to ~1 V). However, the formation of (3) in aqueous solution at low pH (<1.0) was indicated from the fact (Table 4) that the spectra of such solutions are close to those of (3) in acetonitrile. Above pH 1.0, the deprotonated species predominates in solution showing that (3) is a strong acid.

Correlations. The $E_{298}{}^0$ values of some representative complexes of $[Ru(bipy)_2]^{2+}$ in CH_3CN are as follows: $[Ru(bipy)_2Cl_2]$, 0.30;[22] $[Ru(bipy)_2(en)]^{2+}$, 0.96;[21] and $[Ru(bipy)_3]^{2+}$, 1.29 V [21] (en = $NH_2CH_2CH_2NH_2$). The redox potentials of $[Ru(bipy)_2(L)]^+$ and $[Ru(bipy)_2(HL)]^{2+}$ are close to that of $[Ru(bipy)_2(en)]^{2+}$ but are considerably less than that of $[Ru(bipy)_3]^{2+}$. In the redox sense, isonitrosoketones stabilise ruthenium(II) to a lesser extent than bipy. The value of $E_{298}{}^0$ for an electrode reaction depends on a number of free energy terms.[29] However, in related systems run in the same solvent, the gross role of specific factors can still be meaningfully explored. In the present case, the energy of the t_{2g} orbital is such a factor. This orbital is indirectly stabilised by metal-ligand σ-interaction. It is directly stabilised by an increase in π-interaction with the empty ligand π* level ($t_{2g} \longrightarrow \pi^*$). In going from $[Ru(bipy)_2Cl_2]$ to $[Ru(bipy)_2(L)]^+$ or $[Ru(bipy)_2(HL)]^{2+}$, Cl,Cl co-ordination is replaced by N,O co-ordination and the σ-effect alone is expected to make $E_{298}{}^0$ of the latter species more positive (more stable t_{2g} level). In addition the π-contribution which exists (i.r. data) in the latter species makes the $[Ru(bipy)_2(L)]^+$ potential even more positive. Consequently the potential comes close to the value of σ-*NN* co-ordination as in $[Ru(bipy)_2(en)]^{2+}$. In $[Ru(bipy)_3]^{2+}$ all co-ordinating atoms are N and the extent of π-interaction is considerable resulting in the high value of $E_{298}{}^0$. In a closely related group of complexes the correlation of $E_{298}{}^0$ with m.l.c.t. band energy has been considered.[18-20,22-24] Within the $[Ru(bipy)_2(L)]^+$ and $[Ru(bipy)_2(HL)]^{2+}$ series, the correlation is poor; the m.l.c.t. band energy spreads over a considerable range while $E_{298}{}^0$ changes relatively slightly.

The oxidised complex, $[Ru^{III}(bipy)_2(L)]^{2+}$ (4). The oxidised species are labile and attempts to isolate them in the crystalline state have not succeeded thus far. However, their spectra could be recorded using coulometrically oxidised solutions. Data are given in Table 6. An intense band appears in the region 550—600 nm. This is probably of l.m.c.t. ($\pi \longrightarrow t_{2g}$) origin.[1,9,30-32]

In $[Ru(bipy)_3]^{3+}$, $[Ru(bipy)_2Cl_2]^+$, $[Ru(bipy)_2(L')Cl]^{2+}$, and $[Ru(bipy)(L'-L')]^{3+}$ (L′ = tertiary phosphines; L′-L′ = chelating diphosphines), one or more l.m.c.t. transitions (π-orbital on bipy) occur [9,21,31] in the visible region. On the other hand, in $[RuX_2(HL)(L)]$ (X = Cl or Br) l.m.c.t. occurs [1] to the π-level of the (HL)(L) moiety. Thus there is an ambiguity about the identity of the π-level in the l.m.c.t. spectra of $[Ru(bipy)_2(L)]^{2+}$ (4).

For the group of $[Ru(bipy)_2]^{3+}$ complexes including $[Ru(bipy)_2(L)]^{2+}$ considered above, the l.m.c.t. band energy is found to vary approximately linearly with the $E_{298}{}^0$ of the Ru^{III}-Ru^{II} couple (Figure 4). As $E_{298}{}^0$ becomes more positive the energy of the l.m.c.t. band decreases and both are related to the progressive stabilisation of the t_{2g} level. Whereas excessive significance need not be attached to the linearity, the results do suggest that the visible transition in $[Ru(bipy)_2(L)]^{2+}$ is likely to have considerable π(bipy) $\longrightarrow t_{2g}$ character. The l.m.c.t. band of $[Ru(bipy)_2(L')Cl]^{2+}$ was earlier assigned [9] to Cl $\longrightarrow$ Ru. This is untenable on energy considerations.[33] The observed linear $E_{298}{}^0$-ν correlation shows that the transition actually involves the π-level of the bipy ligand.

Ligand reduction. Most of the complexes display one (or more) one-electron electrochemical response(s) in the region −1.54 to −1.75 V *versus* s.c.e. (Table 5). Thus the complexes can add one or more electrons in one or more steps which are quasi-reversible or irreversible. It is believed that the reductions involve the unsaturated organic ligand rather than the

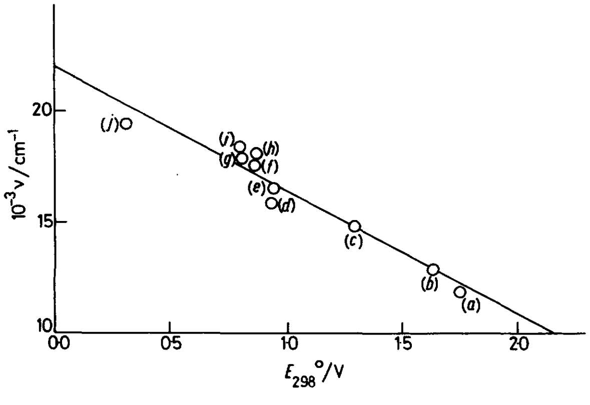
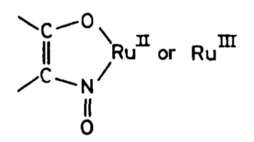


Figure 4. Correlation of $E_{298}{}^{\circ}(\text{Ru}^{\text{III}}\text{–Ru}^{\text{II}})$ with l.m.c.t. band energy in ruthenium(III) complexes: (*a*) $[\text{Ru(bipy)}_2(cis\text{-Ph}_2\text{PCH=CHPPh}_2)]^{3+}$ (ref. 9); (*b*) $[\text{Ru(bipy)}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]^{3+}$ (ref. 9); (*c*) $[\text{Ru(bipy)}_3]^{3+}$ (refs. 21, 31); (*d*) (4) L = L^3; (*e*) $[\text{Ru(bipy)}_2(\text{PPh}_3)\text{Cl}]^{2+}$ (ref. 9); (*f*) (4), L = L^6; (*g*) $[\text{Ru(bipy)}_2(\text{PBu}^n{}_3)\text{Cl}]^{2+}$ (ref. 9); (*h*) (4), L = L^5; (*i*) (4), L = L^4; and (*j*) $[\text{Ru(bipy)}_2\text{Cl}_2]^+$ (refs. 21, 31)



(5)

metal. Ruthenium complexes of such ligands generally undergo [1,9,25,34,35] reduction below −1.0 V.

Conclusions and Comparison with $[\text{RuX}_2(\text{HL})(\text{L})]$.—We conclude that $[\text{Ru(bipy)}_2(\text{L})]^+$ constitutes a group of stable ruthenium(II) complexes. The $E_{298}{}^0$ values of the $\text{Ru}^{\text{III}}\text{–Ru}^{\text{II}}$ couple follow the rational order: $[\text{Ru(bipy)}_2\text{Cl}_2] < [\text{Ru(bipy)}_2(\text{L})]^+ \approx [\text{Ru(bipy)}_2(\text{en})]^{2+} < [\text{Ru(bipy)}_3]^{2+}$. The ruthenium(III) complex $[\text{Ru(bipy)}_2(\text{L})]^{2+}$ is relatively unstable. In contrast $[\text{Ru}^{\text{III}}\text{X}_2(\text{HL})(\text{L})]$ is stable ($E_{298}{}^0$ ~0.5 V) while $[\text{Ru}^{\text{II}}\text{X}_2(\text{HL})(\text{L})]^-$ is unstable.[1] In both $[\text{Ru(bipy)}_2(\text{L})]^+$ and $[\text{RuX}_2(\text{HL})(\text{L})]$, the carbonyl bond order is shifted from free ligand values to lower frequencies. A sizable contribution from configuration (5) thus occurs quite generally in ruthenium complexes of isonitrosoketones. Another common feature is the occurrence of charge-transfer bands: m.l.c.t. (metal–ligand) in $[\text{Ru}^{\text{II}}(\text{bipy})_2(\text{L})]^+$ and $[\text{Ru}^{\text{II}}\text{X}_2(\text{HL})(\text{L})]^-$ and l.m.c.t. (ligand–metal) in $[\text{Ru}^{\text{III}}(\text{bipy})_2(\text{L})]^{2+}$ and $[\text{Ru}^{\text{III}}\text{X}_2(\text{HL})(\text{L})]$. The protonation of $[\text{Ru(bipy)}_2(\text{L})]^+$ to $[\text{Ru(bipy)}_2(\text{HL})]^{2+}$ merely shifts the $E_{298}{}^0$ of the metal redox couple by ~100 mV to the positive side of s.c.e. The effect of deprotonation of $[\text{RuX}_2(\text{HL})(\text{L})]$ to $[\text{RuX}_2(\text{L})_2]^-$ is more dramatic.[1] Here the electron transfer pathway is blocked and the metal redox couple is no longer observed within the accessible voltage range. We recently reported an example of such an extreme control of electron transfer *via* proton transfer in copper(II) chemistry.[27]

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