A dinuclear bis(bipyridine)ruthenium(II) complex, [(bpy)₂Ruᴵᴵ{L²⁻}Ruᴵᴵ(bpy)₂]²⁺, incorporating an unusual non-innocent bridging ligand containing a *p*-benzoquinonediimine fragment: synthesis, structure, redox, and UV/VIS/NIR and EPR spectroelectrochemical properties

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The reaction of [Ru(bpy)₂(EtOH)₂]²⁺ (bpy = 2,2′-bipyridine) with the symmetrical binucleating phenolatodiimine ligand HOC₆H₄N=CHC₆H₄CH=NC₆H₄OH (H₂L¹) in ethanol under dinitrogen results in the unexpected formation of the diruthenium complex [(bpy)₂Ruᴵᴵ{OC₆H₄N=C₆H₃(=NH)O}Ruᴵᴵ(bpy)₂](ClO₄)₂ **1**. In this complex, the bridging ligand (Lˢq,ˢq)²⁻ contains two inequivalent *o*-iminophenolate N,O-chelating binding sites, each formally at the semi-quinone oxidation level, linked such that there is a *p*-benzoquinonediimine bridge between the two Ru centres. The crystal structures of H₂L¹ and of **1** have been determined. Complex **1** is electrochemically active and undergoes two reversible oxidations and two reversible reductions which, on the basis of UV/VIS/NIR and EPR spectroelectro-chemical evidence, comparison with related systems and consideration of the redox potentials, we assign as centred on the bridging ligand. The two oxidations (at +0.12 and +0.35 V *versus* SCE) result in formation of a neutral, fully quinonoidal bridging ligand Lq,q; in the 'mixed-valence' mono-oxidised state, a near-IR transition (1570 nm) is ascribed to an intra-ligand charge transfer from the non-oxidised (semiquinone-like) to the oxidised (quinone-like) terminus. The two reductions (at −0.98 and −1.38 V *versus* SCE) are localised on the central *p*-benzoquinonediimine unit of the bridging ligand, affording the *p*-benzosemiquinone radical and then a *p*-diamide unit. In addition, at more extreme potentials, two oxidations at +1.49 and +1.70 V *versus* SCE are ascribed to Ru(II)/Ru(III) couples, and the reduction at −1.81 V *versus* SCE is bpy-based.

Introduction

The metal ion-mediated transformation of organic molecules is known to be a fundamentally important chemical process which leads to the formation of unusual products otherwise difficult, or even impossible, to synthesize by following conventional synthetic routes.[1] In the present article we report an unusual reaction where the diimine-based potentially bridging ligand H₂L¹ is selectively transformed into (L²⁻) (see Scheme 1) on coordination to {Ru(bpy)₂}²⁺ fragments, affording the unusual dinuclear complex [(bpy)₂Ruᴵᴵ{μ-L}-Ruᴵᴵ(bpy)₂](ClO₄)₂ (**1**). To the best of our knowledge, the present work demonstrates for the first time how coupling of *ortho*-aminophenol moieties can lead to unusual new bridging ligands.

Polynuclear ruthenium polypyridyl complexes are currently of interest for both their electrochemical and photophysical properties, which lead to potential uses in diverse areas such as photosensitisers for photochemical conversion of solar energy,[2] molecular electronic devices[3] and as photoactive DNA cleavage agents for therapeutic purposes.[4] The degree of electronic communication between the metal centres through the bridging ligand controls the ground and excited state properties of such complexes. Therefore, the development of polynuclear metal complexes incorporating new types of bridging ligand, which can mediate electronic coupling through their π-symmetry orbitals by either electron-transfer or hole-transfer mechanisms, is an area of considerable interest.[5]

Herein, we report the synthesis of the new complex **1**, its structure, redox and spectroscopic properties, and the results of a spectroelectrochemical study spanning five oxidation states which shows that the extensive redox activity is centred on the bridging ligand.

Results and discussion

Synthesis and characterisation of complex 1

The ligand H₂L¹, with potentially two iminophenol bidentate compartments, was prepared by condensation of terephthalde-hyde with 2-aminophenol in a molar ratio of 1 : 2 in absolute ethanol. In addition to a satisfactory elemental analysis, the single crystal X-ray structure of H₂L¹ was obtained and is shown in Fig. 1. The presence of an inversion centre at the middle of the central phenyl ring makes the two halves of H₂L¹ equivalent; bond distances and angles are unremarkable. The
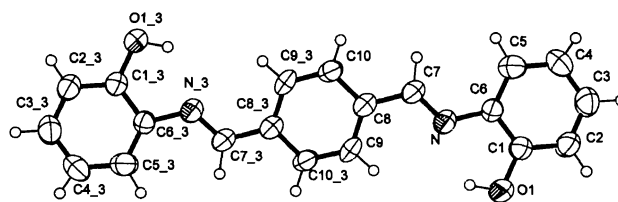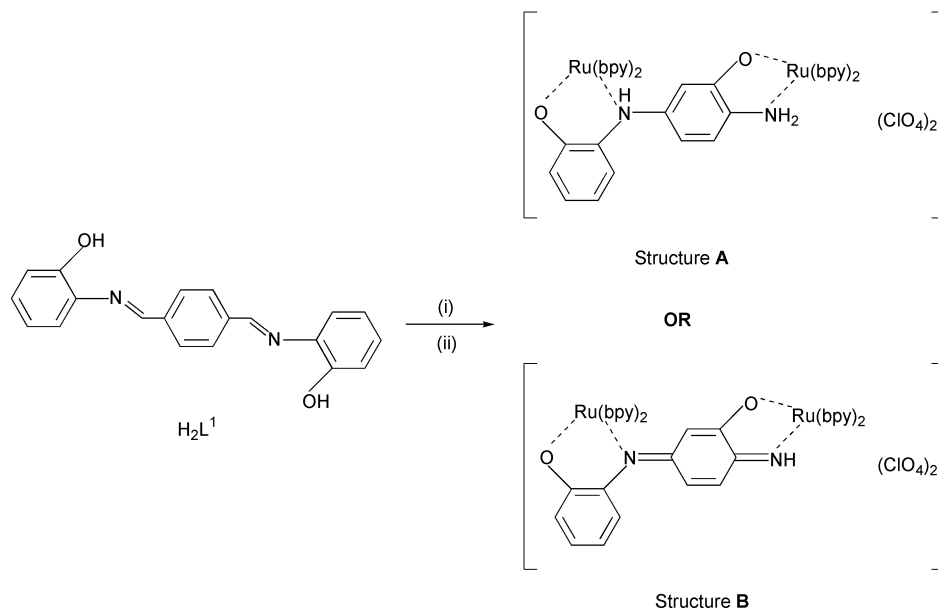

Fig. 1 Crystal structure of H₂L¹; 50% probability ellipsoids.

DOI: 10.1039/b107307a

Scheme 1   (i) [Ru(bpy)$_2$(EtOH)$_2$]$^{2+}$, CH$_3$COONa; (ii) Aqueous NaClO$_4$. Structure **B** is the correct formulation of complex **1** (see main text).

^{1}H NMR spectrum of H$_2$L^1 in (CD$_3$)$_2$SO confirms the two-fold symmetry: although not all of the signals are individually resolved, the correct number of signals consistent with the structure are observed and some assignments are possible (see Experimental section).

Reaction of H$_2$L^1 with [Ru(bpy)$_2$(EtOH)$_2$]$^{2+}$ (bpy = 2,2′-bipyridine) in the presence of sodium acetate in dry ethanol for 12 h affords a dark violet solution, from which pure complex **1** was isolated as its perchlorate salt in 60% yield by chromatographic purification on alumina. In complex **1**, the initial bridging ligand H$_2$L^1 has been selectively transformed into the new bridging ligand (L)$^{2-}$, in which hydrolysis of the imine groups of H$_2$L^1 followed by intermolecular head-to-tail oxidative coupling of the resultant aminophenol fragments leads to formation of the new N–C bond of (L)$^{2-}$ (Scheme 1, structure **B**). We note that this process appears to be very similar to that which occurs in the oxidative polymerisation of aniline to polyaniline;[6] the closely related molecule *o*-methoxyaniline also undergoes oxidative coupling in this way.[7]

The nature of this new complex was not immediately obvious, as its analysis and mass spectrum did not accord with any simple complex based on the starting ligand H$_2$L^1. Identification of the complex was achieved by determining the crystal structure (Fig. 2; see also Tables 1 and 2), which shows a di-
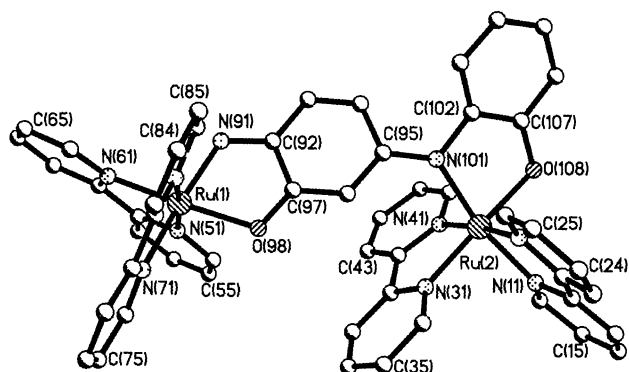

Fig. 2   Crystal structure of the dinuclear dication of complex **1**.

nuclear complex consisting of two {Ru(bpy)$_2$}$^{2+}$ fragments connected by a bis(N,O-bidentate) bridging ligand, as shown in Scheme 1; in addition to the complex cation, the unit cell also contains two perchlorate anions and two water molecules that are hydrogen bonded to the perchlorate ions [the non-bonded O(30) · · · O(12) and O(31) · · · O(23) separations are 2.78 and 2.94 Å, respectively, typical of O–H · · · O hydrogen-bonding interactions].

On the basis of the connectivity and the charge on the complex cation (+2), there are actually two possibilities for the structure of the complex, as shown in Scheme 1: the reduced *p*-diamine form (structure **A**), or the oxidised *p*-benzoquinonediimine (*p*-bqdi) form (structure **B**), depending on the degree of oxidation that occurs during coupling of the 2-aminophenol fragments (polyaniline can in fact contain varying numbers of *p*-diamine and *p*-bqdi units depending on the conditions used to prepare it).[6] Careful examination of the structural parameters allows structure **B** to be identified as the correct one. The most obvious indicator of the ligand oxidation state is the short Ru(1)–N(91) separation of 2.002(8) Å, which is typical of the short bonds that occur between Ru(II) and imine-type ligands, due to the π back-bonding interaction;[8,9] these are much shorter than typical Ru(II)–N separations for an amine ligand (2.1–2.2 Å).[10] The corresponding bond length Ru(2)–N(101) at the alternate metal is rather longer, at 2.077(8) Å, but this is simply ascribable to a steric effect at this much more hindered site. Such stretching of a Ru–N bond to accommodate adjacent bulky substituents is commonplace in complexes of *e.g.* 6-substituted pyridines;[11] the 'unhindered' Ru(1)–N(91) separation of 2.002(8) Å is therefore a more reliable indicator of the oxidation state of the ligand. In addition, the expected arrangement of formally single and double bonds for a quinonoidal system in the bridging *p*-bqdi fragment is apparent. For example the C=N double bonds C(92)–N(91) and C(95)–N(101) have lengths of 1.331(12) and 1.345(12) Å respectively, whereas the single bond C(102)–N(101) has a length of 1.429(11) Å. The C–C/C=C separations around the ring C(92)–C(97) follow the expected 'quinone-like' pattern (Table 2), whereas in the other ring [C(102)–C(107)], all of the C–C separations are much closer to one another, as befits an aromatic ring. Other factors such as C–O, Ru–O and Ru–N separations can be indicative to some extent of ligand oxidation state in complexes of this type,[12] but for ruthenium complexes in particular, the variations are not large and the relatively high e.s.d.'s of the parameters in this structure preclude such an analysis. The structural parameters of the bridging *p*-bqdi fragment are however sufficient to show that structure **B** in Scheme 1 is the correct canonical form, with a double C=N and single C–O bond and a single negative charge associated with each binding site.

In addition to the crystal structure, confirmation of the

Table 1 Crystallographic data for H_2L^1 and $1 \cdot 2H_2O$

Compound	H_2L^1	$1 \cdot 2H_2O$
Empirical formula	$C_{20}H_{16}N_2O_2$	$C_{52}H_{44}Cl_2N_{10}O_{12}Ru_2$
Fw	316.34	1274.01
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
$a/Å$	8.5030(15)	12.320(4)
$b/Å$	6.008(4)	14.781(5)
$c/Å$	15.527(3)	15.394(5)
$a/°$	90	83.096(5)
$\beta/°$	92.090(10)	77.626(5)
$\gamma/°$	90	73.646(5)
$V/Å^3$	792.7(6)	2622.1(14)
Z	2	2
Instrument used	Nonius MACH3	Bruker SMART-CCD
T/K	293(2)	173(2)
$\rho_{calcd}/g\ cm^{-3}$	1.325	1.614
Absorption coefficient/mm^{-1}	0.087	0.751
Data, restraints, parameters	1399, 0, 141	9228, 0, 703
Final R_1, wR_2	0.0574, 0.1708	0.0772, 0.1912

Table 2 Selected bond distances (Å) and angles (°) for $1 \cdot 2H_2O$

Ru(1)–N(91)	2.002(8)	Ru(2)–N(41)	2.025(10)
Ru(1)–N(51)	2.038(8)	Ru(2)–N(21)	2.028(10)
Ru(1)–N(61)	2.038(9)	Ru(2)–N(31)	2.037(7)
Ru(1)–N(81)	2.051(7)	Ru(2)–N(11)	2.059(10)
Ru(1)–N(71)	2.054(7)	Ru(2)–O(108)	2.073(7)
Ru(1)–O(98)	2.093(6)	Ru(2)–N(101)	2.077(8)
N(91)–Ru(1)–N(51)	90.4(3)	N(41)–Ru(2)–N(21)	173.6(3)
N(91)–Ru(1)–N(61)	95.6(3)	N(41)–Ru(2)–N(31)	79.2(3)
N(51)–Ru(1)–N(61)	78.4(4)	N(21)–Ru(2)–N(31)	94.5(3)
N(91)–Ru(1)—N(81)	94.9(3)	N(41)–Ru(2)–N(11)	98.9(4)
N(51)–Ru(1)–N(81)	174.4(3)	N(21)–Ru(2)–N(11)	79.8(4)
N(61)–Ru(1)–N(81)	99.0(3)	N(31)–Ru(2)–N(11)	89.0(3)
N(91)–Ru(1)–N(71)	171.3(3)	N(41)–Ru(2)–O(108)	94.9(4)
N(51)–Ru(1)–N(71)	96.7(3)	N(21)–Ru(2)–O(108)	91.3(3)
N(61)–Ru(1)–N(71)	90.8(3)	N(31)–Ru(2)–O(108)	172.9(3)
N(81)–Ru(1)–N(71)	78.3(3)	N(11)–Ru(2)–O(108)	88.1(3)
N(91)–Ru(1)–O(98)	79.1(3)	N(41)–Ru(2)–N(101)	86.3(3)
N(51)–Ru(1)–O(98)	96.4(3)	N(21)–Ru(2)–N(101)	96.2(3)
N(61)–Ru(1)–O(98)	172.6(3)	N(31)–Ru(2)–N(101)	103.0(3)
N(81)–Ru(1)–O(98)	86.6(3)	N(11)–Ru(2)–N(101)	167.7(3)
N(71)–Ru(1)–O(98)	95.0(2)	O(108)–Ru(2)–N(101)	80.3(3)
N(91)–C(92)	1.331(12)	N(101)–C(102)	1.429(11)
C(92)–C(93)	1.430(13)	C(102)–C(103)	1.398(14)
C(92)–C(97)	1.456(12)	C(102)–C(107)	1.394(16)
C(93)–C(94)	1.359(14)	C(103)–C(104)	1.370(15)
C(94)–C(95)	1.481(13)	C(104)–C(105)	1.39(2)
C(95)–C(96)	1.398(12)	C(105)–C(106)	1.379(18)
C(96)–C(97)	1.375(12)	C(106)–C(107)	1.414(15)
C(97)–O(98)	1.309(10)	C(107)–O(108)	1.343(14)
C(95)–N(101)	1.345(12)		

structure of complex **1** was provided by its electrospray mass spectrum, which shows a molecular ion centred at m/z 1240, corresponding to the intact molecule with both perchlorate anions, and a much stronger peak at m/z 520 for the doubly-charged cation $\{C_{52}H_{42}N_{10}O_2Ru_2\}^{2+}$ resulting from loss of the two perchlorate anions. Also, **1** gives an elemental analysis consistent with its formulation, and it behaves as a 1 : 2 electrolyte (see Experimental section). In the IR spectrum, the NH vibration of the coordinated bridging ligand occurs at 3310 cm^{-1}; vibrations due to perchlorate anions are observed at 1120 and 630 cm^{-1}.[13] An intense peak at 1450 cm^{-1} can be tentatively ascribed to a C=C vibration of the p-benzoquinonediimine unit, lowered by the effect of back-bonding from two d^6 metal centres which will reduce the π bond order in the ring (in free p-benzoquinonediimine this vibration occurs at 1591 cm^{-1}).[14]

It is significant that under identical reaction conditions, but in the absence of $[Ru(bpy)_2(EtOH)_2]^{2+}$, H_2L^1 remains unaltered, which indicates the important role of the $\{Ru(bpy)_2\}^{2+}$ fragments in facilitating the oxidative transformation $(L^1)^{2-} \longrightarrow$

$(L)^{2-}$ in the complex. Since the new bridging ligand $(L)^{2-}$ is derived from two coupled 2-aminophenol fragments, we also checked to see if complex **1** could be prepared from reaction of $[Ru(bpy)_2(EtOH)_2]^{2+}$ with 2-aminophenol, but this reaction did not afford **1**. These observations together suggest that initial coordination of $(L^1)^{2-}$ to the $\{Ru(bpy)_2\}^{2+}$ fragments is an essential step in the conversion process.

Redox properties of 1

The redox properties of **1** were studied in acetonitrile solution using a platinum working electrode. It exhibits two reversible one-electron oxidation processes at $E_{1/2} = 0.12$ ($\Delta E_p = 60$) and 0.35 V ($\Delta E_p = 70$ mV) *versus* SCE (Fig. 3); the one-electron nature of both of these was confirmed by constant potential coulometry. At higher potential are two further oxidation processes, which are irreversible, at 1.49 and 1.70 V *versus* SCE. Differential pulse voltammetry established that these are also one-electron processes. At negative potentials, **1** exhibits three
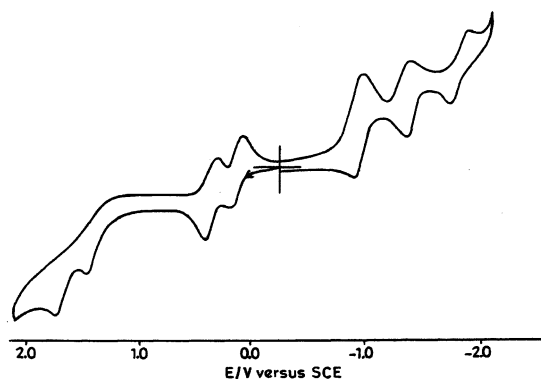
Fig. 3 Cyclic voltammograms of **1** in CH₃CN at a Pt working electrode (scan rate, 50 mV s⁻¹).

reductions at $E_{1/2}$ = −0.98 (ΔE_p = 70), −1.38 (ΔE_p = 70) and −1.81 V (ΔE_p = 100 mV) *versus* SCE; these are symmetric and the first (according to spectroelectrochemical measurements, see later) is chemically reversible, although the second results in slow decomposition. Given the presence of a *p*-bqdi fragment on the bridging ligand of **1**, we assign the first two of these to successive reductions of this fragment to give a *p*-benzosemiquinonediimine monoanion (*p*-bsqdi), and then a *p*-diamidobenzene dianion. This behaviour is exactly the same as that shown by *o*-bqdi ligand fragments chelated to Ru(II) centres, which have been extensively studied by Lever[15] and also by us.[8] For example, in the complex [Ru(bpy)₂-(*o*-bqdi)]²⁺ the first two reductions of the bqdi ligand are at −0.47 and −1.15 V *versus* SCE in MeCN.[15] The third reduction at −1.81 V *versus* SCE is in the region characteristic of bpy-based reductions.[16]

Given the nature of the bridging ligand, there are two possible assignments for the oxidation processes. The more obvious assignment is that the first two couples at +0.12 and +0.35 V *versus* SCE are successive Ru(II)/Ru(III) couples, with the irreversible oxidations at higher potentials being either ligand-centred couples or Ru(III)/Ru(IV) couples.[9,17] The 230 mV separation between the Ru(II)/Ru(III) couples would arise partly from the slight difference in their environments, but principally from an electronic interaction across the conjugated *p*-benzoquinonediimine bridging fragment.[18–20] However, these redox potentials are significantly less positive than those for Ru(II)/Ru(III) couples in essentially identical N₅O coordination environments based on neutral imine and anionic phenolate donors, which typically occur at potentials a few hundred mV more positive than this;[9,21] estimation of metal-centred redox potentials based on Lever's electrochemical ligand parameters gives the same conclusion.[22]

The alternative assignment of the redox data is that the couples at +0.12 and +0.35 V *versus* SCE are ligand centred, resulting in formation of a wholly quinonoidal bridging ligand in two one-electron steps *via* a radical intermediate (Scheme 2). Thus, in (L)²⁻ the two iminophenolate units can each be regarded as being at the semiquinone oxidation level, such that the bridging ligand is denoted as (L^{sq,sq})²⁻. Successive oxidation of each of these results in the 'mixed-valence' radical (L^{sq,q})·⁻ and then the diamagnetic L^{q,q} forms. This exactly parallels the behaviour shown by complex **2** in Scheme 2, in which the diamagnetic 'bis-semiquinone' bridging ligand in **2**^{sq,sq} undergoes two successive one-electron oxidations to give **2**^{q,q}.[23] The analogous N-donor ligand in complex **3** (Scheme 2) undergoes exactly the same behaviour, with the exception that the reduced form **3**^{sq,sq} is unstable, but the principle is identical.[24] The correspondence between the behaviour of **1** and of complexes **2** and **3** is evident; in fact the three series of complexes have isoelectronic π-systems for a given oxidation state, and the bridging ligand in **1** is effectively a positional isomer of those in **2** and **3** but with a mixed donor set. In agreement with this

Table 3 Spectroelectrochemical data (CH₂Cl₂, 243 K)

Complex	λ_{max}/nm ($10^{-3}\,\varepsilon$/dm³ mol⁻¹ cm⁻¹)
1²⁻	910 (3.4),[a] 590 (sh), 539 (17.8), 372 (26.0), 295 (89.7),[b] 246 (60.2)[b]
1⁻	1306 (14.4),[c] 574 (17.9), 479 (18.5), 411 (19.5), 367 (21.9), 294 (85.9),[b] 246 (58.5)[b]
1	860 (24.8),[d] 525 (18.0), 386 (13.5), 344 (15.3), 292 (80.5),[b] 246 (51.0)[b]
1⁺	1570 (9.1),[e] 984 (19.2),[f] 892 (23.1),[f] 567 (14.7), 453 (12.5), 291 (84.2),[b] 244 (56.2)[b]
1²⁺	607 (27.3),[g] 397 (9.8), 280 (62.1),[b] 253 (52.2)[b]

[a] (L^{cat,cat})⁴⁻ ⟶ bpy LLCT. [b] bpy centred π ⟶ π*. [c] Ru(II) ⟶ (L^{sq, cat})·³⁻ MLCT. [d] Ru(II) ⟶ (L^{sq, sq})²⁻ MLCT. [e] Intra-ligand charge transfer of (L^{sq, q})·⁻. [f] Ru(II) ⟶ (L^{sq, q})·⁻ MLCT. [g] Ru(II) ⟶ L^{q,q} MLCT.

assignment we note that the potentials for the **1**/(**1**)⁺ and (**1**)⁺/(**1**)²⁺ interconversions, which involve N,O-donor ligand fragments, lie nicely between those of the corresponding redox potentials of the O,O- and N,N-donor ligands in **2** and **3** (Scheme 2). The same does not apply to the two reductions [the couples **1**/(**1**)⁻ and (**1**)⁻/(**1**)²⁻] because these are more localised on the central bqdi (N-donor) unit, and these two redox potentials are accordingly much closer to those of **3** (where each redox process involves an N,N-donor unit) than of **2** (Scheme 2).

The irreversible oxidations of **1** at +1.49 and +1.70 V *versus* SCE are now assigned as Ru(II)/Ru(III) couples. For comparison, in the mononuclear complex [Ru(bpy)₂(sq)]⁺ (sq = 1,2-benzosemiquinone anion) the reversible ligand-centred oxidation to [Ru(bpy)₂(q)]²⁺ (q = 1,2-benzoquinone) at +0.31 V *versus* SCE is followed by an irreversible Ru(II)/Ru(III) couple at +1.40 V.[25]

With respect to the two possible structures **A** and **B** that were suggested in Scheme 1, it is clear that the observed redox behaviour of **1** is totally different from that of the [(bpy)₂Ru-(*o*-aminophenolate)]⁺ unit (*cf.* the components of structure **A** in Scheme 1), in which irreversible ligand-centred oxidation occurs at modest potentials followed by metal-based oxidation at much higher potential.[15]

UV/VIS/NIR spectroelectrochemical studies on 1

The electronic spectrum of **1** in dichloromethane solution at 243 K displays two strong transitions at 860 and 525 nm (Table 3, Fig. 4), as well as the usual intense intra-ligand trans-
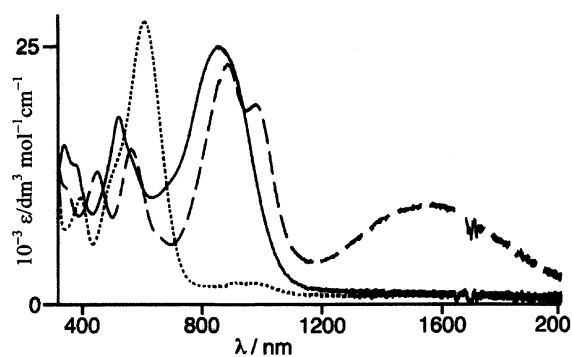

Fig. 4 Electronic spectra of **1** (—), (**1**)⁺ (- - -) and (**1**)²⁺ (· · ·) (CH₂Cl₂, 243 K).

itions in the UV region. The 525 nm band can be assigned as the expected Ru(II) ⟶ bpy MLCT transition.[16] The red-shift of this transition in **1** compared to that of [Ru(bpy)₃]²⁺ (450 nm)[16] is consistent with replacement of one bipyridine ligand by the weaker field σ-donor ligand (L)²⁻, which will raise the energy of the d(π) metal orbitals. The other known {Ru^{II}(bpy)₂}-based complexes having a RuN₅O chromophore, *viz.* [Ru(bpy)₂L]⁺
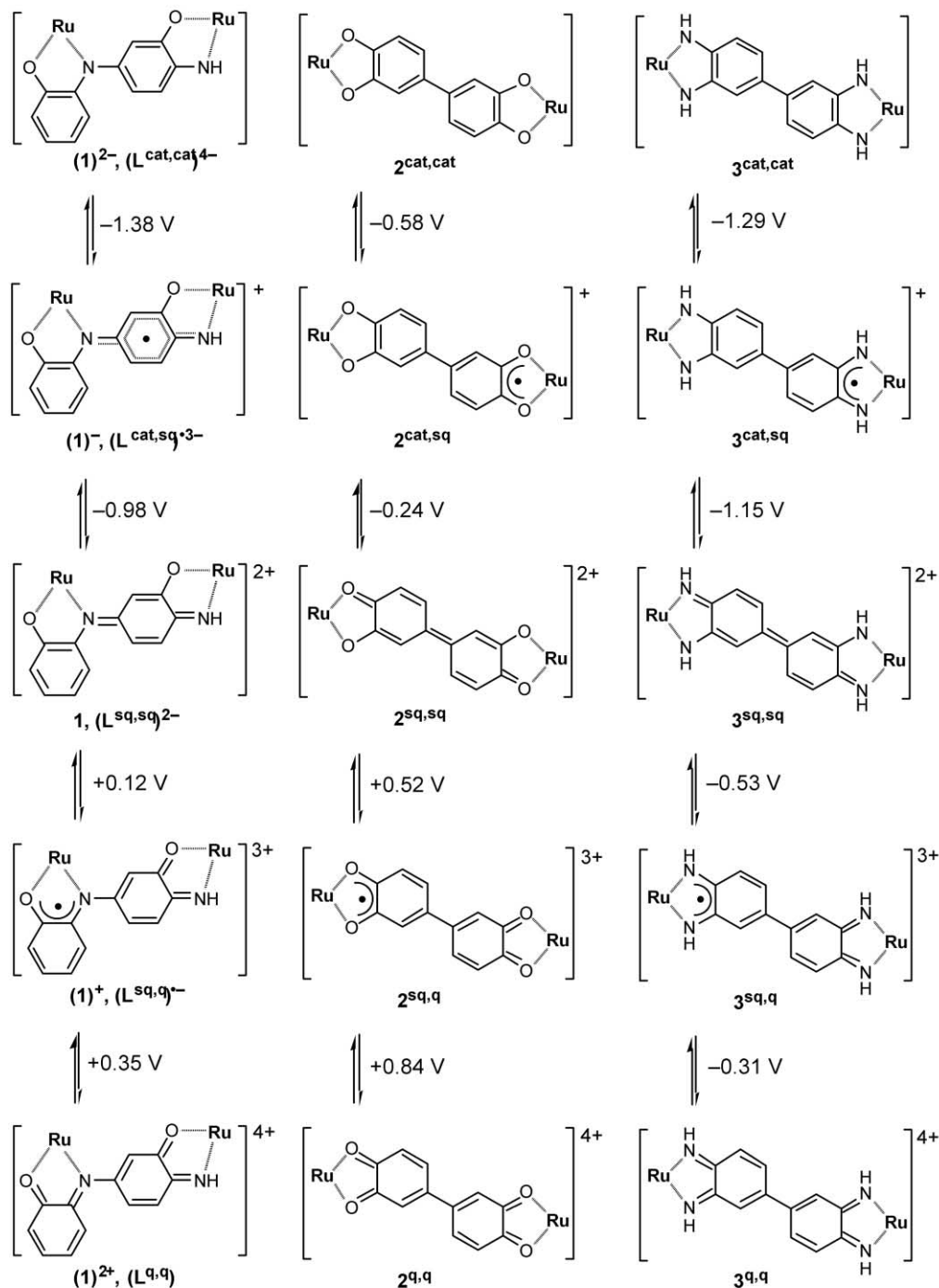
Scheme 2 Ligand-centred redox activity of complex **1** (left), and its correspondence with the ligand-centred redox activity of complexes **2** (centre; see ref. 23) and **3** (right; see ref. 24). Redox potentials are quoted *versus* SCE. Note that for (**1**)$^+$, the choice of which N,O site is in the quinone form and which is in the semiquinone radical form is arbitrary.

(L = pyridine-2-phenolato,[21] pyridine-2-olate,[26] 3,3'-dihydroxy-2,2'-bipyridine,[21] and phenolatoimine fragments,[9] have their Ru(II) ⟶ bpy MLCT transitions at 570, 500, 496 and 477–507 nm, respectively. The intense transition at 860 nm can only be sensibly assigned as an MLCT transition involving the LUMO of the *p*-bqdi fragment of the bridging ligand (L^{sq,sq})$^{2-}$: since the bridging ligand reduces before the terminal bpy ligands, it follows that the MLCT transition to the bqdi unit will be at lower energy than those involving the bpy ligands.[8,15]

UV/VIS/NIR spectroelectrochemical studies of **1** were performed in dichloromethane solution at 243 K (Fig. 4 and 5) using a thermostatted OTTLE cell. The following assignments of electronic spectra are based on comparisons with related compounds rather than calculations, but the picture that emerges is sensible and internally consistent. Electrochemical oxidation of **1** at +0.25 V *versus* SCE generates (**1**)$^+$ in which,
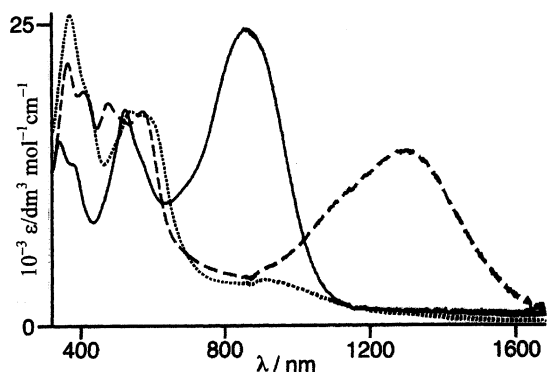

Fig. 5 Electronic spectra of **1** (—), (**1**)$^-$ (- - -) and (**1**)$^{2-}$ (· · ·) (CH$_2$Cl$_2$, 243 K).

following assignment of the redox processes (above), a ligand-centred radical $(L^{sq,q})^{\bullet-}$ is formed in which the bridging ligand is mid-way between its starting dianionic form and the fully oxidised, neutral bis-quinone form $L^{q,q}$. The result of this is that the Ru(II) $\longrightarrow$ $(L^{sq,sq})^{2-}$ MLCT transition of **1** at 860 nm is red-shifted and split into two closely-spaced components at 892 and 984 nm. The red-shift is in agreement with the behaviour shown by complex **2** (Scheme 2), where oxidation from the $2^{sq,sq}$ to the $2^{sq,q}$ state resulted in a red-shift of the Ru(II) $\longrightarrow$ (bridging ligand) MLCT transition from 1080 to 1225 nm.[23] The presence of two components to the Ru(II) $\longrightarrow$ $(L^{sq,q})^{\bullet-}$ MLCT transition of $(\mathbf{1})^+$ is consistent with the inherent asymmetry of the bridging ligand, which means that the redox process is localised at one terminus such that distinct 'semiquinone' and 'quinone' termini will be present. The two metal fragments would therefore have distinct MLCT energies, as seen. Also present in the spectrum of $(\mathbf{1})^+$ is an intense, low energy transition at 1570 nm ($\varepsilon = 9100$ dm^3 mol^{-1} cm^{-1}), which we ascribe to an intra-ligand charge transfer between the 'semiquinone' and 'quinone' termini of $(L^{sq,q})^{\bullet-}$. This is analogous to an inter-valence charge-transfer transition between metal ions in different oxidation states in a mixed-valence dinuclear complex,[5,18–20] and indicates that: (i) the first redox process is localised at one end of the bridging ligand—as was also apparent from the presence of two distinct Ru(II) $\longrightarrow$ $(L^{sq,q})^{\bullet-}$ MLCT transitions—and (ii) there is a strong electronic coupling between the two fragments. Exactly the same behaviour has been observed by Lever for complex $3^{sq,q}$ (Scheme 2), where a strong sq $\longrightarrow$ q intra-ligand charge-transfer transition was seen in the NIR region at *ca.* 1300 nm ($\varepsilon = 10\,000$ dm^3 mol^{-1} cm^{-1}).[24]

On further oxidation of the complex to give $(\mathbf{1})^{2+}$, the intra-ligand charge-transfer transition at 1570 nm disappears. The two closely-spaced Ru(II) $\longrightarrow$ $(L^{sq,q})^{\bullet-}$ transitions of $(\mathbf{1})^+$ also disappear and are replaced by a higher energy Ru(II) $\longrightarrow$ $L^{q,q}$ MLCT transition at 607 nm, which is entirely consistent with ligand-centred oxidation to give a quinone. For example, oxidation of $[Ru(bpy)_2(sq)]^+$ to $[Ru(bpy)_2(q)]^{2+}$ causes the lowest energy MLCT transition to move from 890 to 640 nm,[25] and similar behaviour is shown by many related complexes.[27]

We also examined the spectrum of the reduced forms of **1** to confirm our assignment of the structure of the bridging ligand. On one-electron reduction of **1**, the Ru(II) $\longrightarrow$ $(L^{sq,sq})^{2-}$ MLCT transition at 860 nm disappeared and was replaced by a transition of comparable intensity, but at much lower energy, *viz.* 1306 nm (Fig. 4). This red-shift of the lowest energy MLCT transition is completely consistent with ligand-centred reduction to give a *p*-benzosemiquinonediimine (*p*-bsqdi) radical (Scheme 2), with the new transition being an MLCT transition to the SOMO of the semiquinonediimine fragment, in agreement with numerous precedents.[8,15,25,27] The transitions in the 400–600 nm region [Ru(II) $\longrightarrow$ bpy MLCT] are relatively little affected. Following the notation used above to describe the oxidised forms of the bridging ligand [$(L^{sq,sq})^{2-}$ $\longrightarrow$ $(L^{sq,q})^{\bullet-}$ $\longrightarrow$ $(L^{q,q})$, *etc.*], the mono-reduced form of the ligand in $(\mathbf{1})^-$ is described as $(L^{cat,sq})^{\bullet3-}$ (Scheme 2), where 'cat' denotes the fully reduced dianionic catecholate form of each binding site [*cf.* the reduced forms of complex **2**]. From an electron-counting point of view, this is reasonable, but it takes no account of the point that, since the reduction occurs at the central *p*-bqdi unit (*cf.* the redox potentials) to give a *p*-bsqdi radical fragment which spans both coordination sites, this 'mixed-valence' state is delocalised, with both sites being approximately equivalent (we found no evidence, for example, of an intra-ligand cat $\longrightarrow$ sq transition associated with localised termini). This is in contrast to the oxidised mixed-valence state $(L^{sq,q})^{\bullet-}$, where a localised description is more appropriate.

Further reduction of the complex to the $(\mathbf{1})^{2-}$ state [involving a second reduction of the bridging ligand, *i.e.* $(L^{cat,sq})^{\bullet3-}$ $\longrightarrow$ $(L^{cat,cat})^{4-}$, Scheme 2] results in the disappearance of the Ru(II) $\longrightarrow$ $(L^{cat,sq})^{\bullet3-}$ MLCT transition at 1306 nm, as the

vacancy in the SOMO is filled. Instead, the lowest energy MLCT transition in the spectrum of $(\mathbf{1})^{2-}$ is now the Ru(II) $\longrightarrow$ bpy MLCT manifold in the 500–600 nm range; a new (relatively weak and poorly defined) transition at *ca.* 910 nm may be ascribed to a $(L^{cat,cat})^{4-}$ $\longrightarrow$ bpy ligand-to-ligand charge transfer, by analogy with related complexes which contain π-donor and π-acceptor ligands bound to the same metal centre.[8,15] Re-oxidation of this material to the starting state **1** showed that a small amount of decomposition of the doubly-reduced complex (*ca.* 5%) had occurred on the prolonged timescale of the spectroelectrochemical experiment. For this reason, examination of the spectra of the triply-reduced species (double reduction of the bridging ligand, followed by a bpy-based reduction) was not attempted.

EPR studies on $(\mathbf{1})^+$ and $(\mathbf{1})^{2+}$

We examined the EPR spectra of the oxidised forms of **1** (see Fig. 6) by performing a conventional bulk electrolysis in CH_2Cl_2
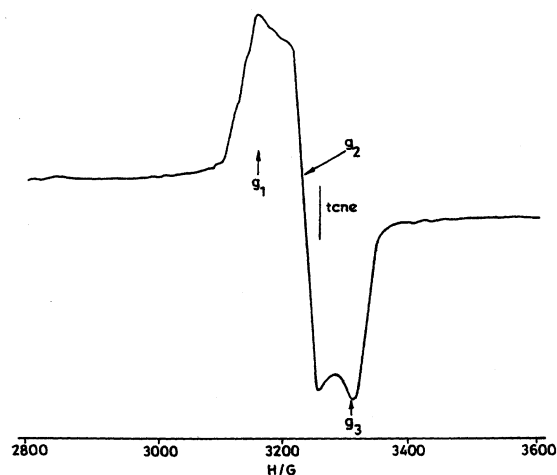

Fig. 6 EPR spectrum of $(\mathbf{1})^+$ as a frozen CH_2Cl_2 solution at 77 K.

and transferring the electrolysis product to an EPR tube. The mono-oxidised complex $(\mathbf{1})^+$ generated in this way is light blue and exhibits a rhombic EPR spectrum ($g_1 = 2.096$, $g_2 = 2.015$ and $g_3 = 1.972$) in dichloromethane at 77 K. The anisotropy of this is too small to be a metal-centred radical [a low-spin Ru(III) complex].[26,28] Instead, in agreement with the conclusions drawn from the electrochemical and spectroelectrochemical results, we assign this to the largely ligand-centred radical $(L^{sq,q})^{\bullet-}$, whose small deviation from free spin (g_{av} based on the above components is 2.028) arises from only a small amount of unpaired spin density on the Ru atoms. The doubly-oxidised deep blue species $(\mathbf{1})^{2+}$ did not give an EPR spectrum at 77 K, in agreement with the diamagnetic nature of the fully oxidised quinonoidal form of the bridging ligand ($L^{q,q}$).

Experimental

Materials

Physical measurements

Solution electrical conductivity was checked using a Systronic conductivity bridge 305. Infrared spectra were taken on a

Nicolet spectrophotometer with samples prepared as KBr pellets. UV/VIS/NIR spectroelectrochemistry studies were performed at 243 K in an optically transparent thin layer electrode (OTTLE) cell mounted in the sample compartment of a Perkin Elmer Lambda 19 spectrophotometer; the cell and the method used have been described previously.[31] ^{1}H NMR spectra were obtained on a 300 MHz Varian FT-NMR spectrometer. Cyclic voltammetric and coulometric measurements were carried out using a PAR model 273A electrochemistry system. A platinum working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode (SCE) were used in a standard three-electrode configuration. TEAP was the supporting electrolyte and the solution concentration was *ca.* 10^{-3} mol dm^{-3}; the scan rate used was 50 mV s^{-1}. A platinum gauze working electrode was used in coulometric experiments. All electrochemical experiments were carried out under dinitrogen atmosphere and all redox potentials are uncorrected for junction potentials. The EPR measurements were made with a Varian model 109C E-line X-band spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid nitrogen). The spectrum was calibrated by using tetracyanoethylene ($g = 2.0023$). The elemental analyses were carried out with a Perkin-Elmer 240C elemental analyser. The electrospray mass spectrum was recorded on a JEOL SX 102/DA-6000 mass spectrometer.

Preparation of ligand (H$_2$L^1) and complex (1)

HOC$_6$H$_4$N=CHC$_6$H$_4$CH=NC$_6$H$_4$OH (H$_2$L^1). To a stirred solution of terephthaldehyde (1 g, 0.7 mmol) in dry ethanol (25 cm^3) was added 2-aminophenol (1.52 g, 1.4 mmol). The stirring was continued for 1 h. The solid product thus obtained was collected by filtration and recrystallised from hot ethanol. Yield 2.5g (80%). Anal. calcd for C$_{20}$H$_{16}$N$_2$O$_2$: C, 75.9; H, 5.1; N, 8.9; found: C, 75.1; H, 5.2; N, 9.1%. ^{1}H NMR (DMSO-d^6) δ (J/Hz): OH, 9.07; H-7, 8.79; H-9/10, 8.16; H-5, 7.26 (6.1); H-3, 7.11 (6.0, 7.2); H-2, 6.91 (5.4); H-4, 6.86 (7.9, 7.3).

[(bpy)$_2$Ru(L^{2-})Ru(bpy)$_2$](ClO$_4$)$_2$ (1). The starting complex [Ru(bpy)$_2$Cl$_2$]·2H$_2$O (300 mg, 0.58 mmol) and AgClO$_4$ (241 mg, 1.17 mmol) were dissolved in ethanol (25 cm^3) and the mixture was heated to reflux with stirring for 1 h. The initial violet solution changed to orange–red. It was then cooled and filtered through a sintered-glass funnel. The ligand H$_2$L^1 (92 mg, 0.29 mmol) was then added to the above filtrate {containing [Ru(bpy)$_2$(EtOH)$_2$]$^{2+}$} followed by sodium acetate (48 mg, 0.58 mmol). The resulting mixture was refluxed overnight under dinitrogen. The precipitate which formed on cooling was filtered and washed thoroughly with cold ethanol and benzene. The product **1** was purified by using an alumina column. A violet band was eluted by using an acetonitrile–methanol (1 : 10) mixture. Finally, the product was recrystallised from acetonitrile–benzene (1 : 5). Yield 245 mg (60%). Anal. calcd. for C$_{52}$H$_{40}$N$_{10}$Cl$_2$O$_{10}$Ru$_2$·2H$_2$O: C, 49.0; H, 3.5; N, 11.0; found: C, 48.7; H, 3.7; N, 10.7%. Λ_M/Ω^{-1} (cm^2 mol^{-1}; MeCN, 298 K): 248.

Crystallography

The single crystals of H$_2$L^1 were grown by slow evaporation of a benzene solution; crystals of **1·2H$_2$O** were grown by slow diffusion of an acetonitrile solution of **1** into benzene, followed by slow evaporation. Significant crystal, data collection and refinement parameters are listed in Table 1. The structures were both solved and refined by full-matrix least squares on F^2 using the SHELX suite of programs.[32] The structure of H$_2$L^1 was determined using a Nonius MACH3 four-circle diffractometer at the National Single Crystal Diffractometer Facility, Indian Institute of Technology, Bombay; the structure of **1·2H$_2$O** was determined using a Bruker SMART diffractometer with a CCD area detector at the University of Bristol. Neither structural

determination presented any significant problems, although the crystals of **1·2H$_2$O** were small and weakly diffracting which means that this structure determination is of only moderate quality. In particular, higher than usual thermal parameters for some atoms of the bipyridine ligands may be ascribed to disorder which could not be resolved because of the weakness of the data, even when collected at 173 K.

CCDC reference numbers 164245 and 164246.

See http://www.rsc.org/suppdata/dt/b1/b107307a/ for crystallographic data in CIF or other electronic format.

Conclusion

We have observed the direct involvement of the {Ru(bpy)$_2$}$^{2+}$ fragment in facilitating the decomposition and rearrangement of the ligand H$_2$L^1 to give the new bridging ligand (L^{sq,sq})$^{2-}$ by selective head-to-tail coupling of two *o*-aminophenol fragments, followed by oxidation to give a central *p*-benzoquinonediimine unit. The bridging ligand is redox-active and undergoes two reversible oxidations to give, ultimately, a neutral, diamagnetic bis-quinone bridge; and two reversible reductions of the central *p*-benzoquinonediimine unit to give *p*-benzosemiquinonediimine and then *p*-diamide units. Further studies are in progress to understand the mechanism of the conversion of H$_2$L^1 $\longrightarrow$ (L^{sq,sq})$^{2-}$ in **1**, along with the general applicability of this type of reaction in the preparation of other unusual bridging ligands.

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