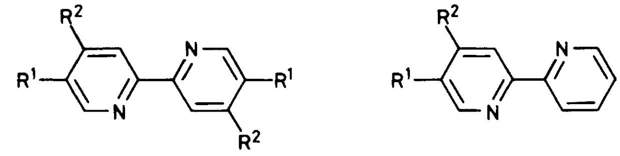
Preparation and Characterisation of 2,2′-Bipyridine-4,4′-disulphonic and -5-sulphonic Acids and their Ruthenium(II) Complexes. Excited-state Properties and Excited-state Electron-transfer Reactions of Ruthenium(II) Complexes containing 2,2′-Bipyridine-4,4′-disulphonic Acid or 2,2′-Bipyridine-4,4′-dicarboxylic Acid

Susan Anderson, Edwin C. Constable, Kenneth R. Seddon,*‡ and Janet E. Turp
Oxford-Imperial Energy Group, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR
James E. Baggott and Michael J. Pilling*
Oxford-Imperial Energy Group, Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ

We report the syntheses of 2,2′-bipyridine-4,4′-disulphonic acid (H_2bp-4,4′-ds) and 2,2′-bipyridine-5-sulphonic acid (Hbp-5-s), and several ruthenium(II) complexes derived therefrom, including $[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}$, $[Ru(bipy)(bp\text{-}4,4'\text{-}ds)_2]^{2-}$ (bipy = 2,2′-bipyridine), $[Ru(bipy)_2(bp\text{-}4,4'\text{-}ds)]$, and $[Ru(bp\text{-}5\text{-}s)_3]^-$ and their 2,2′-bipyridine-4,4′-dicarboxylic acid (H_2bpdc) analogues, *viz.* $[Ru(bpdc)_3]^{4-}$, $[Ru(bipy)(bpdc)_2]^{2-}$, and $[Ru(bipy)_2(bpdc)]$. Some novel thioalkyl derivatives of 2,2′-bipyridine, including 4,4′-di(methylthio)-2,2′-bipyridine, 4,4′-di(ethylthio)-2,2′-bipyridine, and 4,4′,6,6′-tetra(methylthio)-2,2′-bipyridine, were also prepared and characterised during the course of this investigation. The luminescent states of the complexes $[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}$, $[Ru(bipy)(bp\text{-}4,4'\text{-}ds)_2]^{2-}$, $[Ru(bpdc)_3]^{4-}$, $[Ru(bipy)(bpdc)_2]^{2-}$, and $[Ru(bipy)_2(bpdc)]$ were studied using variable-temperature lifetime measurements. Studies of the quenching of $\{[Ru(bipy)_3]^{2+}\}^*$, $\{[Ru(bipy)_2(bpdc)]\}^*$, $\{[Ru(bipy)(bp\text{-}4,4'\text{-}ds)_2]^{2-}\}^*$, and $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ by 1,1′-dimethyl-4,4′-bipyridinium bromide (methyl viologen) in aqueous solution as a function of ionic strength have demonstrated that the effects of charge in these electron-transfer reactions can be understood in terms of conventional theories of ionic reactions whilst, at the same time, confirming the effective charges of the ruthenium(II) complex ions. The rate constants for the quenching of $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ and $\{[Ru(bipy)(bp\text{-}4,4'\text{-}ds)_2]^{2-}\}^*$ by copper(II) ions in neutral aqueous solution show unusual (non-Arrhenius) temperature dependences. A novel kinetic scheme involving parallel inner- and outer-sphere quenching mechanisms has been proposed to account for the observed behaviour. The luminiscence decay of $\{[Ru(bipy)_2(bpdc)]\}^*$ in the presence of aqueous copper(II) ions at pH 3.5 is non-exponential. This is interpreted in terms of a combination of static and dynamic quenching effects.

Interest in the complex cation tris(2,2′-bipyridine)ruthenium(II) has flourished in the past seven years.[1,2] Not only does the species undergo unique photo-induced electron-transfer reactions,[3] but it is also under investigation as a photocatalyst for the direct homogeneous photodecomposition of water,[4] and as a component in photogalvanic cells[5] and photoelectrochemical cells for the production of dihydrogen.[6] More recently, a detailed investigation[7] of the photogalvanic systems $[Ru(bipy)_3]^{2+}/[Fe(H_2O)_6]^{3+}$ and $[Ru(tmphen)_3]^{2+}/[Fe(H_2O)_6]^{3+}$ (bipy = 2,2-bipyridine, tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) found the cells to be of limited practical value, owing to several constraints: one such constraint was the relatively low solubility of the ruthenium complexes. Thus, for several reasons, it was a matter of some interest to develop syntheses for complexes of the type $[Ru(L\text{–}L)_3]^{n+}$ (L–L = substituted 2,2′-bipyridine derivatives, $2 \geqslant n \geqslant -4$), to impart a greater solubility and to study the effect of the overall charge on the complex upon the excited-state electron-transfer reactions of these species. In particular, we have recently[8,9] studied the quenching of $\{[Ru(bipy)_3]^{2+}\}^*$ by aqueous copper(II) complexes and found that, despite the fact that these reactions fall in the 'normal' region[10] of reaction exothermicity, the quenching rate constants show a strong deviation from the predictions of classical, adiabatic Marcus theory.[11] A pre-equilibrium step involving a configuration change within the inner co-ordination sphere of the copper(II) cation was proposed,[8] and complexes of the type $[Ru(L\text{–}L)_3]^{n+}$ ($2 \geqslant n \geqslant -4$) would enable this postulate to be investigated further.

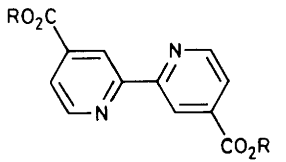


R^1	R^2		R^1	R^2	
H	SO_3H	H_2bp-4,4′-ds	H	SO_3H	Hbp-4-s
SO_3H	H	H_2bp-5,5′-ds	SO_3H	H	Hbp-5-s

A logical choice of ligand for preparing such complexes is 2,2′-bipyridine-4,4′-disulphonic acid (H_2bp-4,4′-ds) but there were no reports of the synthesis of this ligand in the literature. The only reported sulphonic acid derivatives of 2,2′-bipyridine are the products from the direct reaction of 2,2′-bipyridine with sulphuric acid at 300 °C (a mixture of 2,2′-bipyridine-5,5′-disulphonic acid and 2,2′-bipyridine-5-sulphonic acid)[12] and from the thermolysis of the 'bipy–SO_3 (1/1) adduct' (2,2′-bipyridine-5-sulphonic acid, Hbp-5-s).[13] Summers and co-workers[14,15] have confirmed these results (but see later) and have demonstrated that the best yields of Hbp-5-s were

---

† *Present address:* School of Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ.



R
H H_2bpdc
Me dmbpdc

obtained by the direct sulphonation of bipy with oleum in the presence of mercury(II) sulphate at 220 °C. Accordingly, we have reinvestigated the synthetic routes to sulphonated 2,2'-bipyridine derivatives, and have developed, *inter alia*, a route to H_2bp-4,4'-ds. We also report here the synthesis of several ruthenium(II) complexes of these sulphonated derivatives, along with complexes of the related ligand, 2,2'-bipyridine-4,4'-dicarboxylic acid (H_2bpdc).

The ligands and complexes have been characterised by a variety of spectroscopic techniques, and the excited-state properties, and some excited-state electron-transfer reactions, of the ruthenium(II) complexes have also been investigated and are reported here in some detail.

Experimental

General Procedures.—The blue 'ruthenium(II)' stock solution was prepared *exactly* as described elsewhere,[16] as was Ru(bipy)Cl_3.[16] The blue 'ruthenium(II)' solution is extremely air-sensitive, and was handled by standard Schlenk techniques. [Ru(bipy)$_2$$Cl_2$] was prepared by the methods described by Whitten and co-workers[17] and Meyer and co-workers.[18] The complex tris(dimethyl 2,2'-bipyridine-4,4'-dicarboxylate)ruthenium(II) dichloride, [Ru(dmbpdc)$_3$]Cl_2, was prepared by a standard method.[18] 2,2'-Biquinoline was prepared by the method of Haginiwa and Higuchi[19] or purchased from G. F. Smith Chemical Company. Commercial '$RuCl_3 \cdot xH_2O$' (see ref. 2) was obtained from Johnson-Matthey, 4,7-diphenyl-1,10-phenanthrolinedisulphonic acid from G. F. Smith Chemical Company, 4-methylpyridine (distilled once prior to use) and 2,2'-bipyridine from B.D.H., and Sephadex LH-20 from Pharmacia. Electronic absorption spectra were recorded upon a Perkin-Elmer PE330 spectrophotometer, ^1H n.m.r. spectra (δ quoted as positive to high frequency of $SiMe_4$) were recorded using a JEOL PMX-60 spectrometer, ^{13}C n.m.r. spectra (δ quoted as positive to high frequency of $SiMe_4$) were recorded with a Bruker WH 90 spectrometer, and mass spectra were obtained at 70 eV (*ca.* 1.1×10^{-17} J) on a MSS 501 mass spectrometer. Microanalytical data were supplied by the Analytical Department of the Inorganic Chemistry Laboratory, Oxford University.

2,2'-Bipyridine-5-sulphonic Acid.—(*i*) *In sulphuric acid.* 2,2'-Bipyridine (15.6 g, 0.1 mol) was cautiously added to concentrated sulphuric acid (40 g), and the mixture heated to 300 °C for 10 h, after which time a deep red syrup had been obtained. This was allowed to cool to room temperature, when it was cautiously quenched in water (200 cm^3; 18 °C). Powdered barium carbonate was added, and the mixture left until no further CO_2 was evolved. The solution, which had a pH of 5, was filtered to remove any unreacted $BaCO_3$, and was extracted with $CHCl_3$ (5×50 cm^3). The extracts were dried ($MgSO_4$), and evaporated to dryness to give 2,2'-bipyridine (9.0 g), m.p. 68—70 °C. The aqueous solution was evaporated to dryness *in vacuo* to give a red residue (5.0 g, 50% based upon unrecovered bipy) of 2,2'-bipyridine-5-sulphonic acid, m.p. >300 °C (Found: C, 50.00; H, 3.50; N, 11.30. Calc. for $C_{10}H_8N_2O_3S$: C, 50.85; H, 3.40; N, 11.85%). Recrystallisation from aqueous methanol gave a very pale brown powder [Found: C, 50.95; H, 3.40; N, 12.20%; mass spectrum *m*/*z* (relative intensity) 236 (*M*, 18), 200 (13), 156 (31), 155 (21), 129 (14), 128 (21), 127 (48), 126 (100)]. Neither the crude product, nor the recrystallised material, gave a green flame test, nor a precipitate when aqueous solutions were mixed with sulphuric acid (2 mol dm^{-3}).

(*ii*) *In oleum with mercury*(II) *sulphate.* 2,2'-Bipyridine (4.0 g, 0.025 mol) was added slowly to oleum (5.2 cm^3, d = 1.92 g cm^{-3}, 20% SO_3) and $HgSO_4$ (0.1 g), maintained at 0 °C in an ice-bath. The solution so obtained was heated to 220 °C for 24 h under a stream of dry dinitrogen. The reaction mixture was allowed to cool, and the remaining sulphuric acid removed by distillation *in vacuo*, using a vacuum line. The brown residue was then dissolved in water (10 cm^3) and boiled with activated charcoal (0.3 g). After filtration, the filtrate was again boiled, and EtOH was added until crystallisation commenced. The pale pink solid so obtained was collected by filtration, and washed with propanone to give Hbp-5-s$\cdot H_2O$, m.p. >330 °C (Found: C, 47.50; H, 3.50; N, 10.80. Calc. for $C_{10}H_8N_2O_3S \cdot H_2O$: C, 47.25; H, 3.95; N, 11.00%). A further 0.53 g of product was recovered from the mother-liquor.

When the reaction was repeated using double the quantities of oleum and $HgSO_4$, for 36 h, 1.08 g of Hbp-5-s (Found: C, 47.55; H, 3.45; N, 10.75%) were obtained.

2,2'-Bipyridine-5,5'-disulphonic Acid in Admixture with 2,2'-Bipyridine-5-sulphonic Acid.—(*i*) *In oleum.* 2,2'-Bipyridine (15.6 g, 0.1 mol) was heated to 300 °C with a mixture of sulphuric acid (25 cm^3) and oleum (5.0 cm^3, d = 1.92 g cm^{-3}, 20% SO_3) for 4 h. After this period the clear red syrup began to char, and the reaction mixture was allowed to cool. The product was boiled with water (250 cm^3), and the deep red solution filtered to remove carbon. The filtrate was then boiled with $BaCO_3$ (150 g) for 20 min, filtered hot, and extracted with $CHCl_3$ (5×50 cm^3). The $CHCl_3$ extracts were dried ($MgSO_4$) and evaporated to give bipy (5.6 g, 35%). The aqueous solution was then evaporated to dryness, to give a pale pink solid, m.p. >360 °C (Found: C, 37.85; H, 2.45; N, 9.50. Calc. for a 3:1 mixture of the barium salts of Hbp-5-s and H_2bp-5,5'-ds: C, 37.45; H, 2.10; N, 8.75%).

(*ii*) *In sulphuric acid with mercury*(II) *sulphate.* 2,2'-Bipyridine (5.00 g, 0.032 mol) was maintained at 280—300 °C for 4 h with sulphuric acid (9.00 cm^3, 0.168 mol) and $HgSO_4$ (0.1 g). The deep red syrup was quenched in water (60 cm^3) and neutralised with $BaCO_3$ (35 g). The $BaSO_4$ and excess $BaCO_3$ were removed by filtration, and the filtrate extracted with $CHCl_3$ (1.0 g bipy recovered). The aqueous solution was then evaporated to dryness to give a pale brown solid (Found: C, 44.80; H, 3.00; N, 10.90; S, 13.90. Calc. for a 3:2 mixture of the barium salts of Hbp-5-s and H_2bp-5,5'-ds: C, 44.75; H, 2.90; N, 10.45; S, 16.75%).

Reaction of 4,4'-Dinitro-2,2'-bipyridine N,N'*-Dioxide with Sodium Sulphite.*—4,4'-Dinitro-2,2'-bipyridine *N*,*N'*-dioxide (1.4 g, 0.005 mol) was added to a mixture of water (40 cm^3) and methanol (20 cm^3); sodium sulphite (1.3 g, 0.01 mol) was added and the suspension heated to reflux for 0.5 h, after which period an orange solution had been obtained. This was filtered, and the filtrate evaporated to dryness. The residue was dissolved in water (20 cm^3) and hydrochloric acid (70 cm^3, 12 mol dm^{-3}) added. The NaCl was removed by filtration, the solution concentrated, and the process repeated. Finally, the solution was saturated with HCl, filtered, and evaporated to give an orange residue, which was recrystallised from methanol to give yellow crystals, m.p. >300 °C (Found: C, 33.20; H, 2.85; N, 9.90%).

When the crude orange reaction mixture was passed down a Dowex 50W-XS ion exchange column, and the pale yellow eluate evaporated to dryness, it gave pale yellow microcrystals, m.p. > 300 °C (Found: C, 33.50; H, 3.75; N, 11.95; S, 14.60%).

4,4′,6,6′-*Tetra*(*methylthio*)-2,2′-*bipyridine*.—A solution of sodium thiomethoxide was prepared by saturating a solution of sodium hydride (0.18 g, 0.075 mol) in methanol (20 cm^3) with MeSH. 4,4′-Dinitro-2,2′-bipyridine *N,N′*-dioxide (0.95 g, 0.0034 mol) was added, and the solution heated to reflux for 1.5 h, after which time a brown solution had been obtained. Cooling gave colourless needles of 4,4′,6,6′-tetra(methylthio)-2,2′-bipyridine, m.p. 178—180 °C; mass spectrum *m/z* 340(*M*) only; ^{1}H n.m.r., δ(CDCl$_3$, 60 MHz) 2.56 (6 H, s), 2.70 (6 H, s), 6.91 (2 H, d, J = 2), 7.77 (2 H, d, J = 2 Hz). Evaporation of the mother-liquor gave a brown oil, which was not further investigated.

4,4′-*Di*(*methylthio*)-2,2′-*bipyridine*.—4,4′-Dichloro-2,2′-bipyridine (0.3 g, 0.0013 mol) was added to a solution of NaSMe (0.02 mol, prepared *in situ*, see above) in methanol (20 cm^3), and the mixture heated to reflux for 20 h. After this period the solution was filtered hot, and allowed to cool, to give white needles (0.25 g, 76%) of 4,4′-di(methylthio)-2,2′-bipyridine, m.p. 153.5—156 °C (Found: C, 58.55; H, 4.85; N, 11.40. Calc. for $C_{12}H_{12}N_2S_2$: 58.05; H, 4.85; N, 11.30%); mass spectrum *m/z* (relative intensity) 250 (11), 249 (24), 248 (*M*, 100), 247 (37), 232 (14), 231 (5), 202 (48), 187 (16); ^{1}H n.m.r., δ (CDCl$_3$, 60 MHz) 2.50 (6 H, s), 6.95 (2 H, dd, J = 5.0, 2.0), 8.08 (2 H, d, J = 2), 8.23 (2 H, d, J = 5 Hz).

6-*Chloro*-6′-*methylthio*-2,2′-*bipyridine*.—6,6′-Dichloro-2,2′-bipyridine (0.5 g, 0.002 mol) was added to a solution of NaH (0.1 g, 0.004 mol) in propan-2-ol (20 cm^3), which had been saturated with MeSH. *N,N*-Dimethylmethanamide (10 cm^3) was added, and the mixture heated to reflux for 12 h, filtered hot, and quenched in water (75 cm^3). The white precipitate was collected by filtration, and recrystallised from methanol to give white needles of 6-chloro-6′-methylthio-2,2′-bipyridine, m.p. 93—94 °C; mass spectrum *m/z* (relative intensity) 238 (36), 237 (26), 236 (*M*, 100), 235 (41), 224 (15), 191 (24), 190 (58), 189 (42); ^{1}H n.m.r., δ (CDCl$_3$, 60 MHz) 2.65 (3 H, s), 7.18 (1 H, d), 7.45 (1 H, d), 7.60 (1 H, t), 7.71 (1 H, t), 8.09 (1 H, dd), 8.35 (1 H, dd); ν(CCl) = 785, 740 cm^{-1}.

No reaction was observed when the reaction was conducted in methanol (20 cm^3) for 2 h.

2,2′-*Bipyridine*-4(1H),4′(1′H)-*dithione*.—Potassium hydroxide (5.0 g, 0.9 mol) was dissolved in methanol (20 cm^3) and the solution saturated with hydrogen sulphide. This solution was evaporated to dryness, and the residue added to *N,N*-dimethylmethanamide (50 cm^3). 4,4′-Dichloro-2,2′-bipyridine (0.5 g, 0.0022 mol) was added to this solution, which was then heated to reflux for 4 h. The green reaction mixture was filtered from inorganic material, and the filtrate evaporated to dryness *in vacuo*, to give a yellow residue. This was treated with water (20 cm^3), and the pH of the suspension adjusted to 7 with dilute hydrochloric acid (2 mol dm^{-3}). The residue was collected by filtration and dried *in vacuo*. Although extremely insoluble, the material could be purified by Soxhlet extraction (EtOH), or by dissolution in alkali followed by acidification, m.p. 315—317 °C (decomp.) (Found: C, 53.65; H, 3.85; N, 12.80. Calc. for $C_{10}H_8N_2S_2$: C, 54.50; H, 3.65; N, 12.70%); mass spectrum *m/e* 220 (*M*) only.

4,4′-*Di*(*ethylthio*)-2,2′-*bipyridine*.—The above preparation of 2,2′-bipyridine-4(1*H*),4′(1′*H*)-dithione was repeated, and the crude yellow solid obtained by evaporation of the solvent was washed with water (10 cm^3) and heated to reflux with iodoethane (25 cm^3) for 6 h. The solution was evaporated to dryness, and the white solid so obtained extracted with boiling ethanol (40 cm^3). On cooling the EtOH extract, white needles of 4,4′-di(ethylthio)-2,2′-bipyridine were deposited, m.p. 98—99 °C (Found: C, 60.40; H, 5.30; N, 9.75. Calc. for $C_{14}H_{16}N_2S_2$: C, 60.85; H, 5.85; N, 10.15%), mass spectrum *m/z* (relative intensity) 278 (9), 277 (23), 276 (*M*, 85), 261 (15), 248 (100), 243 (30), 219 (11), 216 (36); ^{1}H n.m.r., δ (CDCl$_3$, 60 MHz) 1.40 (6 H, t, J = 8), 3.00 (4 H, q, J = 8), 6.95 (2 H, dd, J = 1.5, 5.0), 8.05 (2 H, d, J = 1.5), 8.25 (2 H, d, J = 5 Hz).

Disodium 2,2′-*Bipyridine*-4,4′-*disulphonate*.—This is a five-step synthesis from bipy, giving a yield of *ca.* 51% from the known 4,4′-dinitro-2,2′-bipyridine *N,N′*-dioxide.

(*i*) 2,2′-*Bipyridine* N,N′-*dioxide*.[20] **WARNING:** This reaction is potentially explosive. 2,2′-Bipyridine (10 g, 64 mmol), hydrogen peroxide (13 cm^3, 100 vol.), and glacial ethanoic acid (75 cm^3) were heated at 80 °C for 3 h. Hydrogen peroxide (9 cm^3, 100 vol.) was added, and heating was continued for 4 h. The colourless solution was cooled to room temperature and added slowly to propanone (1 l), precipitating a white solid of 2,2′-bipyridine *N,N′*-dioxide which was collected by filtration and air dried (11 g, 90%). This product was commonly used as obtained from the above preparation, but recrystallisation from a large volume of ethanol gave transparent white plates, m.p. 312—315 °C (decomp.) (lit.,[20] 297 °C) (Found: C, 64.20; H, 4.20; N, 14.90. Calc. for $C_{10}H_8N_2O_2$: C, 63.85; H, 4.30; N, 14.90%).

(*ii*) 4,4′-*Dinitro*-2,2′-*bipyridine* N,N′-*dioxide*.[21] To a mixture of 2,2′-bipyridine *N,N′*-dioxide (5 g, 27 mmol) and oleum–sulphuric acid (1:2 v/v, 15 cm^3) in an ice-bath, nitric acid (fuming, 10 cm^3) was added slowly. The mixture was heated to 100 °C for 4 h, with the reflux condenser fitted with a calcium chloride drying tube. After this time it was cooled to room temperature, and *cautiously* poured onto crushed ice (50 g) and water (50 cm^3) to give a yellow solid. This was collected by filtration, washed with water and air dried to give 4,4′-dinitro-2,2′-bipyridine *N,N′*-dioxide (3.75 g, 49%), m.p. 272—275 °C (lit.[21] 274 °C) (Found: C, 43.55; H, 2.25; H, 20.05. Calc. for $C_{10}H_6N_4O_6$: C, 43.15; H, 2.15; N, 20.15%).

(*iii*) 4,4′-*Dichloro*-2,2′-*bipyridine* N,N′-*dioxide*.[21] Glacial ethanoic acid (120 cm^3), ethanoyl chloride (80 cm^3, 1.02 mol), and 4,4′-dinitro-2,2′-bipyridine *N,N′*-dioxide (7.5 g, 27 mmol) were heated at 100 °C for 2 h. The cooled mixture was poured onto ice (500 g) (**WARNING:** this step must be performed behind a safety screen, and with eye and hand protection) and the solution neutralised with sodium hydroxide solution (30% w/v) to give a white solid. This was collected by filtration, washed with water, and air dried (7 g, 98%), m.p. 276—282 °C (lit.,[21] 261 °C) (Found: C, 46.90; H, 2.50; N, 12.05. Calc. for $C_{10}H_6Cl_2N_2O_2$: C, 46.70; H, 2.35; N, 10.90%).

(*iv*) 2,2′-*Bipyridine*-4,4′-*disulphonic acid* N,N′-*dioxide*. Two alternative procedures are described, the first leading to the free acid, the second to its sodium salt.

(*a*) Sodium sulphite (26 g, 0.16 mol) and 4,4′-dichloro-2,2′-bipyridine *N,N′*-dioxide (7 g, 26 mmol) were heated to reflux in ethanol–water (1:1 v/v, 100 cm^3) for 18 h under dinitrogen. The resultant solution was evaporated to dryness to give a white solid which was dissolved in water (10 cm^3). Concentrated hydrochloric acid (10 cm^3) was added, precipitating a white solid (sodium chloride). This was removed by filtration, the colourless filtrate evaporated to dryness and the precipitation of sodium chloride (as described above) repeated twice. The final colourless filtrate was evaporated to dryness to give a white solid, 2,2′-bipyridine-4,4′-disulphonic acid *N,N′*-dioxide (4 g, 36%).

(*b*) 4,4′-Dichloro-2,2′-bipyridine *N,N′*-dioxide (3.5 g, 0.013 mol) and Na_2SO_3 (13.0 g, 0.1 mol) were heated to reflux in ethanol–water (1:3 v/v, 100 cm^3) for 40 h. The solution was filtered hot, and the filtrate treated with concentrated hydrochloric acid (200 cm^3). The precipitate was removed by filtration, the filtrate concentrated to 50 cm^3, and the acidification process repreated three times. The solution was finally evaporated to dryness, dissolved in the minimum volume of water, and passed down a Dowex 50W-X8 cation-exchange column. The eluate was evaporated to 20 cm^3, neutralised with $NaHCO_3$, and concentrated to crystallisation point to give the disodium salt of 2,2'-bipyridine-4,4'-disulphonic acid *N,N'*-dioxide (80%).

(*v*) *Disodium* 2,2'-*bipyridine*-4,4'-*disulphonate*. The disodium salt of 2,2'-bipyridine-4,4'-disulphonic acid *N,N'*-dioxide (2.0 g, 0.0055 mol) was dissolved in water (20 cm^3), and the solution degassed. $[NH_4]VO_3$ (5.0 g, 0.043 mol) was added to hydrochloric acid (60 cm^3, 6 mol dm^{-3}), and the mixture degassed. Zinc dust (8 g, 0.12 mol) was added to the orange vanadium(V) solution, and the colour of the solution changed, through blue and green, to violet. This violet solution was added, under dinitrogen, to the sulphonic acid solution, whence an instantaneous colour change to green occurred. This solution was then neutralised by the addition of aqueous sodium hydroxide solution (4 mol dm^{-3}), and the pale green precipitate formed was removed by filtration and washed with hot water (5 × 100 cm^3). The filtrate and washings were combined, and concentrated (to *ca.* 200 cm^3), or taken to dryness, with subsequent recrystallisation of the residue from water, to yield white crystals of Na_2[bp-4,4'-ds]·$2H_2O$ (1.1 g, 65%) (Found: C, 29.95; H, 2.30; N, 6.80. Calc. for $C_{10}H_{10}N_2Na_2O_8S_2$: C, 30.30; H, 2.55; N, 7.05%); ^{1}H n.m.r., δ[$(CD_3)_2SO$, 60 MHz] 7.66 (2 H, dd, *J* = 5. 2), 8.60 (2 H, d, *J* = 2), 8.76 (2 H, d, *J* = 5 Hz); ^{1}H n.m.r., δ (D_2O, 60 MHz), 7.68 (2 H, dd, *J* = 6, 1.5), 8.25 (2 H, d, *J* = 1.5), 8.65 (2 H, d, *J* = 6 Hz); ^{13}C n.m.r., δ(D_2O), 127.077 (C^3), 129.505 (C^5), 159.442 (C^4), 161.276 (C^6), 164.675 (C^2).

2,2'-*Biquinolinedisulphonic Acid*.—2,2'-Biquinoline (1.28 g, 0.005 mol) was dissolved in oleum (8.0 cm^3, *d* = 1.92 g cm^{-3}, 20% SO_3), and the solution maintained at 100 °C for 30 h, after which time it was cooled, and poured into water (15 cm^3). The yellow solid was collected by filtration, and air dried at 100 °C, to give 2,2'-biquinolinedisulphonic acid (0.53 g), m.p. >360 °C (Found: C, 52.40; H, 2.80; N, 6.95; S, 14.50. Calc. for $C_{18}H_{12}N_2O_6S_2$: C, 51.90; H, 2.90; N, 6.75; S, 15.40%).

2,2'-*Bipyridine*-4,4'-*dicarboxylic Acid*.[17]—(*i*) 4,4'-*Dimethyl*-2,2'-*bipyridine*. 4-Methylpyridine (700 cm^3) was heated to reflux with 10% palladium on charcoal (28 g) for 3 d. Benzene (250 cm^3) was added and heating continued for a further 1 h. The hot solution was filtered, and the recovered catalyst washed with hot benzene (2 × 100 cm^3). The combined filtrate and washings were evaporated under reduced pressure to *ca.* 100 cm^3 to give white crystals, which were collected by filtration and recrystallised from ethyl ethanoate to give large colourless crystals of 4,4'-dimethyl-2,2'-bipyridine (30 g, 2%), m.p. 170—173 °C (lit.,[22] 171—172 °C) (Found: C, 78.3; H, 6.9; N, 15.3. Calc. for $C_{12}H_{12}N_2$: C, 78.25; H, 6.55; N, 15.20%).

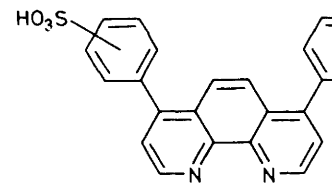
(*ii*) 2,2'-*Bipyridine*-4,4'-*dicarboxylic acid*. 4,4'-Dimethyl-2,2'-bipyridine (1.6 g, 8.7 mmol) and K[MnO_4] (10 g, 63 mmol) were heated to reflux in water (100 cm^3) for 12 h. The finely divided 4,4'-dimethyl-2,2'-bipyridine gradually disappeared and the purple solution gradually deposited a brown precipitate. The mixture was filtered and the brown precipitate washed with water (2 × 30 cm^3). The filtrate and washings were combined, and extracted with diethyl ether to remove unreacted starting material. The aqueous fraction was reduced to half its original volume under low pressure and concentrated hydrochloric acid (10 cm^3) was added slowly to precipitate a white flocculent solid, which was then collected by filtration, washed with water, ethanol, and diethyl ether and air dried (Found: C, 59.1; H, 3.7; N, 11.4. Calc. for $C_{12}H_8N_2O_4$: C, 59.0; H, 3.30; N, 11.50%).

Tetrasodium Tris(2,2'-*bipyridine*-4,4'-*disulphonato*)*ruthenate*(II) *Tetrahydrate*.—The blue 'ruthenium(II)' solution (3 cm^3, 0.3 mmol) was added slowly to a degassed solution of Na_2[bp-4,4'-ds]·$2H_2O$ (0.47 g, 1 mmol) in water (30 cm^3) at 60 °C. The green-blue solution produced was heated at reflux under dinitrogen for 4 h to give a red solution, filtered hot, and the filtrate evaporated to dryness under reduced pressure. This produced a red solid which was dissolved in water (5 cm^3) and reprecipitated by adding ethanol (50 cm^3); the reprecipitated solid was isolated by filtration, washed with ethanol and dried. This product was then dissolved in the minimum volume of water (*ca.* 5 cm^3) and chromatographed (Sephadex LH-20, 30 × 2 cm column, water as eluant) giving one coloured band only. This was collected and evaporated to dryness to give Na_4[Ru(bp-4,4'-ds)$_3$]·$4H_2O$ (Found: C, 29.8; H, 2.3; N, 7.0; Na, 7.6; S, 15.7. Calc. for $C_{30}H_{24}N_6Na_4O_{22}RuS_6$: C, 29.75; H, 2.15; N, 6.95; Na, 7.60; S, 16.20%).

Tetrasodium Tris(2,2'-*bipyridine*-4,4'-*dicarboxylato*)*ruthenate*(II) *Hexahydrate*.—Aqueous sodium hydroxide (*ca.* 3 cm^3, 2 mol dm^{-3}) was added to a suspension of H_2bpdc (0.5 g, 1.7 mmol) in water (30 cm^3), in order to dissolve the solid. Hydrochloric acid (2 mol dm^{-3}) was slowly added to this solution until a slight cloudiness was apparent. The solution was then degassed, and an aliquot of blue 'ruthenium(II)' solution (5 cm^3, 0.5 mmol) was added. The resultant green-blue solution was heated at reflux under dinitrogen for 4 h, by which time it was deep red in colour. It was filtered hot, and the volume of the filtrate reduced (to *ca.* 5 cm^3) under low pressure. Methanol was added dropwise to the solution until a red solid began to precipitate; the solution was then kept at 0 °C for 4 h, and the resultant red crystals collected by filtration. Recrystallisation from water–methanol gave red microcrystals of Na_4[Ru(bpdc)$_3$]. They were dissolved in water (5 cm^3) and chromatographed (Sephadex LH-20, 30 × 2 cm column, water as eluant). A single red band was observed; it was collected and evaporated to dryness to give a red solid, Na_4[Ru(bpdc)$_3$]·$6H_2O$ (Found: C, 41.8; H, 3.2; N, 8.05. Calc. for $C_{36}H_{30}N_6Na_4O_{18}Ru$: C, 42.20; H, 2.90; N, 8.20%).

Sodium Tris(2,2'-*bipyridine*-5-*sulphonato*)*ruthenate*(II).—The blue 'ruthenium(II)' solution (0.3 mmol, 3 cm^3) was transferred into a degassed solution of Na[bp-5-s] (0.25 g, 1 mmol) in water (30 cm^3). The mixture was heated at reflux under dinitrogen for 5 h, filtered hot, and the red filtrate evaporated to low volume (*ca.* 5 cm^3) under reduced pressure. To this solution was added ethanol (50 cm^3) to precipitate an amorphous red solid, which was collected by filtration, washed with ethanol and air dried. It was dissolved in water (2 cm^3) and chromatographed (Sephadex LH-20, 30 × 2 cm column, water as eluant); one red band and one purple band were observed and collected separately. The red band, which contained the desired complex, was evaporated to dryness to give a red solid, Na[Ru(bp-5-s)$_3$]. The purple band was shown to be Na[Ru(bp-5-s)$_2Cl_2$] by its reactivity with bipy, and by electronic absorption spectroscopy.

Tetrasodium Tris[1,10-*phenanthrolinediyl*-4,7-*di*(*benzenesulphonato*)*ruthenate*(II) *Hexahydrate*.—The blue 'ruthenium(II)' solution (0.5 mmol, 5 cm^3) was transferred into a degassed solution of disodium 1,10-phenanthrolinediyl-4,7-di(benzenesulphonate), Na_2[phendbs] (1 g, 2 mmol), in water (20 cm^3) and the mixture was heated at reflux under dinitrogen for 12 h. The resultant red solution was filtered hot, and the red filtrate evaporated to dryness to give an orange-brown solid. This was recrystallised from water–ethanol, and then dissolved in water



H_2phendbs

($5 cm^3$) and chromatographed (Sephadex LH-20, 30 × 2 cm column, water as eluant). The red band observed was collected (other purple and brown bands were not investigated) and evaporated to dryness to give a brown solid (Found: C, 45.3; H, 2.6; N, 4.3. Calc. for $C_{72}H_{54}N_6Na_4O_{24}RuS_6$: C, 45.15; H, 2.85; N, 4.40%).

Bis(2,2′-*bipyridine*)(2,2′-*bipyridine*-4,4′-*disulphonato*)*ruthenium*(II) *Dihydrate*.—Bis(2,2′-bipyridine)dichlororuthenium(II) (0.24 g, 0.5 mmol) and Na_2[bp-4,4′-ds] (0.24 g, 0.8 mmol) were heated to reflux in water ($40 cm^3$) for 2 h. The resultant red solution was filtered hot and the filtrate was reduced in volume (to *ca.* $10 cm^3$) under reduced pressure. To this solution was added methanol ($20 cm^3$); the mixture was cooled at 0 °C and the resultant red needles collected by filtration. They were recrystallised from water–methanol and a saturated solution of the solid in water ($2 cm^3$) was chromatographed (Sephadex LH-20, 30 × 2 cm column, water as eluant) to give one red band. This was collected and evaporated to dryness; the resultant red solid was recrystallised once more from water–methanol to give bright red microcrystals of $[Ru(bipy)_2(bp\text{-}4,4'\text{-}ds)]\cdot 2H_2O$ (Found: C, 47.0; H, 3.2; N, 10.9; Ru, 13.2; S, 8.2. Calc. for $C_{30}H_{26}N_6O_8RuS_2$: C, 47.1; H, 3.45; N, 11.00; Ru, 13.20; S, 8.50%).

Disodium (2.2′-*Bipyridine*)*bis*(2,2′-*bipyridine*-4,4′-*disulphonato*)*ruthenate*(II) *Hexahydrate*.—(2,2′-Bipyridine)trichlororuthenium(III) (0.04 g, 0.1 mmol) and Na_2[bp-4,4′-ds] (0.1 g, 0.3 mmol) were heated together under reflux in water ($30 cm^3$) for 36 h; the mixture dissolved to give a green solution which became red after 24 h. It was filtered hot, and the red filtrate was evaporated to low volume (*ca.* $5 cm^3$) under reduced pressure. This solution was chromatographed (Sephadex LH-20, 30 × 2 cm column, water as eluant) and the single red band was eluted and evaporated to dryness to give a red solid, $Na_2[Ru(bipy)(bp\text{-}4,4'\text{-}ds)_2]\cdot 6H_2O$ (Found: 34.4; H, 3.3; N, 7.9. Calc. for $C_{30}H_{32}N_6Na_6O_{18}RuS_4$: C, 34.65; H, 3.10; N, 8.10%).

Bis(2,2′-*bipyridine*)(2,2′-*bipyridine*-5-*sulphonato*)*ruthenium*(II) *Chloride*.—Bis(2,2′-bipyridine)dichlororuthenium(II) (0.24 g, 0.5 mmol) and Na[bp-5-s] (0.12 g, 0.5 mmol) were heated to reflux in water ($30 cm^3$) for 2 h. The solution changed from purple to red in colour. It was filtered hot, and the filtrate was evaporated to low volume ($3 cm^3$) under reduced pressure. The resultant red liquid was chromatographed (Sephadex LH-20, 30 × 2 cm column, water as eluant) and the red-orange band collected and evaporated to dryness. The solid was characterised by electronic absorption spectroscopy.

Bis(2,2′-*bipyridine*)(2,2′-*bipyridine*-4,4′-*dicarboxylic acid*)-*ruthenium*(II) *Dichloride Hexahydrate*.—Aqueous NaOH (*ca.* $3 cm^3$, 2 mol dm^{-3}) was added to a suspension of H_2bpdc (0.24 g, 1.1 mmol) in water ($30 cm^3$) to dissolve the solid; hydrochloric acid (2 mol dm^{-3}) was then added slowly until a faint cloudiness was apparent. Bis(2,2′-bipyridine)dichlororuthenium(II) (0.4 g, 1 mmol) was added to this solution and the purple mixture was heated to reflux for 3 h; it changed to deep red after *ca.* 1.5 h. The solution was filtered hot and the red filtrate evaporated to low volume ($5 cm^3$) under reduced pressure. The resultant deep red solution was chromatographed (Sephadex LH-20, 30 × 2 cm column, water as eluant) and the single red band observed was collected and evaporated to dryness to give a deep red solid. This was recrystallised from ethanol to give crystals of $[Ru(bipy)_2(H_2bpdc)]Cl_2\cdot 6H_2O$ (Found: C, 45.6; H, 3.6; N, 10.2. Calc. for $C_{32}H_{36}Cl_2N_6O_{10}Ru$: C, 45.95; H, 4.3; N, 10.05%).

Disodium (2,2′-*Bipyridine*)*bis*(2,2′-*bipyridine*-4,4′-*dicarboxylato*)*ruthenate*(II) *Hexahydrate*.—(2,2′-Bipyridine)trichlororuthenium(III) (0.1 g, 0.25 mmol) and 2,2′-bipyridine-4,4′-dicarboxylic acid (0.15 g, 0.6 mmol) were suspended in water and heated for 3 d at reflux; the mixture dissolved to give a green solution which changed to red after 24 h. The solution was filtered hot and the red filtrate was evaporated to dryness under reduced pressure to give a brown solid. This was recrystallised from water–ethanol to give red-brown crystals; a solution of this solid in water ($5 cm^3$) was chromatographed (Sephadex LH-20, 30 × 3 cm column, water) to give one red band which was collected and evaporated to dryness. The resultant red crystals were recrystallised from water–ethanol to give $Na_2[Ru(bipy)(bpdc)_2]\cdot 6H_2O$ (Found: C, 45.4; H, 3.7; N, 9.2. Calc. for $C_{34}H_{32}N_6Na_2O_{14}Ru$: C, 45.60; H, 3.60; N, 9.40%).

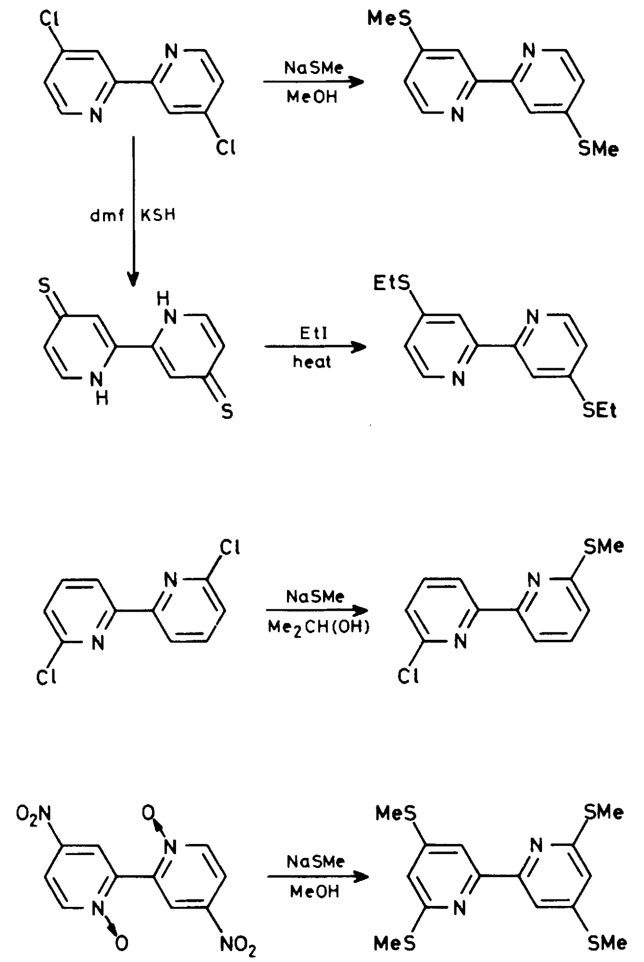
Lifetime Measurements.—The method of time-correlated single-photon counting, used for the measurement of luminescence lifetimes, has been described previously.[8,23,24] The luminescence decays were analysed as single exponentials unless otherwise stated; plots of ln(counts) *vs.* channel number (time) were linear for 3—4 mean ($1/e$) lifetimes. The flash lamp (Ortec) was used in the 'free-running' mode with a repetition rate of 10—15 kHz and pulse width (full-width at half-maximum) $\leqslant 3$ ns. Deconvolution techniques were not employed. The count ratio (true stop/true start) was kept below *ca.* 1.3% and so no corrections for photon pile-up were made. Analysis of the decay data was performed by linear regression to plots of ln(counts) *vs.* channel number, weighted by the number of counts in each channel.[24]

Curvilinear regression routines were applied for the analysis of the spontaneous decay data in terms of a quadratic expression described in a previous publication.[8] For the reactions of $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ with copper(II) ions in various media, activation parameters derived from non-linear Arrhenius plots were obtained using an iterative fitting technique.

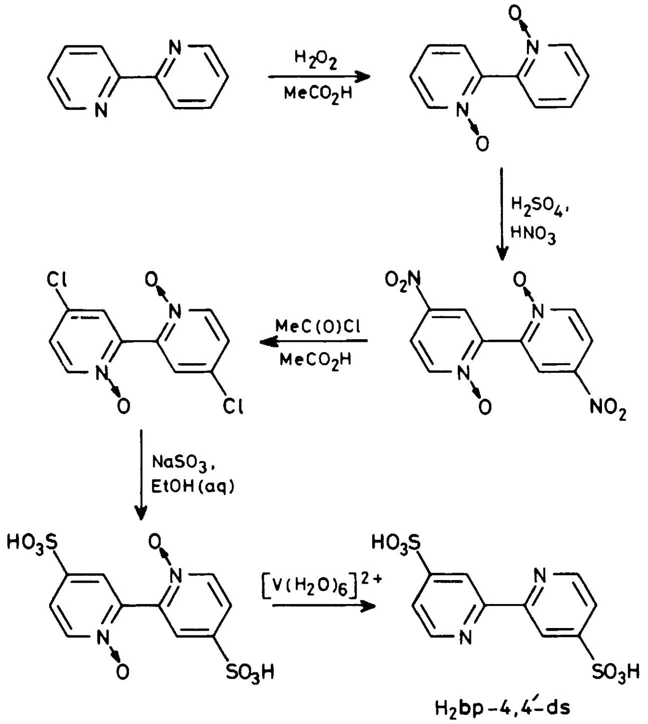
AnalaR grade $CuSO_4\cdot 5H_2O$ (B.D.H.) and Koch-Light Laboratories' $Cu[ClO_4]_2\cdot 6H_2O$ were used in the quenching experiments. For the ionic strength studies methyl viologen supplied by Koch-Light Laboratories was used; B.D.H. AnalaR grade $NaClO_4$ and Na_2SO_4 were used as supporting electrolytes, and B.D.H. AnalaR grade H_2SO_4 was used where indicated. Samples were prepared in doubly distilled water, D_2O (99.8%) supplied by Fluorochem Ltd., or in methanol (B.D.H. AnalaR).

Results and Discussion

Ligand Syntheses.—Attempts to prepare sulphonated derivatives of 2,2′-bipyridine by the direct sulphonation of either bipy or 2,2′-bipyridine *N*,*N*′-dioxide under relatively mild conditions were unsuccessful. Thus, bipy was recovered unchanged after heating to reflux with chlorosulphonic acid in tetrachloromethane solution for 2 h, to reflux with neat chlorosulphonic acid for 2 h, or to 100 °C with chlorosulphonic acid in concentrated sulphuric acid for 4 h. Similarly, no sulphonated derivatives of bipy could be isolated from the treatment of 2,2′-bipyridine *N*,*N*′-dioxide with concentrated sulphuric acid at



Scheme 1. Synthetic routes to novel alkylthio-derivatives of 2,2'-bipyridine (dmf = *N,N*-dimethylmethanamide)



Scheme 2. The synthesis of 2,2'-bipyridine-4,4'-disulphonic acid from 2,2'-bipyridine

100 °C, with oleum (20% SO_3) at 100 °C, with concentrated sulphuric acid at 200 °C, or with concentrated sulphuric acid at 200 °C in the presence of $HgSO_4$. However, when bipy was treated with concentrated sulphuric acid, under conditions similar to those described by Otroshchenko *et al.*[12] (*i.e.* 300 °C for 10 h), a deep red syrup was obtained which upon quenching in water and neutralising with $BaCO_3$ produced (after extraction of unreacted bipy with $CHCl_3$) the monosulphonated derivative, Hbp-5-s, in good yield. No evidence for the reported H_2bp-5,5'-ds also being formed was obtained, but some of this material was formed if oleum was substituted for sulphuric acid. Similarly, we confirm the report of Summers and co-workers[14] that treatment of bipy with oleum at 220 °C in the presence of $HgSO_4$ for 24 h yields only Hbp-5-s, and find that raising the reaction temperature to *ca.* 290 °C induces the formation of some H_2bp-5,5'-ds, which could not be separated from the major monosulphonated product. A potentiometric titration of pure Hbp-5-s in water, against aqueous NaOH, confirmed that it was a strong, monobasic acid, showing behaviour rather similar to pyridine-3-sulphonic acid.

Pyridine-4-sulphonic acids have generally been prepared by the reaction of a pyridine derivative bearing a labile substituent in the 4-position with a suitable sulphur nucleophile.[25] Thus, for our first attempts at the synthesis of H_2bp-4,4'-ds, we investigated the reactions of various 4,4'-disubstituted 2,2'-bipyridines and their *N,N'*-dioxides with sulphide or sulphite anions, since the oxidation of pyridine-4-thiones to sulphonic acids has several literature precedents.[25] Thus, 4,4'-dinitro-2,2'-bipyridine *N,N'*-dioxide (prepared, essentially, according to Maerker and Case[21a]) was treated with sodium sulphite (see Experimental section), to yield a yellow, non-stoicheiometric product of empirical formula $C_{6.1}H_{8.22}N_{1.87}O_5S$. The solubility of this product suggested that one of the nitro-groups may have been displaced by a sulphite, but all attempts to purify this compound or isolate a characterisable derivative were unsuccessful. Treatment of aqueous 4,4'-dinitro-2,2'-bipyridine *N,N'*-dioxide with Na_2S, NaSH, or H_2S led to the formation of highly coloured, insoluble products (assumed to be azo- or hydrazo-derivatives), which were not investigated further. The reaction with NaSMe, however, did yield an isolable (if unexpected) derivative, 4,4',6,6'-tetra(methylthio)-2,2'-bipyridine, which was identified by mass spectrometry and ^1H n.m.r. spectroscopy. This compound represents the first thioalkyl derivative of 2,2'-bipyridine, and a number of similar derivatives were thus prepared. Treatment of 4,4'-dichloro-2,2'-bipyridine with methanolic NaSMe gave near-quantitative yields of 4,4'-di(methylthio)-2,2'-bipyridine, but similar treatment of 6,6'-dichloro-2,2'-bipyridine gave no reaction. However, changing the reaction solvent to propan-2-ol resulted in the formation of 6-chloro-6'-methylthio-2,2'-bipyridine. No reaction was observed between 4,4'-dichloro-2,2'-bipyridine and either aqueous sodium sulphite or aqueous ethanolic NaSH. Nevertheless, treatment of 4,4'-dichloro-2,2'-bipyridine with KSH in *N,N'*-dimethylmethanamide leads to the formation of an extremely insoluble, involatile material, the intractable nature of which prevented spectroscopic characterisation. However, as this material reacted with iodoethane to give white 4,4'-di(ethylthio)-2,2'-bipyridine, it was deduced that the yellow, intractable solid was 2,2'-bipyridine-4(1*H*),4'(1'*H*)-dithione, or a polymer of similar composition. The reactions leading to the various alkylthio-derivatives of 2,2'-bipyridine are summarised in Scheme 1. Unfortunately, the dithione derivative showed no apparent activity towards aqueous $K[MnO_4]$ solution.

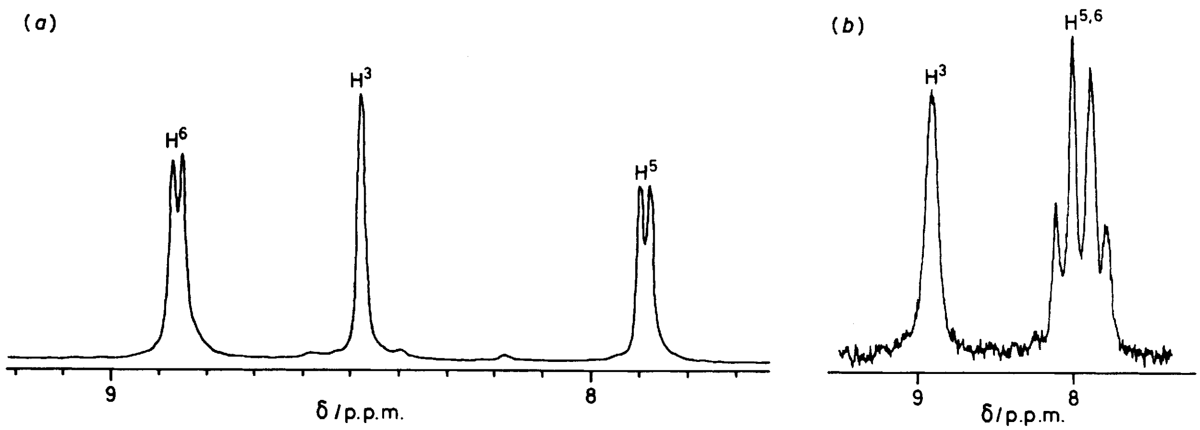


Figure 1. Hydrogen-1 n.m.r. spectra of (*a*) H_2bp-4,4′-ds in D_2O and (*b*) $[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}$ in $(CD_3)_2SO$

The key step in the eventual synthesis of H_2bp-4,4′-ds (see Scheme 2) turned out to be the treatment of 4,4′-dichloro-2,2′-bipyridine *N,N*′-dioxide[21] with aqueous ethanolic sodium sulphite, to give 2,2′-bipyridine-4,4′-disulphonic acid *N,N*′-dioxide. However, as this product was only soluble in water, the normal reagents (*e.g.* PCl_3 or $SOCl_2$) for the deoxygenation of the nitrogen atom could not be used, and the presence of the sulphonic acid group precluded catalytic hydrogenation. Moreover, both SO_2 and $NaBH_4$ proved ineffective for this particular deoxygenation reaction. However, it had been reported that $[V(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ were effective reagents for the deoxygenation of pyrazine *N*-oxides,[26] and indeed $[V(H_2O)_6]^{2+}$ proved an excellent reagent for the formation of H_2bp-4,4′-ds from its *N,N*′-dioxide. Two equivalents of vanadium(II) were needed for each equivalent of the *N,N*′-dioxide, and the reduction was essentially instantaneous. The H_2bp-4,4′-ds was isolated as its disodium salt, and the free acid was obtained by ion exchange.

A potentiometric titration of pure H_2bp-4,4′-ds in water, against aqueous NaOH solution, confirmed that it behaved as a strong dibasic acid. Its ^1H n.m.r. spectrum is illustrated in Figure 1, and the assignments indicated were confirmed by decoupling experiments.

Finally in this section, it was attempted to sulphonate 2,2′-biquinoline. No sulphonation occurred after heating 2,2′-biquinoline to reflux with pyridine–SO_3 (1/1) in pyridine for 6 h, but after treatment with sulphuric acid at 100 °C for 30 h, a yellow solid was obtained, which analysed well for 2,2′-biquinolinedisulphonic acid. However, as no satisfactory ^1H n.mr. data could be obtained for this material [owing to its low solubility in both D_2O and $(CD_3)_2SO$], its substitution pattern could not be determined.

Complex Syntheses.—We have described elsewhere[16] the reasons for the use of the blue 'ruthenium(II)' solution[27] for the synthesis of pure tris(di-imine)ruthenium(II) derivatives, and the use of $[Ru(bipy)_2Cl_2]$ and $Ru(bipy)Cl_3$ for the syntheses of $[Ru(bipy)_2(phen)]^{2+}$ and $[Ru(bipy)(phen)_2]^{2+}$ (phen = 1,10-phenanthroline), respectively.[28] We report here the successful use of similar procedures for the preparations of $Na_4[Ru(bp\text{-}4,4'\text{-}ds)_3]\cdot 4H_2O$, $Na_4[Ru(bpdc)_3]\cdot 6H_2O$, $Na_4[Ru(phendbs)_3]\cdot 6H_2O$ [H_2phendbs = 1,10-phenanthrolinediyl-4,7-di(benzenesulphonic acid)], $Na[Ru(bp\text{-}5\text{-}s)_3]$, $[Ru(bipy)_2(bp\text{-}4,4'\text{-}ds)]\cdot 2H_2O$, $Na_2[Ru(bipy)(bp\text{-}4,4'\text{-}ds)_2]\cdot 6H_2O$, $[Ru(bipy)_2(bp\text{-}5\text{-}s)]Cl$, $[Ru(bipy)_2(H_2bpdc)]Cl_2\cdot 6H_2O$, and $Na_2[Ru(bipy)(bpdc)_2]\cdot 6H_2O$, a range of tris(di-imine)ruthenium(II) complexes carrying charges varying between +2 and −4. The solubility imparted, in particular, by the sulphonic acid groups creates some difficulties with purification procedures, but gel-permeation chromatography through Sephadex LH-20 proved an invaluable method for removing trace impurities. None of the sulphonated derivatives showed an oxidation wave within the redox range of water, but $[Ru(bipy)_2(H_2bpdc)]^{2+}$ in water showed a reversible cyclic voltammetric wave at 1.29 V (*vs.* normal hydrogen electrode) {*cf.* $[Ru(bipy)_3]^{2+}$ at 1.26 V}. This leads[29] to a value of −0.88 V for the $[Ru(bipy)_2(bpdc)]^+$/$\{[Ru(bipy)_2(bpdc)]\}^*$ couple, similiar to that (−0.84 V) for $[Ru(bipy)_3]^{3+}$/$\{[Ru(bipy)_3]^{2+}\}^*$. The electronic absorption spectra of these complexes in water are as expected, all

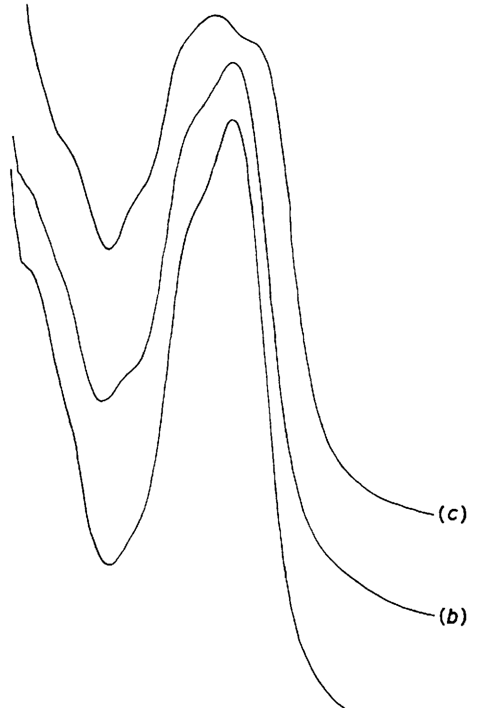


Figure 2. The electronic spectra in aqueous solution of (*a*) $[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}$, (*b*) $[Ru(bipy)(bp\text{-}4,4'\text{-}ds)_2]^{2-}$, and (*c*) $[Ru(bipy)_2(bp\text{-}4,4'\text{-}ds)]$

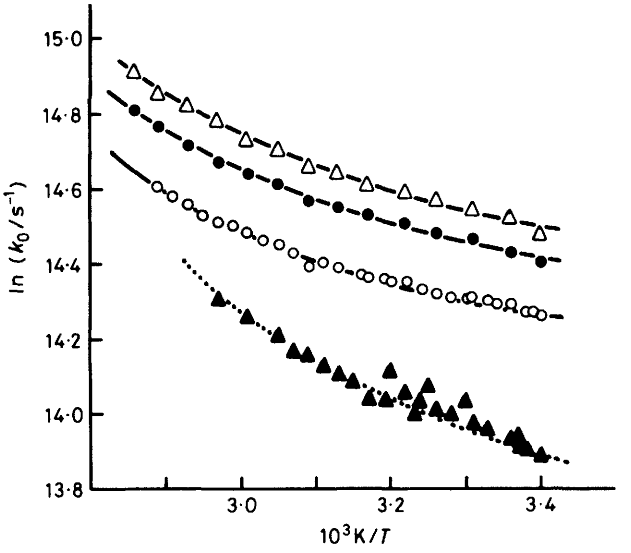


Figure 3. Temperature dependence of the rate constant for spontaneous decay of a selection of excited ruthenium(II) complexes (*ca.* 5 × 10^{-5} mol dm^{-3}) containing bpdc ligands: (○), {[Ru(bpdc)$_3$]$^{4-}$}*; (●), {[Ru(bipy)(bpdc)$_2$]$^{2-}$}*; (△), {[Ru(bipy)$_2$(bpdc)]}* in a NaOH–KH$_2$PO$_4$ buffer solution; (▲), {[Ru(dmbpdc)$_3$]$^{2+}$}*. The temperature dependence of the spontaneous decay of {[Ru(dmbpdc)$_3$]$^{2+}$}* is represented by a dashed line as this complex was found to be unstable, presumably with respect to hydrolysis of the ester groups, at high temperatures

exhibiting intense (ε ~ 10^4 dm^3 mol^{-1} cm^{-1}) metal ⟶ ligand (L) charge transfer [$(t_{2g})^6 \longrightarrow \pi_L$*] transitions in the range 21 300—23 200 cm^{-1}: typical spectra are illustrated in Figure 2. The emission spectra of the complexes all exhibit a single unresolved band in homogeneous aqueous solution, in the range 15 000—16 400 cm^{-1}. The ^{1}H n.m.r. spectrum of [Ru(bp-4,4′-ds)$_3$]$^{4-}$ in (CD$_3$)$_2$SO is illustrated in Figure 1. It exhibits an AB quartet (centred at 7.91 p.p.m.) due to the 5,5′ and 6,6′ protons, and a low-field singlet (8.82 p.p.m.) due to the 3,3′ protons. The low-field shift of the 3,3′-protons, which is characteristic of 2,2′-bipyridine derivatives co-ordinated to ruthenium,[30] is enhanced by the inductive effect of the adjacent -SO$_3^-$ groups.

Spontaneous Decay Measurements.—The bimolecular rate constant, k_q, for quenching of the excited states of the ruthenium(II) complexes was determined by subtracting the spontaneous decay constant, k_0, from the observed decay constant, k_{obs}, in the presence of a quencher, at concentration [Q], at each temperature: equation (1). Thus, determinations of

$$k_q = (k_{obs} - k_0)/[Q] \qquad (1)$$

the quenching constants required a prior determination of the k_0 values over a range of temperatures and Arrhenius plots for the latter are shown in Figure 3 for the compounds containing 2,2′-bipyridine-4,4′-dicarboxylate ligands, and in Figure 4 for those containing 2,2′-bipyridine-4,4′-disulphonate ligands. In order that the data may be readily used at a precision close to that obtained experimentally, the data were fitted to the quadratic expression (2) and the parameters *A*, *B*, and *C*, together with excited-state lifetimes ($\tau_0 = 1/k_0$) at 298 K are shown in Table 1. The value of τ_0 for {[Ru(bipy)$_2$(bpdc)]}* agrees well with the value of 0.52 μs reported by Gaines.[31]

$$\ln(k_0) = A + B/T + C/T^2 \qquad (2)$$

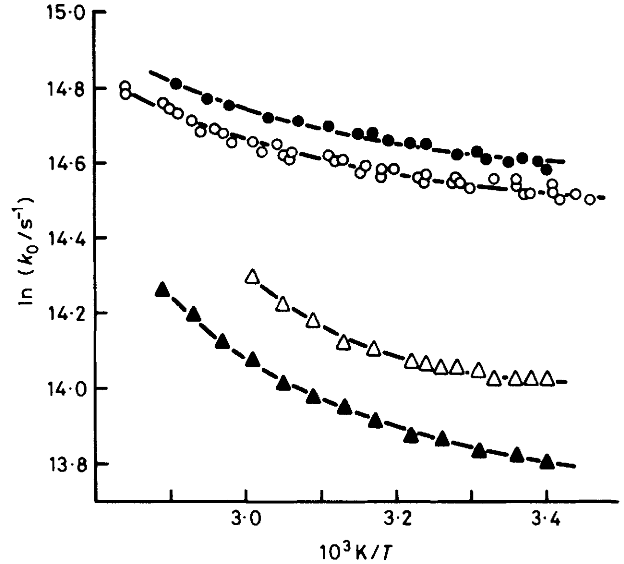


Figure 4. Temperature dependence of the rate constant for spontaneous decay of a selection of excited ruthenium(II) complexes (*ca.* 5 × 10^{-5} mol dm^{-3}) containing bp-4,4′-ds ligands: (●), {[Ru(bipy)(bp-4,4′-ds)$_2$]$^{2-}$}* in neutral aqueous solution; (○), {[Ru(bp-4,4′-ds)$_3$]$^{4-}$}* data from measurements in both neutral aqueous solution and 0.25 mol dm^{-3} H$_2$SO$_4$; (△), {[Ru(bp-4,4′-ds)$_3$]$^{4-}$}* in CH$_3$OH; (▲), {[Ru(bp-4,4′-ds)$_3$]$^{4-}$}* in D$_2$O

Table 1. Emission lifetimes[a] and quadratic coefficients[b] for some ruthenium(II) complex (*ca.* 5 × 10^{-5} mol dm^{-3}) excited states

Complex	*A*	$10^{-3}B$/K	$10^{-5}C$/K^2	τ_0/μs
[Ru(bipy)$_2$(bpdc)]^0	24.949	−5.8582	8.1913	0.53[c] 0.50[d]
[Ru(bipy)(bpdc)$_2$]$^{2-}$	24.692	−5.7979	8.1687	0.54
[Ru(bpdc)$_3$]$^{4-}$	25.367	−6.3460	9.0687	0.62
[Ru(dmbpdc)$_3$]$^{2+}$[e]				0.89
[Ru(bipy)(bp-4,4′-ds)$_2$]$^{2-}$	19.487	−2.6305	3.5122	0.46
[Ru(bp-4,4′-ds)$_3$]$^{4-}$	22.708	−4.7417	6.8677	0.48
[Ru(bp-4,4′-ds)$_3$]$^{4-}$ in MeOH				0.87
[Ru(bp-4,4′-ds)$_3$]$^{4-}$ in D$_2$O	33.415	−11.545	17.002	0.99

[a] At 298 K in aqueous solution unless otherwise stated. [b] Coefficients refer to the expression $\ln(k_0) = A + B/T + C/T^2$. [c] pH 3.5. [d] NaOH–KH$_2$PO$_4$ buffer solution, pH 7.4. [e] dmbpdc = dimethyl 2,2′-bipyridine-4,4′-dicarboxylate.

Some problems were encountered with the complex {[Ru(bipy)$_2$(bpdc)]^0}*, which was found to exhibit multiple luminescence at temperatures above 313 K. This presumably arose from independent emission from the free species and from the mono- and di-protonated forms.[32,33] The problem was overcome by studying the emission in a NaOH-KH$_2$PO$_4$ buffer solution (pH 7.4 at 298 K), which ensured that the protonation steps were suppressed.[32] Problems were also encountered with tris(dimethyl 2,2′-bipyridine-4,4′-dicarboxylate)ruthenium(II) dichloride which was found to be unstable, presumably with respect to ester hydrolysis at elevated temperatures; the data given for this complex in Figure 3 and Table 1 should, therefore, be treated with some caution. Figure 4 shows the dramatic effect on the lifetime of {[Ru(bp-4,4′-ds)$_3$]$^{4-}$}* of changing the solvent to D$_2$O or CH$_3$OH, suggesting that hydrogen bonding may be an important determinant in the decay processes of this excited state.[34] All of the complexes containing bp-4,4′-ds which

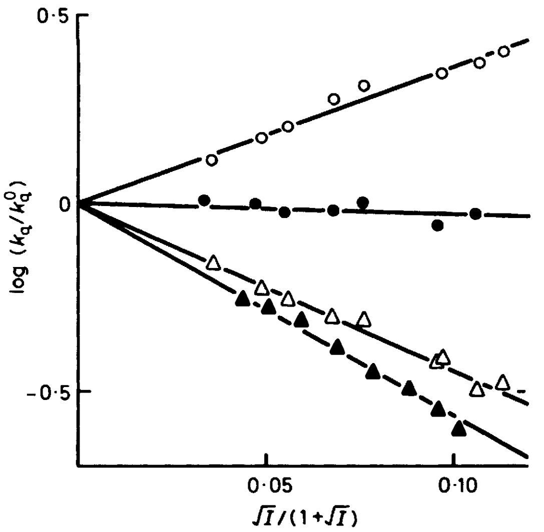


Figure 5. Variation with ionic strength of log (k_q/k_q^0) for the electron-transfer quenching of a series of excited ruthenium(II) complexes (*ca.* 5 × 10^{-5} mol dm^{-3}) by methyl viologen in aqueous solution at 298 K: (○), {[Ru(bipy)$_3$]$^{2+}$}*; (●), {[Ru(bipy)$_2$(bpdc)]}*; (△), {[Ru(bipy)(bp-4,4′-ds)$_2$]$^{2-}$}*; (▲), {[Ru(bp-4,4′-ds)$_3$]$^{4-}$}*

were investigated showed single exponential decays apart from {[Ru(bipy)$_2$(bp-4,4′-ds)]}*, which showed very weak emission with a multi-exponential decay. In consequence, results for this complex are not shown.

Ionic Strength Studies.—The incorporation of carboxylic or sulphonic acid groups in 2,2′-bipyridine ligands of ruthenium(II) complexes has allowed a series of complex ions to be produced with varying formal charges. Previous experimental work on the nature of the mechanism of electron transfer from excited ruthenium(II) complexes to aqueous copper(II) ions has been restricted to the use of dipositive ruthenium(II) complexes[8,35] and no attempt has been made to assess the importance of coulombic effects in the excited-state quenching mechanism. The high ionic strengths employed in previous work[8,35] would, in any case, have reduced the importance of such effects.

The effective charge carried by a reactant may be confirmed by studies of the dependence on ionic strength of the rate of its reaction with a charged quencher. The conventional Debye–Hückel–Brønsted relationship[36] may be used to correlate changes in the quenching rate constant with ionic strength according to equation (3), where k_q is the electron-transfer quenching rate constant, k_q^0 is the value of k_q corresponding to zero ionic strength, and A is the Debye–Hückel constant which is taken to be 0.51 for aqueous dilute solutions at 298 K. However, very low ionic strengths ($I < 0.01$ mol dm^{-3}) must be employed if the assumptions made in the formulation of equation (3) are to be valid. This places severe limitations on the amount

$$\log (k_q/k_q^0) = (2Az_1z_2\sqrt{I})/(1 + \sqrt{I}) \qquad (3)$$

of quencher that can be added to the system. For example, using Cu_{aq}^{2+} with a bimolecular quenching rate constant of *ca.* 10^8 dm^3 mol^{-1} s^{-1}, *ca.* 2 × 10^{-3} mol dm^{-3} of quencher is required to produce changes in the observed rate of luminescence decay of *ca.* 10%. Thus, quencher concentrations are required which are comparable to, or even greater than, the supporting electrolyte concentrations needed for the study of kinetic salt effects. A more satisfactory electron-transfer oxidant for the purposes of this study is methyl viologen (1,1′-dimethyl-4,4′-bipyridinium bromide), which quenches the {[Ru(bipy)$_3$]$^{2+}$}* luminescence with a bimolecular rate constant close to the diffusion-controlled limit.[37] {[Ru(bipy)$_2$(bpdc)]}* has also been shown to react with methyl viologen in aqueous solution at a comparable rate.[31] With quenching rate constants of the order of 10^9—10^{10} dm^3 mol^{-1} s^{-1}, only very small amounts of quencher are required to produce measurable changes in the observed rate of luminescence decay, and thus very low ionic strengths can be achieved. The use of methyl viologen has an additional advantage in that effects arising as a result of the generation of a range of complexed forms of the quencher are not expected. Logan[38] has demonstrated that diffusion-controlled reactions show the same dependence on ionic strength as activation-controlled reactions. Rate constants for the quenching of {[Ru(bipy)$_3$]$^{2+}$}* by a series of viologen salts have been shown to correlate well with the overall change in free energy of reaction as calculated using redox potentials, implying that these reactions are quite well categorised electron-transfer processes.[39]

Table 2. Excited-state electron-transfer quenching of {[Ru(bipy)$_3$]$^{2+}$}* and related complexes by methyl viologen: ionic strength dependence for aqueous solutions at 298 K

Complex	$10^{-9}k_q^0$/ dm^3 mol^{-1} s^{-1}	Slope[a] Expt.	Theory
[Ru(bipy)$_3$]$^{2+}$	0.28 ± 0.02	+3.8 ± 0.6	+4.08
[Ru(bipy)$_2$(bpdc)]	1.91 ± 0.28	−0.4 ± 1.0	0
[Ru(bipy)(bp-4,4′-ds)$_2$]$^{2-}$	15.9 ± 0.2	−4.5 ± 0.4	−4.08
[Ru(bp-4,4′-ds)$_3$]$^{4-}$	22.9 ± 0.2	−5.6 ± 0.4	−8.16

[a] Slope of a plot of log (k_q) *vs.* $\sqrt{I}/(1 + \sqrt{I})$ over a range of ionic strengths. Theoretically, this has a value $2Az_1z_2$ where $A = 0.51$, z_1 is the formal charge on the excited ruthenium(II) complex, and z_2 is the formal charge on the quencher (2+). Two standard deviations quoted. In calculating the ionic strengths, account has been taken of the concentration of ruthenium(II) complex present (5 × 10^{-5} mol dm^{-3}), the concentration of quencher ($< 10^{-3}$ mol dm^{-3}), and the concentration of added Na$_2$SO$_4$.

Figure 5 shows rate constants obtained for the quenching of four excited complexes of ruthenium(II) bearing charges +2, 0, −2, and −4 which were studied in aqueous solution at 298 K over a range of ionic strengths (varied in the range 10^{-3}—10^{-2} mol dm^{-3} with Na$_2$SO$_4$). The k_q^0 values, derived from linear least-squares fitting to plots of log (k_q) *vs.* $\sqrt{I}/(1 + \sqrt{I})$ are given in Table 2, together with the theoretical and experimentally derived values of the slopes of these plots (*i.e.* $2Az_1z_2$). These values for the quenching of {[Ru(bipy)$_3$]$^{2+}$}* by methyl viologen are in reasonable agreement with previously reported estimates of k_q^0, and z_1z_2 in aqueous solution,[40] although the slope of the plot in Figure 5 is much closer to the expected value of 4.08 than that of the earlier work. This is probably a consequence of the much lower ionic strengths employed in the present study.

A comparison of the behaviour observed experimentally and the predictions of the Debye–Hückel–Brønsted relationship shows good agreement for the excited complexes bearing charges of +2, 0, and −2, verifying that under these experimental conditions the expected overall charge is observed. The tendency for {[Ru(bipy)$_2$(bpdc)]}* to display a small negative ionic strength dependence in its reaction with methyl viologen has been observed previously,[31] and is probably due to its highly dipolar structure. For the reaction between {[Ru(bp-4,4′-ds)$_3$]$^{4-}$}* with methyl viologen, the agreement is less good. This could result from one, or all, of the following effects.

(*i*) As the charge on the ion increases the range of validity of

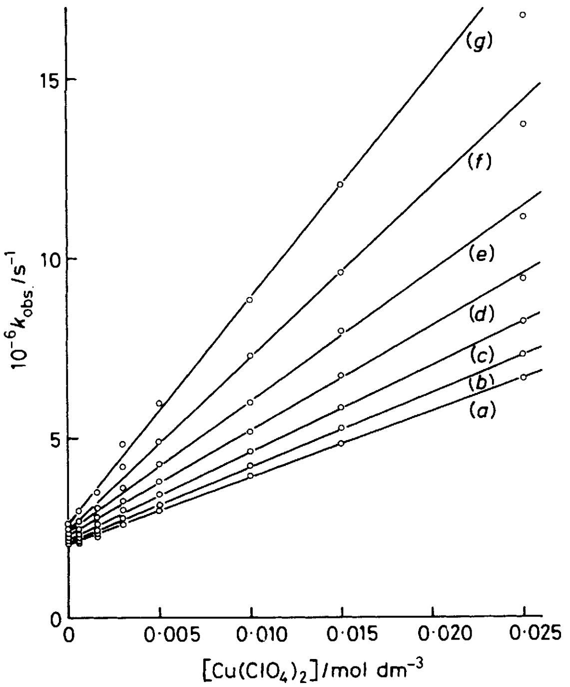


Figure 6. Variation of the observed rate constant of decay of $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ luminescence with concentration of copper(II) ions added as $Cu[ClO_4]_2$. Ionic strength maintained at 0.2 mol dm^{-3} using $NaClO_4$ as the supporting electrolyte at (*a*) 298, (*b*) 307, (*c*) 315, (*d*) 324, (*e*) 333, (*f*) 341, and (*g*) 350 K. The concentration of the ruthenium(II) complex was *ca.* 5 × 10^{-5} mol dm^{-3}

Debye–Hückel theory is reduced. For an ion carrying a charge −4, the radius of the ionic atmosphere at $\sqrt{I}$ = 0.05 is *ca.* 6 nm, whilst the distance at which an ion of charge −4 has an interaction energy, with an ion of charge +1, equal to k_BT (k_B = Boltzmann constant), is *ca.* 3 nm at 300 K. Thus the basic assumption which permits linearisation of the Boltzmann equation in Debye–Hückel theory is of questionable validity.

(*ii*) For an ion of charge −4, the assumption of a continuum dielectric, unaffected by the reactants, may not be valid.

(*iii*) A significant degree of protonation may occur, tending to reduce the overall charge.

The Reaction of $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ *with Aqueous Copper*(II) *Ions.*—Figure 6 shows the variation of the observed first-order rate constant for decay of $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ as a function of the concentration of $Cu[ClO_4]_2$ over the temperature range 298—350 K. Each measurement was made under identical conditions of ionic strength (I = 0.2 mol dm^{-3} maintained with $NaClO_4$ as the supporting electrolyte) and pH 5—6. No marked deviation from linearity can be discerned in the plots in Figure 6, each possessing a linear correlation coefficient ⩾0.995. The quenching rate constants derived from the slopes of these plots are presented in the form of an Arrhenius plot in Figure 7, which is clearly non-linear.

As the data refer to neutral aqueous solution it is possible that hydrolysis of the Cu^{2+}_{aq} ion might be responsible for this anomalous temperature dependence. Hydrolysis occurs to give a small amount of $[Cu(OH)]^+_{aq}$ in solution according to equations (4) and (5), and values of pK_1 of between 7.3 and 8.0

$$Cu^{2+}_{aq} + H_2O \rightleftharpoons [Cu(OH)]^+_{aq} + H_3O^+ \qquad (4)$$

$$K_1 = [Cu(OH)^+_{aq}][H_3O^+]/[Cu^{2+}_{aq}][H_2O] \qquad (5)$$

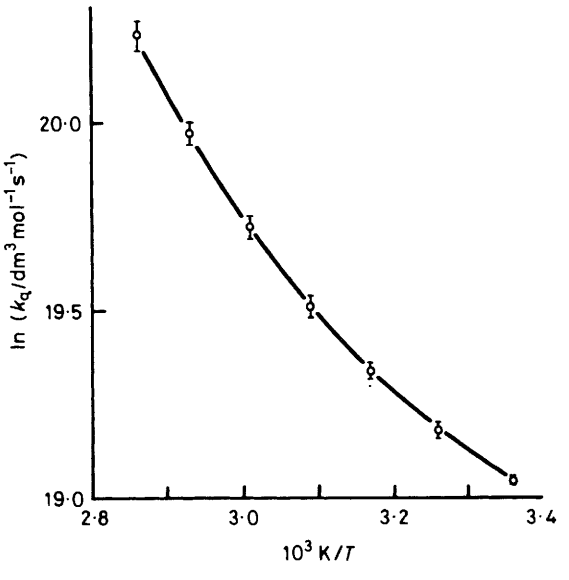


Figure 7. Temperature dependence of the rate constant for quenching of $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ (*ca.* 5 × 10^{-5} mol dm^{-3}) luminescence by aqueous copper(II) ions. Rate constants were obtained at each temperature by linear least-squares fitting to the plots shown in Figure 6. Error bars represent single standard deviations

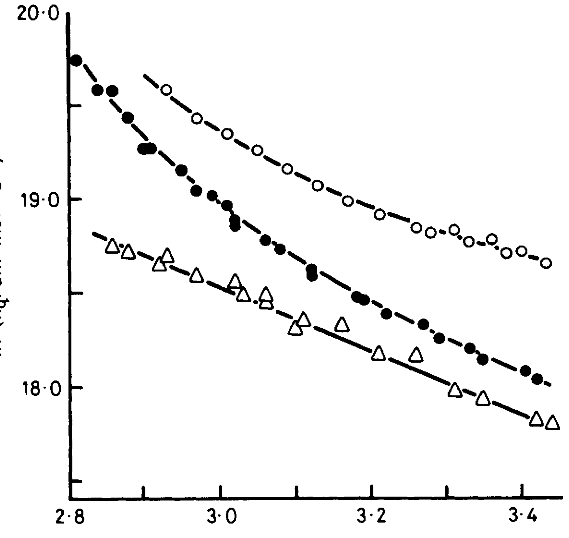
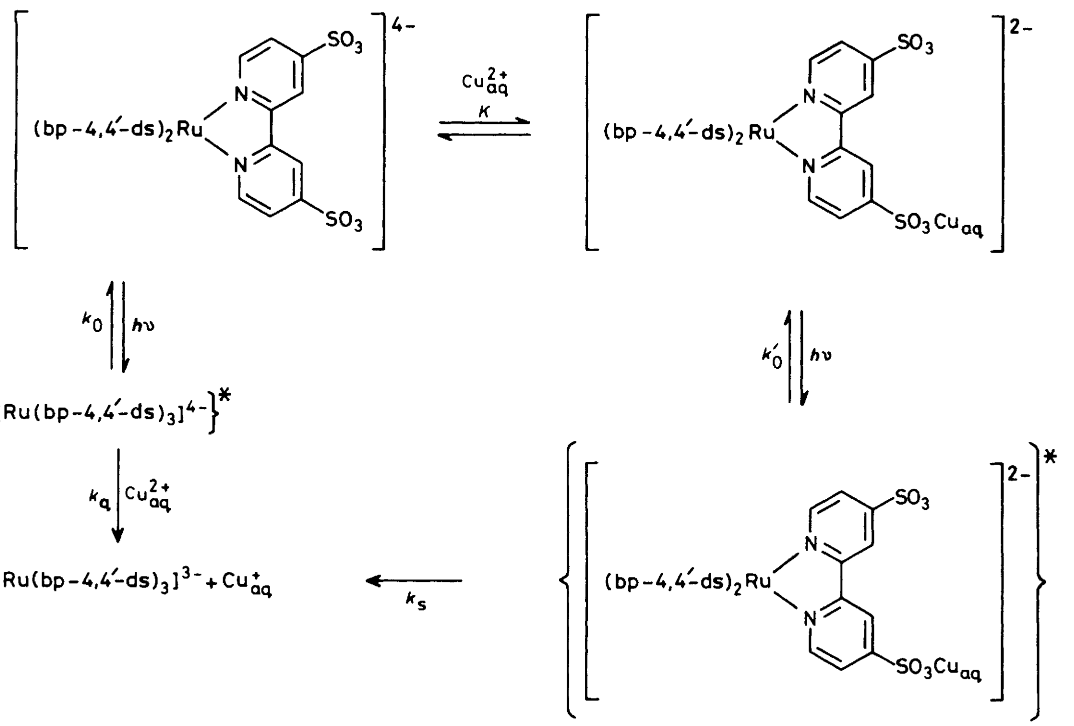


Figure 8. Temperature dependence of a selection of excited-state quenching reactions involving copper(II) ions, showing that the anomalous curvature arises as a consequence of the presence of SO_3^- substituents: (○), $\{[Ru(bipy)(bp\text{-}4,4'\text{-}ds)_2]^{2-}\}^*$ in neutral aqueous solution; (●), $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ in 0.25 mol dm^{-3} H_2SO_4; (△), $\{[Ru(bipy)_3]^{2+}\}^*$ in 0.25 mol dm^{-3} H_2SO_4 (data from ref. 8). In all cases copper(II) was added as the sulphate salt. For neutral solutions I = 0.2 mol dm^{-3}, while for acidic solution I = 0.8—1.0 mol dm^{-3}. The concentration of the ruthenium(II) complex was *ca.* 5 × 10^{-5} mol dm^{-3}

have been reported for zero ionic strength solutions.[41] At pH 6, 99% of the dissolved copper(II) is present as Cu^{2+}_{aq} [or Cu^{2+}_{aq} and $(CuSO_4)_{aq}$ for sulphate media] and less than 1% is present as the hydroxide,[42] and dissimilarities in the rates of quenching of $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ by Cu^{2+}_{aq} and $[Cu(OH)]^+_{aq}$, coupled with a temperature dependence of their relative concentrations, could account for the behaviour illustrated in Figure 7. This idea was examined by repeating the measurements in 0.25 mol



Scheme 3. A possible mechanism for the quenching of $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ by Cu^{2+}_{aq}, assuming static quenching *via* ground-state complex formation

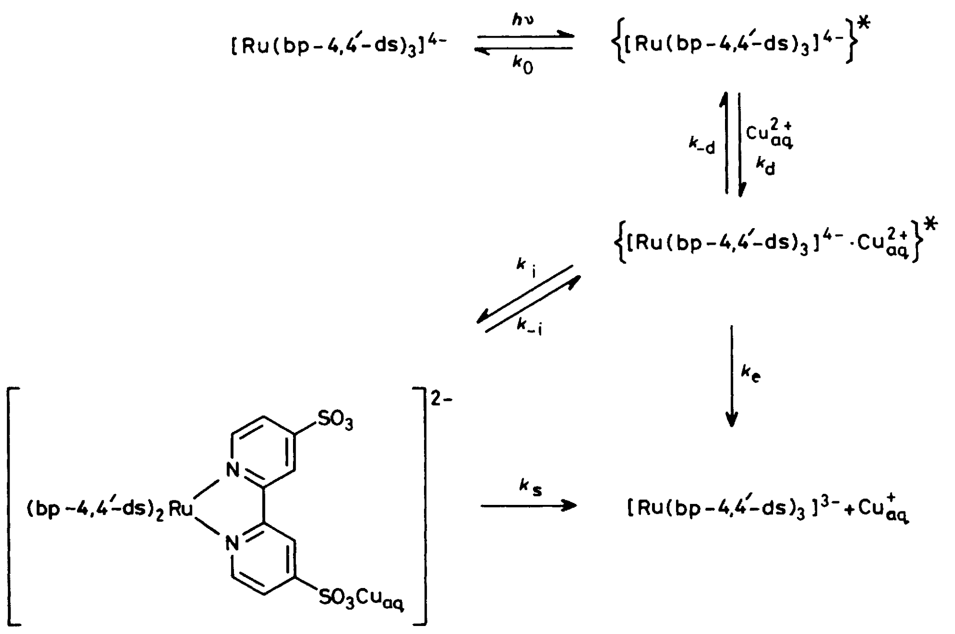
dm^{-3} H_2SO_4 ($I = 0.95$ mol dm^{-3}) in which the copper(II) will be present predominantly in the aqua or inner-sphere $(CuSO_4)_{aq}$ forms. The results are presented in Figure 8, and it is clear that the curvature persists in this system. Variable-temperature studies of the quenching of $\{[Ru(bipy)(bp\text{-}4,4'\text{-}ds)_2]^{2-}\}^*$ by copper(II) (added as the sulphate) in neutral aqueous solution and of $\{[Ru(bipy)_3]^{2+}\}^*$ by copper(II) in 0.25 mol dm^{-3} H_2SO_4 (data from ref. 8) are also included in Figure 8. It can be seen from these data that the anomalous behaviour appears to be related to the presence of SO_3^- substituents on the bipy ligands, and a specific interaction between ligand substituent and quencher is indicated. The likely mode of this interaction is now discussed.

Static Quenching.—The excitation of a complex formed in solution between the ground state of a luminescent species and its quencher leads to significant effects on the observed emission characteristics. If the associated complex decays very rapidly with respect to the decay of excited monomer, then the result will be observed in terms of anomalous upward curvature in a Stern–Volmer plot obtained from steady state measurements. This is known as static quenching, and may be contrasted with the dynamic quenching processes examined in earlier work.[8,35] Some evidence for static quenching phenomena has been obtained for systems involving the quenching of excited ruthenium(II) chelate complexes. Of particular relevance to the present work is the demonstration by Demas and Addington[43] of both dynamic and static processes in the quenching of the luminescence of dicyanobis(1,10-phenanthroline)ruthenium(II) by aqueous copper(II). The static quenching process arises from the interaction between ground-state $[Ru(phen)_2(CN)_2]$ and copper(II) ions *via* a CN bridge.[43] The separation of effects in such a system relies on the assumption that, while static quenching effects are observed in steady-state measurements (revealed by a linear increase in quenching rate constant with quencher concentration), the rapidity of the decay of the excited associated complex means that only dynamic quenching is observed in pulsed experiments. However, if the excited associated complex decays with a lifetime comparable with that of the excited monomer, *i.e.* that of the unassociated ruthenium(II) complex in the presence of quencher, some contribution from static quenching can be expected in luminescence lifetime measurements. This situation is illustrated in Scheme 3, in which a direct interaction between aqueous copper(II) ions and the SO_3^- substituents on the 2,2'-bipyridine ligands has been assumed.

In these circumstances the intensity of emitted light will be made up of two components according to equation (6) where α and β represent the fractions of the total light emitted by the

$$I(t) = \alpha \exp[-(k_0 + k_q[Q])t] + \beta \exp[-(k'_0 + k_s)t] \quad (6)$$

unassociated and associated excited complexes respectively, and will be related to the initial concentrations of the excited complexes in solution. The decay curves obtained using the single-photon counting technique for the $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*/Cu^{II}$ systems shown in Figure 6 were re-examined in an attempt to discover if multiple luminescence, suggested by the form of equation (6), was indirectly affecting the values of the derived decay rate constants, since marked differences in the temperature dependences of the time constants of each of the two components could lead to the curvature in the Arrhenius plot obtained experimentally. No such effects were found, the logarithmic forms of the luminescence decays appearing linear for more than three mean (1/e) lifetimes with values of the reduced chi-squared statistic,[44] χ_v^2, in the range $0.7 < \chi_v^2 < 1.3$, indicating satisfactory correspondence between the experimental decay curves and the fitted single-exponential functions. As we have discussed previously,[28] there are problems in unambiguously assigning bi-exponential behaviour if the decay constants are very similar. However, in the



Scheme 4. A mechanism for the quenching of $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ by Cu^{2+}_{aq}, in which parallel inner- and outer-sphere reactions occur

expression given by equation (6), the first decay constant is linearly dependent upon the concentration of copper(II) ions present in solution (which was varied by more than an order of magnitude), whilst the second decay constant should be independent of $[Cu^{2+}_{aq}]$. Differences of this order of magnitude should be discernible and static quenching occurring on the time-scale of the $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ decay would therefore appear to be unimportant. Further evidence against such an occurrence is the linearity of the plots in Figure 6. This observation does not exclude the possibility that the decay of a hypothetical excited complex formed by association of ground-state $[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}$ and Cu^{2+}_{aq} is present in the measured luminescence decays but with the characteristics of very fast decay with a lifetime comparable with the pulse width of the lamp ($\leqslant 3$ ns). However, such behaviour would not affect the measured decays and so it appears that only dynamic quenching processes are being studied. In consequence the anomalous temperature dependence cannot be ascribed to ground-state complex formation.

Parallel Inner- and Outer-sphere Mechanisms.—An alternative scheme to account for the observed curvature in the Arrhenius plot of Figure 7, which does not require behaviour leading to multi-exponential luminescence decay, is presented in Scheme 4. This kinetic scheme involves the interaction between SO_3^- groups and aqueous copper(II) ions only in the ruthenium(II) complex excited state, and is therefore a second dynamic quenching process which will operate in parallel with outer-sphere electron transfer. That such an interaction takes place only in the excited state is consistent with the view that excitation increases the basicity of the complex, as found in the study of the protonation of $\{[Ru(bipy)_2(bpdc)]\}^*$ by Wrighton and co-workers.[32a] In Scheme 4, k_d and k_{-d} are the forward and reverse rate constants, respectively, for formation of the reactant encounter complex, k_e is the rate constant for outer-sphere electron transfer to form products, k_i and k_{-i} are the forward and reverse rate constants for formation and dissociation of the inner-sphere complex, and k_s is the rate constant for formation of the electron-transfer products from the inner-sphere complex. This is identical to the mechanism proposed by Marshall and Pilling[45] to account for the temperature dependence of the quenching of triplet phenanthrene by lanthanide ions in solution and, following their arguments, the overall quenching rate constant may be expressed in the form of equations (7) and (8).

$$k_q = \frac{k_d k_e}{(k_d + k_i + k_e) - f k_i} + \frac{k_d k_i (1 - f)}{(k_d + k_i + k_e) - f k_i} \qquad (7)$$

$$\text{where } f = k_{-1}/(k_{-i} + k_s) \qquad (8)$$

Equation (7) may be greatly simplified by making some assumptions about the system.[45] For example, k_s is expected to be much greater than k_e because the inner-sphere reaction will be one involving a much greater donor–acceptor orbital overlap than the outer-sphere electron transfer. For the inner-sphere mechanism, the step involving penetration of the SO_3^- group into the primary co-ordination sphere of the aqueous copper(II) ion is expected to be rate-determining and so $k_s \gg k_{-i}$. The observed quenching rate constants are well below the diffusion-controlled limit, whence $k_{-d} \gg (k_i + k_e)$. Thus $f \sim 0$ and equation (9) applies, *i.e.* the bimolecular quenching rate constant

$$k_q \simeq (k_d/k_{-d})(k_i + k_e) \qquad (9)$$

comprises the constants of two rate processes relating to outer-sphere electron transfer and an inner-sphere path involving water displacement from aqueous copper(II). This may be written as equation (10) where $A_1 = (A_d/A_{-d})A_e$ and $A_2 = (A_d/A_{-d})A_i$. This formulation of the quenching rate constant is consistent with the experimental data as given in Figures 6 and 7. Table 3 provides the results of analyses of the reactions of $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ with copper(II) ions in three different media based on equation (10), using an iterative method to evaluate the four parameters.

$$k_q = A_1 \exp(-\Delta E_1/RT) + A_2 \exp(-\Delta E_2/RT) \qquad (10)$$

If the proposed mechanism, Scheme 4, is correct, then the activation parameters listed in Table 3 refer to outer-sphere electron transfer and water displacement from aqueous

Table 3. Rate constants and activation parameters for the quenching of $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ emission by copper(II) ions[a] at 298 K

Medium	Aqueous, pH 5—6	D_2O	0.25 mol dm^{-3} H_2SO_4
$10^{-7}k_q$/dm^3 mol^{-1} s^{-1}	18.7	16.2	7.53
$10^{-8}A_1$/dm^3 mol^{-1} s^{-1}	4.09	2.94	8.37
ΔE_1/kJ mol^{-1}	27.4	19.8	6.4
$10^{-14}A_2$/dm^3 mol^{-1} s^{-1}	1.75	5.71	17.1
ΔE_2/kJ mol^{-1}	38.0	41.5	46.5
$\Delta G_1^{\ddagger}$/kJ mol^{-1}	26.6	26.7	28.5
$\Delta H_1^{\ddagger}$/kJ mol^{-1}	0.2	−0.5	3.9
$\Delta S_1^{\ddagger}$/J K^{-1} mol^{-1}	−87	−91	−83
$\Delta G_2^{\ddagger}$/kJ mol^{-1}	29.7	30.2	32.6
$\Delta H_2^{\ddagger}$/kJ mol^{-1}	35.5	38.9	44.0
$\Delta S_2^{\ddagger}$/J K^{-1} mol^{-1}	+20	+29	+38

[a] Added as $Cu[ClO_4]_2$, $I = 0.2$ mol dm^{-3}, maintained with $NaClO_4$ except for the system in H_2SO_4, where $CuSO_4$ was used with $I = 0.95$ mol dm^{-3}. Errors in activation parameters are estimated to be 5—10%. Values of A_1, A_2, ΔE_1, and ΔE_2 have been obtained by iteratively fitting equation (10) to the data of Figures 7—9. Values of $\Delta G_n^{\ddagger}$, $\Delta H_n^{\ddagger}$, and $\Delta S_n^{\ddagger}$ (n = 1 or 2) have been derived using absolute rate theory as described previously (ref. 8).

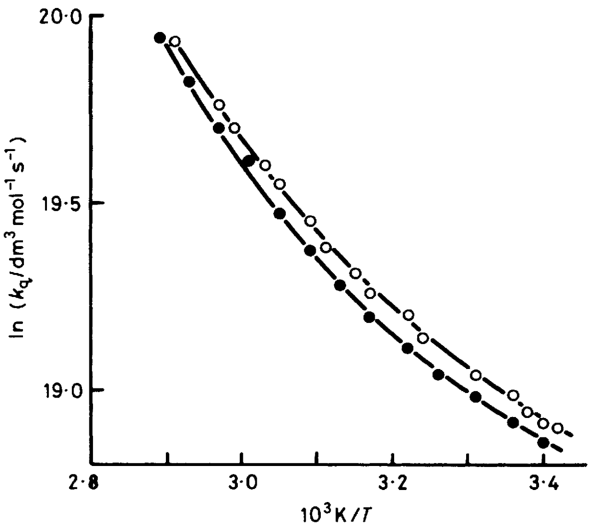


Figure 9. Temperature dependence of the quenching of $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ emission by copper(II) ions in (○) H_2O and (●) D_2O. Copper(II) added as the perchlorate salt in both cases, with $I = 0.2$ mol dm^{-3}. The concentration of the ruthenium(II) complex was *ca.* 5×10^{-5} mol dm^{-3}

copper(II) ions respectively. It is interesting to note that the free energy of activation for the outer-sphere reaction in 0.25 mol dm^{-3} H_2SO_4 is identical to that obtained for the quenching of $\{[Ru(bipy)_3]^{2+}\}^*$ by aqueous copper(II) ions and, indeed, these data can be seen to be subject to the same isokinetic effect.[8]

Displacement of water from Cu^{2+}_{aq} is very rapid due to Jahn–Teller distortion and the consequently low binding energies of two of the water molecules in the primary hydration sphere. The interchange rate constant within the Cu^{2+}_{aq},SO_4^{2-} ion pair is estimated to be $\geqslant 10^7$ s^{-1} at ambient temperatures,[41] indicating that the process involved in the proposed inner-sphere mechanism would be expected to be of this order of magnitude in agreement with experimental observations [*e.g.* in neutral aqueous solution $(k_d/k_{-d})k_i$ is estimated to be 3.9×10^7 dm^3 mol^{-1} s^{-1}]. Few activation parameters are available for copper(II) complex formation involving water displacement, and those that have been reported do not help to clarify the situation in any way.[41]

One unusual feature of the experimental activation parameters given in Table 3 is that, for the proposed inner sphere path, positive entropies of activation are obtained. This would seem to be reasonable if water molecules from the primary coordination sphere of Cu^{2+}_{aq} were being replaced by charged groups, as this will result in the removal of the negatively charged SO_3^- groups from the bulk solution. In addition, both the inner- and outer-sphere paths involve reaction between species of opposite charge, and thus large pre-exponential factors can be expected. Such behaviour is also a feature of the reactions involving the quenching of triplet phenanthrene by copper(II) ions, where a similar mechanism has been proposed.[45] It should also be noted that positive entropies of activation appear to be a feature of some inner-sphere electron-transfer reactions.[46]

Solvent Isotope Effects.—Some measurements were performed on D_2O solvent systems to ascertain the importance or otherwise of specific SO_3^-–solvent interactions (in this case the interaction between ligand substituents and the hydrogen atom of water). These measurements are given in Figure 9 and the activation parameters obtained from these data are presented in Table 3. As in the case for quenching of $\{[Ru(dmphen)_3]^{2+}\}^*$ (dmphen = 4,7-dimethyl-1,10-phenanthroline) by aqueous copper(II) ions, described in an earlier paper,[8] there is little difference between the energetics of this reaction in water and deuterium oxide. This would indicate that hydrogen-bonding interactions are absent or unimportant and that (if the explanation of the observed behaviour in terms of parallel outer- and inner-sphere paths applies) the rate of D_2O loss from $[Cu(D_2O)_6]^{2+}$ is comparable to that for water loss from $[Cu(H_2O)_6]^{2+}$.

Quenching of Excited Complexes containing 2,2′-*Bipyridine*-4,4′-*dicarboxylate Ligands by Aqueous Copper*(II) *Ions.*—The behaviour of excited states of ruthenium(II) complexes containing bpdc ligands with aqueous copper(II) ions was found to be in complete contrast to that observed for complexes containing bp-4,4′-ds ligands. Figure 10 gives some examples of the abnormal decay kinetics obtained for emission of the simplest of the complexes examined, $[Ru(bipy)_2(bpdc)]$, in the presence of various concentrations of Cu^{2+}_{aq}. In the absence of copper(II) [Figure 10(*a*)], the excited state decays in the expected manner at 298 K and a single exponential analysis yields τ_0 = 0.51 µs. Increasing the concentration of copper(II) is seen to increase the deviation of the form of the luminescence decay from the simple exponential decay law.

Referring to the arguments presented in the previous section, some form of static quenching is indicated by the curves in Figure 10. However, the decay curves do not conform to the bi-exponential decay law suggested by equation (6), and attempts to fit the data to a bi-exponential expression produced unsatisfactory results. The situation therefore appears to be more complex than that involving the 1 : 1 association of ground state $[Ru(bipy)_2(bpdc)]$ with Cu^{2+}_{aq}, which is the basis of the arguments leading to equation (6), and some form of aggregation is indicated. Abnormal decay kinetics have been observed for emission from $\{[Ru(bipy)_3]^{2+}\}^*$ in the presence of sodium dodecyl sulphate below the critical micelle concentration,[47] and self-quenching as a result of the formation of clusters containing several molecules of $[Ru(bipy)_3]^{2+}$ was proposed to account for the fast-decay component. Similar emission decay profiles were obtained for the decay of $\{[Ru(tmphen)_3]^{2+}\}^*$ in

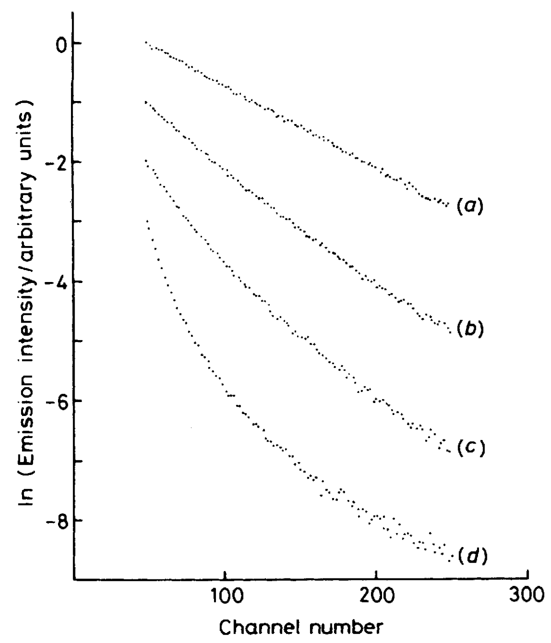


Figure 10. Emission decay profiles obtained at 298 K for $\{[Ru(bipy)_2$-$(bpdc)]\}^*$ (*ca.* 5×10^{-5} mol dm^{-3}) in the presence of various concentrations of aqueous copper(II) ions. Curves (*b*)—(*d*) have been offset for greater clarity. (*a*) The spontaneous decay of emission from $\{[Ru(bipy)_2(bpdc)]\}^*$ in the absence of copper(II), $\tau_0 = 513$ ns; (*b*) $[Cu^{2+}_{aq}] = 1.13 \times 10^{-3}$ mol dm^{-3}; (*c*) $[Cu^{2+}_{aq}] = 2.51 \times 10^{-3}$ mol dm^{-3}; and (*d*) $[Cu^{2+}_{aq}] = 7.6 \times 10^{-3}$ mol dm^{-3}. Copper(II) was added to the system as the perchlorate salt. Only every second channel is shown (3.551 ns per channel)

the presence of large quantities of sulphate ions,[8] where, in extreme cases, some precipitation was observed. The direct interaction between copper(II) ions and the carboxylic acid groups on the substituted 2,2′-bipyridine ligand can be inferred from the data shown in Figure 10. The fact that such behaviour is not observed in the reactions between complexes containing bp-4,4′-ds ligands and copper(II) is further indication that static quenching in the latter systems is not responsible for the anomalous temperature dependence of the quenching rate constant shown in Figure 7.

It is important to note that addition of increasing quantities of $Cu[ClO_4]_2$ to the system $[Ru(bipy)_2(bpdc)]$ in water did have a noticeable effect on the pH of the solution. This effect presumably arises due to hydrolysis of the $[Cu(H_2O)_6]^{2+}$ ion, as given by equation (4). However, the increasing deviation from an exponential decay law for $\{[Ru(bipy)_2(bpdc)]\}^*$ luminescence with increasing copper(II) concentration, as shown in Figure 10, cannot be explained by either the pH changes, or the presence of small amounts of $[Cu(OH)]^+_{aq}$. With regard to the pH effect, non-exponential decays for $\{[Ru(bipy)_2(bpdc)]\}^*$ luminescence were only observed at temperatures above 313 K; the luminescence decays at pH 3.5 and 7.4 obeyed the simple decay law at 298 K, demonstrating that pH changes of this kind have no effect on the form of the decay law. The effect of the presence of $[Cu(OH)]^+_{aq}$ would be to provide a second dynamic quenching channel, as discussed in connection with the experimental results on the quenching of $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$, and would not be expected to affect the form of the decay law unless, perhaps, by increasing the ground-state interaction between $[Ru(bipy)_2(bpdc)]$ and copper(II) ions.

Lifetime Studies.—Summary and conclusions. The spontaneous decay data presented in Figures 3 and 4 are consistent with the interpretation of Ferguson *et al.*[33] that the presence of electron-withdrawing substituents on the bipy ligands results in the localisation of the excited electron on those ligands in complexes such as $\{[Ru(bipy)_2(bpdc)]\}^*$. This is reflected in the fact that the temperature dependences of k_0 for each of the excited complexes studied containing bp-4,4′-ds or bpdc ligands are all very similar and yet different to the behaviour exhibited by $\{[Ru(bipy)_3]^{2+}\}^*$.[8]

The ionic strength studies using methyl viologen as an electron acceptor and the excited states of $[Ru(bipy)_3]^{2+}$, $[Ru(bipy)_2(bpdc)]$, $[Ru(bipy)(bp\text{-}4,4'\text{-}ds)_2]^{2-}$, and $[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}$ as electron donors have shown that the effective charges of these excited complexes affect the rate constant associated with electron-transfer quenching in a manner that can be understood in terms of conventional Debye–Hückel–Brønsted theory. These studies have helped to verify that the expected formal charges correlate very well with the effective charges displayed by the excited complexes in solution.

The quenching of $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ by aqueous copper(II) ions exhibits unusual behaviour which has been interpreted in terms of a parallel inner- and outer-sphere quenching mechanism. Interference effects arising from static quenching have been shown not to be responsible for the observed behaviour. The data therefore indicate that a stronger inner-sphere interaction is obtained between $\{[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}\}^*$ and Cu^{2+}_{aq} than for ground-state $[Ru(bp\text{-}4,4'\text{-}ds)_3]^{4-}$ and Cu^{2+}_{aq}, consistent with the previous conclusions of Wrighton and co-workers[32a] regarding the basicity of excited complexes containing ligands bearing such electron-withdrawing substituents.

Acknowledgements

We wish to thank the S.E.R.C. for the awards of several equipment grants (to M. J. P. and K. R. S.), research fellowships (to J. E. B. and E. C. C.), and an advanced fellowship (to K. R. S.). We also wish to thank the Central Electrical Generation Board for the awards of studentships (to S. A. and J. E. T.) and for generous financial support.

References

1 K. R. Seddon, *Coord. Chem. Rev.*, 1981, **35**, 41; 1982, **41**, 79.
2 E. A. Seddon and K. R. Seddon, 'The Chemistry of Ruthenium,' Elsevier, Amsterdam, 1984, ch. 15.
3 N. Sutin, *J. Photochem.*, 1979, **10**, 19.
4 J-M. Lehn, J-P. Sauvage, and R. Ziessel, *Nouv. J. Chim.*, 1979, **3**, 423.
5 W. J. Albery and A. W. Foulds, *J. Photochem.*, 1979, **10**, 41.
6 B. Durham, W. J. Dressick, and T. J. Meyer, *J. Chem. Soc., Chem. Commun.*, 1979, 381.
7 W. J. Albery, W. R. Bowen, F. S. Fisher, and A. D. Turner, *J. Electronal. Chem. Interfacial Electrochem.*, 1980, **107**, 11.
8 J. E. Baggott and M. J. Pilling, *J. Phys. Chem.*, 1980, **84**, 3012.
9 J. E. Baggott and M. J. Pilling, *J. Chem. Soc., Faraday Trans. 1*, 1981, 261.
10 See, for example, C. R. Bock, J. A. Connor, A. R. Gutierrez, T. J. Meyer, D. G. Whitten, B. P. Sullivan, and J. K. Nagle, *Chem. Phys. Lett.*, 1979, **61**, 522.
11 R. A. Marcus, *Ann. Rev. Phys. Chem.*, 1964, **15**, 155.
12 O. S. Otroshchenko, Yu. V. Kurbatov, and A. S. Sadykov, *Nauchn. Tr., Tashk. Gos. Univ.*, 1964, **263**, 27.
13 Yu. V. Kurbatov, O. S. Otroshchenko, and A. S. Sadykov, *Nauchn. Tr., Tashk. Gos. Univ.*, 1964, **263**, 36.
14 N. H. Pirzhada, O. M. Pojer, and L. A. Summers, *Z. Naturforsch., Teil B*, 1976, **31**, 115.
15 P. M. Pojer and L. A. Summers, *Z. Naturforsch., Teil B*, 1975, **30**, 980.
16 S. Anderson and K. R. Seddon, *J. Chem. Res. S*, 1979, 74.
17 G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *J. Am. Chem. Soc.*, 1977, **99**, 4947.
18 B. P. Sullivan, D. Salmon, and T. J. Meyer, *Inorg. Chem.*, 1978, **17**, 3334.
19 J. Haginiwa and Y. Higuchi, *Yakugaku Zasshi*, 1973, **93**, 144.

20 A. Vinciguerra, P. G. Simpson, and J. V. Quagliano, *Inorg. Chem.*, 1963, **2**, 282.

21 (*a*) G. Maerker and F. H. Case, *J. Am. Chem. Soc.*, 1958, **80**, 2745; (*b*) J. Haginiwa, *Yakugaku Zasshi*, 1955, **75**, 733.

22 F. H. Case, *J. Am. Chem. Soc.*, 1946, **68**, 2574.

23 A. E. W. Knight and B. K. Selinger, *Aust. J. Chem.*, 1973, **26**, 1.

24 C. Lewis, W. R. Ware, L. J. Doemeny, and T. L. Nemzek, *Rev. Sci. Instrum.*, 1973, **44**, 107.

25 E. Klingsberg, (ed.), 'Pyridine and its Derivatives,' Wiley-Interscience, New York, 1961, and later supplements.

26 M. Blesa and H. Taube, *Inorg. Chem.*, 1975, **15**, 1454.

27 D. Rose and G. Wilkinson, *J. Chem. Soc. A*, 1970, 1791; D. N. Klassen, *Inorg. Chem.*, 1976, **15**, 3166.

28 J. E. Baggott, G. K. Gregory, M. J. Pilling, S. Anderson, K. R. Seddon, and J. E. Turp, *J. Chem. Soc., Faraday Trans. 2*, 1983, 195.

29 C-T. Lin, W. Böttcher, M. Chou, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, 1976, **98**, 6536.

30 E. C. Constable and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 1982, 34.

31 G. L. Gaines, jun., *J. Phys. Chem.*, 1979, **83**, 3088.

32 (*a*) P. J. Giordano, C. R. Bock, M. S. Wrighton, L. V. Interrante, and R. F. X. Williams, *J. Am. Chem. Soc.*, 1977, **99**, 3187; (*b*) K-P. Seefeld, D. Möbius, and H. Kuhn, *Helv. Chim. Acta*, 1977, **60**, 2608.

33 J. Ferguson, A. W-H. Mau, and W. H. F. Sasse, *Chem. Phys. Lett.*, 1979, **68**, 21.

34 J. Van Houten and R. J. Watts, *J. Am. Chem. Soc.*, 1975, **97**, 3843; 1976, **98**, 4853.

35 M. A. Hoselton, C-T. Lin, H. A. Schwarz, and N. Sutin, *J. Am. Chem. Soc.*, 1978, **100**, 2383.

36 J. N. Brønsted, *Z. Phys. Chem.*, 1922, **102**, 169.

37 C. R. Bock, J. A. Connor, A. R. Gutierrez, T. J. Meyer, D. G. Whitten, B. P. Sullivan, and J. K. Nagle, *J. Am. Chem. Soc.*, 1979, **101**, 4815.

38 S. R. Logan, *Trans. Faraday Soc.*, 1966, **62**, 3416.

39 E. Amouyal, B. Zidler, P. Keller, and A. Moradpour, *Chem. Phys. Lett.*, 1980, **74**, 314.

40 M. A. J. Rogers and J. C. Becker, *J. Phys. Chem.*, 1980, **84**, 2762.

41 J. Burgess, 'Metal Ions in Solution,' Ellis Horwood, Chichester, 1978.

42 A. J. Paulson and D. R. Kester, *J. Soln. Chem.*, 1980, **9**, 269.

43 J. N. Demas and J. W. Addington, *J. Am. Chem. Soc.*, 1974, **96**, 3663.

44 P. R. Bevington, 'Data Reduction and Error Analysis for the Physical Sciences,' McGraw-Hill, New York, 1969.

45 E. J. Marshall and M. J. Pilling, *J. Chem. Soc., Faraday Trans. 2*, 1978, 579.

46 F. S. Dainton, *Discuss. Faraday Soc.*, 1960, **29**, 125; D. Bunn, F. S. Dainton, and S. Duckworth, *Trans. Faraday Soc.*, 1961, **57**, 1131.

47 J. H. Baxendale and M. A. J. Rogers, *Chem. Phys. Lett.*, 1980, **72**, 424.

Received 22nd November 1984; *Paper* 4/1991