Electronic properties of hydroquinone-containing ruthenium complexes in different oxidation states†

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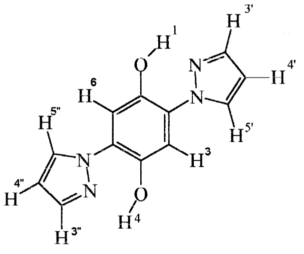
Some novel bis(2,2′-bipyridyl)ruthenium(II) complexes based on the ligands 1,4-dihydroxy-2,5-bis(pyrazol-1-yl)-benzene (H_2L^p) and 1,4-dihydroxy-2,3-bis(pyrazol-1-yl)benzene (H_2L^o) have been prepared and characterized. The spectroscopic properties of the analogous H_2L^p complex containing deuteriated 2,2′-bipyridyl were also studied. The compounds have been oxidized and the electronic properties associated with both oxidation states examined in detail using resonance-Raman and UV/VIS/NIR spectroscopy. In the parent compounds the first redox process is hydroquinone based and the lowest-energy absorption is assigned to a hydroquinone to 2,2′-bipyridyl interligand transition. The products obtained upon oxidation are best described as ruthenium(II)–quinone complexes and their lowest-energy transition is assigned to a Ru^{II} to quinone charge transfer.

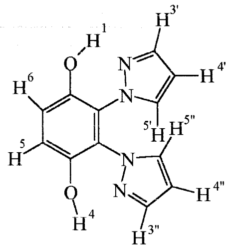
Recently, much attention has been paid to ruthenium–polypyridyl complexes[1] bound to hydroquinone/quinone moieties. Most compounds reported are based upon 1,2-dihydroxy-type ligands where the hydroquinone moiety acts as a 1,2 chelate through two metal–oxygen bonds. In addition, some reports[2,3] deal with mixed nitrogen–oxygen donors where in the former the co-ordination of Ru^{II} to quinonoid rings *via* hydroxyl and amino moieties is examined and in the latter O,N co-ordination *via* a pyridyl nitrogen and a phenolic OH is observed. 1,4-Dihydroxyquinone complexes have been investigated to a considerably lesser extent.[4]

We have recently embarked on a systematic study of complexes where hydroquinone units in combination with other co-ordinating groups are bound to metal centres in a bidentate asymmetric mode. The aim of these studies is to investigate the electronic interaction between the hydroquinone and ruthenium–polypyridyl units. In previously reported cathecholate and hydroquinone complexes, electronic coupling between the ligands and the metal centre is expected to be strong and considerable orbital mixing complicates a detailed description of the properties of the compounds.[2] Detailed investigation on both mono- and di-nuclear complexes[5] is needed to better understand the properties of dihydroxy-type ligands and their interactions with metal centres. Such investigations are not only of interest from the purely inorganic point of view, but are also expected to yield information on the behaviour of hydroquinone-type compounds in biological processes. Indeed recently we reported on the electrochemically induced intramolecular proton transfer in a ruthenium(II)–hydroquinone complex.[6] In addition, the ruthenium(II)–polypyridyl complexes involving O,N bonds are expected to absorb well into the visible region and have therefore potential as dyes in sensitized solar cells.[7]

In this contribution we report on the synthesis and characterization of novel bis(bipyridyl)ruthenium complexes of the type $[Ru(bipy)_2L]^+$ where bipy is 2,2′-bipyridyl and L is 1,4-dihydroxy-2,5-bis(pyrazol-1-yl)benzene (H_2L^p) or 1,4-dihydroxy-2,3-bis(pyrazol-1-yl)benzene (H_2L^o). Employing electrochemistry, spectroelectrochemistry and resonance-Raman spectroscopy, we have carried out a detailed study of the electrochemical and excited-state properties of these complexes in different oxidation states.



H_2L^p



H_2L^o

The synthesis and properties of the hydroquinones as polymer photostabilizers have been investigated by Catalan *et al.*[8] This group also reported on the synthesis of rhodium and iridium carbonyl complexes of H_2L^p.

Experimental

Techniques

Metal complexes were purified on a semipreparative HPLC system using an Applied Chromatography Service (ACS) pump (model RR066) and model 353/UV/VIS detector together with a Magnum-9μ Partisil cation-exchange column (10 mm × 25 cm). The mobile phase was acetonitrile–water (7:3, v/v) containing 0.15 mol dm^{-3} KNO_3. Absorption spectra were measured using a Shimadzu 3100 UV/VIS/NIR spectrophotometer interfaced with an Elonex PC-433.

Electrochemistry was performed in HPLC-grade acetonitrile [dried over activated molecular sieve (type 3A)] using 0.1 mol dm^{-3} tetraethylammonium perchlorate. The working electrode was a 3 mm Teflon-shrouded, glassy carbon electrode, the reference a saturated calomel electrode and the auxiliary electrode a platinum gauze. The cell employed was a three-electrode compartmentalized cell separated by glass frits. Solutions were degassed under argon for 20 min prior to experimentation. An EG&G PAR model 362 scanning potentiostat was employed for cyclic voltammetry (CV) and a model 264A polarographic analyser for differential pulse polarography (DPP). Data were recorded on a Linseis model 17100 x-y recorder at a scan rate of 100 mV s^{-1} for CV and 10 mV s^{-1} for DPP.

Resonance-Raman experiments were recorded using an argon-ion laser as the excitation source in the region 355–528 nm, and a titanium–sapphire laser pumped by an argon-ion source for experiments carried out at wavelengths beyond 700 nm. Backscattering geometry was employed for the spectral

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† *Supplementary data available* (No. SUP 57224, 3 pp.): resonance-Raman spectra. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

Table 1 The 400 MHz ^1H NMR data (δ) for the complexes in CD_3CN

	Hydroquinone				Pyrazole (pyridine)					
Complex	H^3	H^5	H^6	OH^4	$H^{3'}$	$H^{4'}$	$H^{5'}$	$H^{3''}$	$H^{4''}$	$H^{5''}$
$[Ru(bipy)_2(HL^p)]^+$	7.00	—	6.37	10.38	6.44	6.37	8.24	7.71	6.46	7.91
Δδ*	−0.27		−0.90	−0.59	−1.34	−0.20	0.00	−0.07	−0.11	−0.33
$[Ru(bipy)_2(HL^o)]^+$	—	6.39	6.08	7.01	6.39	5.98	6.89	7.68	6.45	7.56
Δδ		−0.37	−0.88	−1.22	−1.27	−0.59	−0.13	−0.02	−0.12	0.54

* Difference between resonances for complexes and free H_2L.

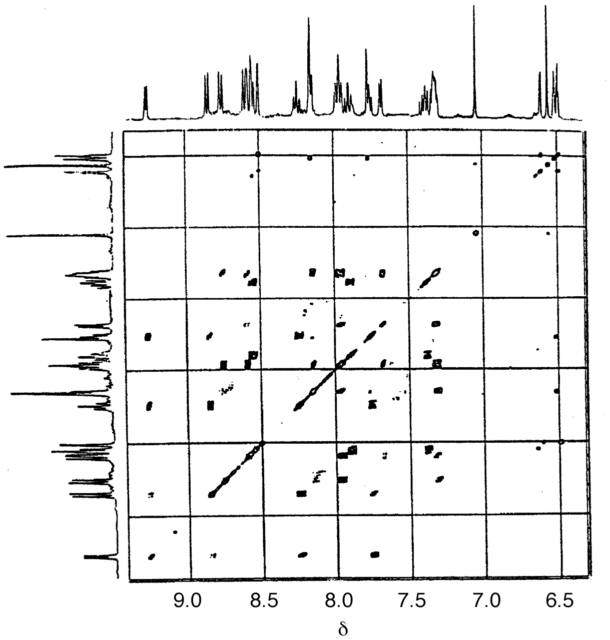

Fig. 1 The 400 MHz ^1H NMR COSY-45 spectrum of $[Ru(bipy)_2(HL^p)]^+$ in CD_3CN

accumulations using a liquid-nitrogen cooled Charged-Coupled Devices multichannel array as the detector.[9] Spectra of electrochemically generated species were recorded using a cell fitted with an optically transparent platinum-gauze electrode (62% transmittance) as working electrode. A silver wire was employed as a pseudo-reference electrode and a platinum wire as auxiliary. Tetrabutylammonium perchlorate (0.1 mol dm^{-3} in dry acetonitrile) was used as supporting electrolyte.

Materials

p-Benzoquinone was recrystallized from water and dried prior to use. 1,4-Dioxane was dried by distillation over $LiAlH_4$ and stored over activated molecular sieves prior to use. All other reagents (Aldrich) were used as received. The compounds H_2L^o and H_2L^p were synthesized and purified as described by Catalan *et al.*,[8] $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ and $[Ru([^2H_8]bipy)_2Cl_2]\cdot 2H_2O$ as described by Meyer and co-workers[10] and $[^2H_8]$2,2′-bipyridyl as reported previously.[11]

$[Ru(bipy)_2(HL^p)]PF_6\cdot 2H_2O$. The compound H_2L^p (0.15 g, 0.6 mmol) was dissolved in ethanol–water (1:1 v/v, 40 cm^3) containing diethylamine (2%, v/v). This solution was deoxygenated with argon, heated and $[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (0.275 g, 0.53 mmol) dissolved in ethanol–water (1:1 v/v, 40 cm^3) was added slowly over 20 min. The mixture was heated under reflux in an argon atmosphere for 4 h after which time the dark purple solution was reduced in volume to approximately 10 cm^3 and neutralized with sulfuric acid. It was allowed to stand for several hours and then filtered to remove any salt formed. A few drops of concentrated aqueous NH_4PF_6 were added and the resulting purple precipitate was filtered off. Two products were identified by HPLC. The first a mononuclear complex and the second dinuclear.[5] The mononuclear product was obtained in a pure form after separation by semipreparative HPLC. It was recrystallized from acetone–water (1:1 v/v). Yield 60% (Found: C, 46.05; H, 3.35; N, 13.1. $C_{32}H_{29}F_6N_8O_4PRu$ requires C, 46.0; H, 3.5; N, 13.4%). The deuteriated analogue, $[Ru([^2H_8]bipy)_2(L^p)]PF_6$ was prepared by the same method.

$[Ru(bipy)_2(HL^o)]NO_3\cdot 2H_2O$. This complex was prepared as above except that no addition of NH_4PF_6 was required. On reduction of the solution volume after semipreparative HPLC the product precipitated spontaneously, and was collected as the nitrate salt. Yield 59% (Found: C, 51.05; H, 3.6; N, 16.35. Calc. for $C_{32}H_{29}N_9O_7Ru$: C, 51.05; H, 3.9; N, 16.75%).

Results and Discussion

General

The complexes can be prepared and purified using standard synthetic techniques. Trace amounts of dinuclear complex formed during reaction can be removed by semipreparative HPLC. The properties of these dinuclear compounds will be dealt with in a separate publication.[5] It is important to note that the complexes are unstable in acidic solution at pH < 4. Such decomposition has been reported elsewhere for phenolate-bound complexes.[12] Proton NMR spectroscopy (see below) and elemental analysis indicate that in the complex the free OH group is protonated and that as expected the co-ordinated hydroxyl group is deprotonated.

^1H NMR spectroscopy

Sharp, well defined resonances were observed for the complexes, confirming the presence of Ru^{II} and the absence of semiquinone radicals. Fig. 1 shows the ^1H NMR correlation (COSY) spectra for $[Ru(bipy)_2(HL^p)]^+$. A complete assignment of resonances was achieved by COSY 45 techniques, and comparison with the deuteriated analogue. However, although all bipyridyl resonances were identified, individual ring assignments were not made. The shifts pertaining to the hydroquinone ligands are shown in Table 1.

The interpretation of the spectra for the complexes is straightforward and described for $[Ru(bipy)_2(HL^p)]^+$; similar arguments may be applied to the other complex. Two singlets are observed for the hydroquinone moiety; COSY experiments show that they are in fact weakly coupled to one another. Both singlets exhibit an upfield shift with respect to free H_2L^p. The first, H^3, a moderate −0.27 ppm while the second, H^6, exhibits a significant shift of −0.9 ppm. This large shift can be explained by a diamagnetic anisotropic interaction with a bipyridyl ring and indicates that the ruthenium centre is bound adjacent to this proton. Both $H^{4'}$ and in particular $H^{3'}$ of the co-ordinated pyrazole experience upfield shifts with respect to free H_2L^p; again this shift may be attributed to diamagnetic anisotropic interaction of the pyrazole protons with the ring current of an adjacent bipyridyl ring. The protons of the remaining unco-ordinated pyrazole $H^{3''}$, $H^{4''}$ and $H^{5''}$ show only weak upfield shifts, remaining essentially unchanged from those of free H_2L^p

Table 2 Electrochemical and spectral data

	E/V *vs.* SCE			
Compound[a]	OH oxidation (*V*)	Bipyridyl reduction	Metal oxidation	Absorbance λ_{max}/nm (log ε)
$[Ru(bipy)_3]^{2+}$	—	−1.35	1.26	—
$[Ru(bipy)_2(HL^p)]^+$	0.42	−1.52, −1.80	1.29[b]	485 (3.76)
$[Ru(bipy)_2(HL^o)]^+$	0.44	−1.60, −1.89	1.30[b]	490 (3.63)

[a] For H_2L^p, *E* = 0.3 (pH 10) and 0.9 V (7) for OH oxidation; for H_2L^o, 0.25 and 0.98 V respectively. [b] Irreversible.

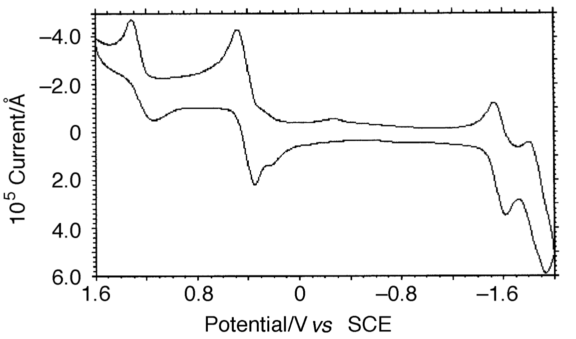

Fig. 2 Cyclic voltammogram of $[Ru(bipy)_2(HL^p)]^+$ in acetonitrile, electrolyte NEt_4ClO_4, scan rate 100 mV s^{-1}

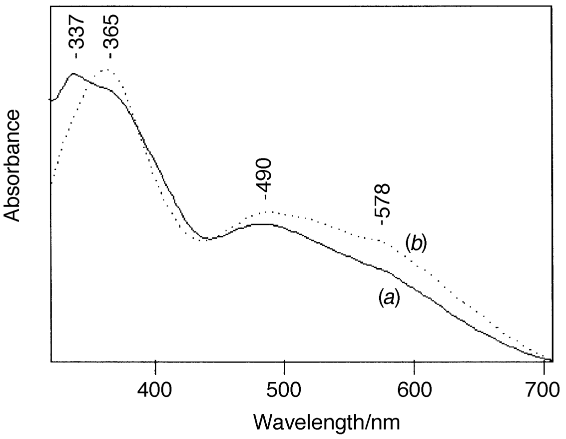

Fig. 3 The UV/VIS absorbance spectra of (*a*) $[Ru(bipy)_2(HL^o)]^+$ and (*b*) $[Ru(bipy)_2(HL^p)]^+$ (1×10^{-4} mol dm^3) in acetonitrile

(see Table 1). The presence of an intramolecular hydrogen bond between the unco-ordinated OH and the pyrazole is maintained in $[Ru(bipy)_2(HL^p)]^+$, confirmed by the downfield shift of the OH proton at δ 10.38.[8] The intramolecularity of this bridge was confirmed by the fact that the resonance is not affected by dilution. No such bridging is present for $[Ru(bipy)_2(HL^o)]^+$, the OH resonance of which is observed at δ 7.01; this is also observed for free H_2L^o, where as a result of steric crowding the pyrazoles are turned out of the plane of the hydroquinone moiety.

Electrochemical properties

Table 2 displays the electrochemical properties of the complexes and the free hydroquinones. Fig. 2 shows the cyclic voltammogram for $[Ru(bipy)_2(HL^p)]^+$. For the free H_2L in neutral solution the first oxidation potential is around 0.9 V. In basic solution as a result of deprotonation of the hydroxyls this potential is dramatically cathodically shifted to around 0.3 V as a result of the large increase in electron density on the negatively charge oxygen groups. The quasi-reversible two-electron oxidation at 0.42 V for $[Ru(bipy)_2(HL^p)]^+$ and at 0.44 V for $[Ru(bipy)_2(HL^o)]^+$ has been assigned to the hydroquinone–quinone oxidation. The two-electron nature of this wave was confirmed by bulk electrolysis/coulometry. It is interesting that despite the asymmetry of the ligand after co-ordination the oxidation occurs in a single two-electron step. The anodic shift of this potential with respect to the free H_2L is expected as a result of co-ordination and is consistent with the behaviour observed for free H_2L in basic solution.

The O,N complexes bound to phenolic moieties reported by Ward and co-workers[3] show behaviour that is remarkably similar to that described here with an irreversible oxidation occurring at strongly anodic potential, 1.3 V in each case. For the present compounds the irreversibility of this oxidation is dependent on the potential scan rate, with the redox process becoming more reversible at faster scan rates. We associate the process with the metal-based Ru^{II}–Ru^{III} oxidation. It is proposed that its irreversibility is related to decomposition of the ruthenium(III)–quinone complex.

Electronic properties

The absorption spectra are shown in Fig. 3 and the data in the visible part of the spectrum are listed in Table 2. The complexes exhibit intense absorbances at wavelengths <300 nm. On the basis of their intensities and by comparison with other ruthenium(II)–polypyridyl complexes[1] these are assigned as π–π* ligand-based transitions. The features around 330–350 nm for each complex are associated with π–π* transitions in hydroquinone moieties; similar absorbances are observed for H_2L which show absorption maxima between 315 and 360 nm and for other complexes containing hydroquinone moieties.[6] In line with other ruthenium(II)–polypyridyl complexes, the visible absorption at 480 nm is assigned as a metal to ligand charge transfer (m.l.c.t.) $Ru(t_{2g})$ to bipy (π*) transition. This assignment is supported by the resonance-Raman and electrochemical data (see below). Table 2 shows that the position of the lowest-energy absorption maxima is red-shifted with respect to $[Ru(bipy)_3]^{2+}$ and other complexes containing strong σ-donor ligands.[1] The values do not fully represent the true extent of the visible absorbance range of these compounds, since it is very broad and tails to approximately 700 nm (see Fig. 3). An intense shoulder tailing to the red from approximately 580 nm is observed. In agreement with Lever and co-workers[2] who reported similar transitions for their $Ru(bipy)_2$–catecholate complexes, we attribute this transition to a π(L)–π*(bipy) transition. For Lever's O,O′- and O,N-co-ordinated catecholate complexes a long-wavelength shoulder is observed at 667 nm.[2] The absorbances associated with π(L)–π*(bipy) transitions for these complexes are at substantially longer wavelengths than observed for the present compounds. The reason for this is unclear, but the values obtained may indicate a higher energy for the hydroquinone ground state in our complexes.

Spectroelectrochemistry

Ultraviolet–visible spectroelectrochemistry was employed to obtain further information concerning the electrochemical and spectroscopic assignments. Oxidation of the solutions was carried out both by electrochemical methods and chemically by the addition of controlled amounts of Ce^{4+}. A typical example for the H_2L^o complex is shown in Fig. 4. For the H_2L^p complex similar features are observed. The spectral changes associated

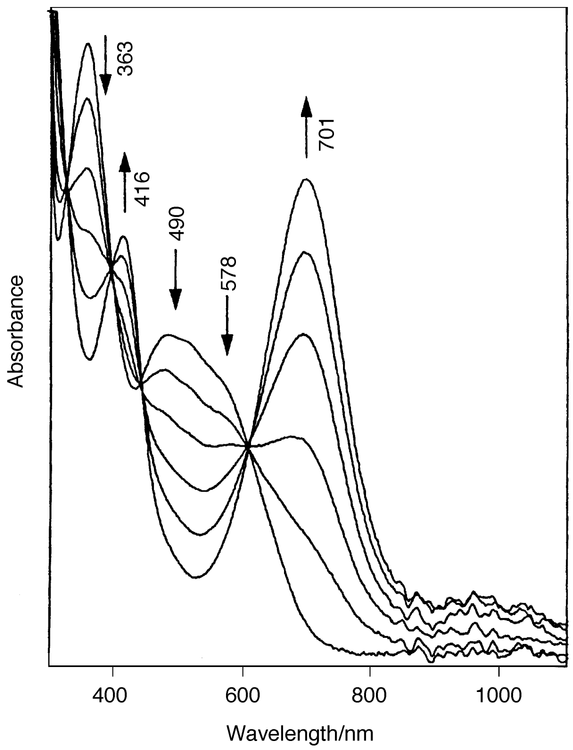

Fig. 4 Spectroelectrochemistry of $[Ru(bipy)_2(HL^o)]^+$ oxidized by addition of cerium(IV) sulfate. Spectra were recorded as a function of time between 0 and 20 min

with the first two-electron oxidation step are reversible, and unstable long-lived intermediates are not present as indicated by the clear isosbestic points at 327, 398, 446 and 614 nm. The figure shows that after the first two-electron oxidation the m.l.c.t. band at 490 nm blue shifts to approximately 416 nm, and a new feature appears at 700 nm for $[Ru(bipy)_2(L^o)]^{2+}$. For $[Ru(bipy)_2(L^p)]^{2+}$ a similar band is observed at 756 nm. The presence of significant absorption features between 400 and 500 nm in the spectrum of the oxidized compound suggests that in the complex the metal centre is still in the ruthenium(II) state, consistent with the interpretation of the electrochemical data. The oxidized complex is therefore most likely the analogous ruthenium(II)–quinone species. After oxidation of the hydroquinone to quinone the $Ru^{II}\rightarrow bipy(\pi_2{}^*)$ m.l.c.t. shifts to the blue as a result of the stabilization of the t_{2g} level when the σ-donating ability of the ligand is decreased. For both the H_2L^o and H_2L^p complexes the spectral changes associated with the oxidation at 1.3 V are irreversible, loss of the intense feature at between 700 and 800 nm and of the band at 416 nm is evident and a yellow complex is obtained. Preliminary characterization of this product suggests it to be a complex in which the pyrazole is bound to the Ru in a monodentate fashion.

Resonance Raman

Resonance-Raman spectroscopy has been used extensively to investigate the nature of the absorption and emission processes in ruthenium–polypyridyl complexes.[13] In this study we have applied the technique to better understand the absorption features of the compounds and of their oxidized analogues. Fig. 5 shows the resonance-Raman spectra of (*a*) $[Ru(bipy)_2(HL^o)]^+$, (*b*) $[Ru(bipy)_2(HL^p)]^+$ and (*c*) $[Ru([^2H_8]bipy)_2(HL^p)]^+$ excited at 457.9 nm. Both the H_2L^p and H_2L^o complexes exhibit very similar features upon 457.9 nm excitation, suggesting that the ligand L is not involved in this transition. The enhanced features in spectra (*a*)–(*c*) at 1606, 1558, 1488, 1268, 1173 and 1023 cm^{-1} are all characteristic of bipy, and this is confirmed by the spectral shifts induced in these bands on deuteriation of bipy. The shift on deuteriation is in the region of 30 cm^{-1}, with the exception of the band at 1486 cm^{-1} which has an unusually large isotopic effect of over 60 cm^{-1}. One feature, however, shows no isotopic effect, *i.e.* the low-intensity band at 1342 cm^{-1}. Interestingly the resonance-Raman spectrum of free H_2L (SUP 57224), excited at 363.8 nm (*i.e.* in resonance with the hydroquinone π–π* transition), has as its most intense feature a band at 1342 cm^{-1}. We therefore conclude that excitation at 457.9 nm causes some pre-resonance enhancement of the ligand-based absorbance on the hydroquinone. In the low-frequency end of the spectrum there are bands at 667 (isotope sensitive) and 374 cm^{-1}; the former has been tentatively associated with a ligand-deformation mode of bipy and the latter with a Ru–N stretching mode.[14] The band at 374 cm^{-1} shows only very weak resonance enhancement as the m.l.c.t. transition exerts little influence on the Ru–N bond. On the basis of these results we conclude that the broad absorption with a maximum near 480 nm is assigned as a $Ru^{II}\rightarrow bipy(\pi^*)$ m.l.c.t. transition. This was anticipated, as the hydroquinone ligands possess no empty low-lying energy levels.

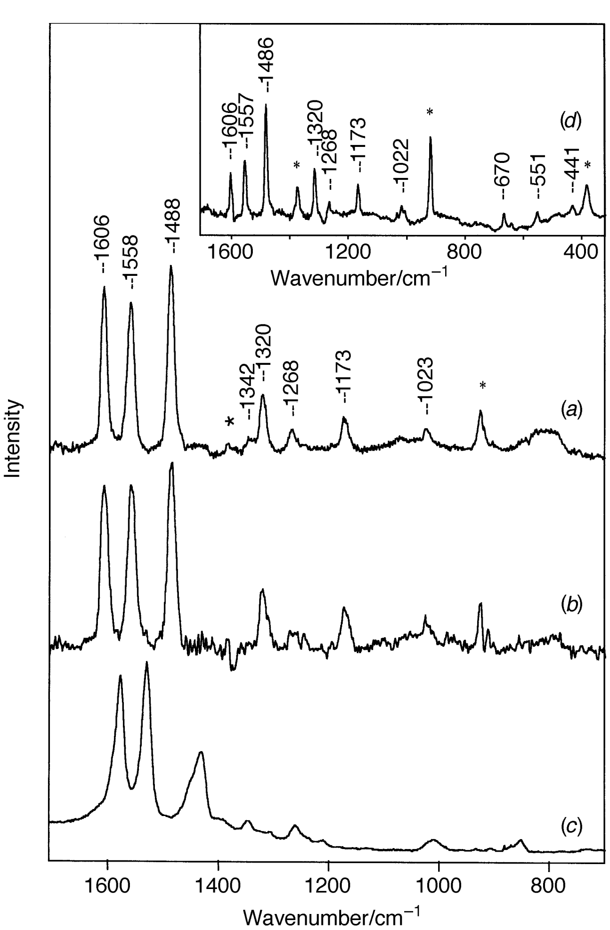

Fig. 5 Resonance-Raman spectra of (*a*) $[Ru(bipy)_2(HL^p)]^+$, (*b*) $[Ru(bipy)_2(HL^o)]^+$, (*c*) $[Ru([^2H_8]bipy)_2(HL^p)]^+$ excited at 457.4 nm and (*d*) $[Ru(bipy)_2(HL^p)]^+$ excited at 632.8 nm in acetonitrile

Fig. 3 shows that, apart from the usual 400–500 nm band, the compounds exhibit a strong shoulder in their absorption spectrum at about 578 nm. To investigate the nature of that transition resonance-Raman spectra were recorded at 632.8 nm. This wavelength was chosen to avoid absorption into the low-energy tail of the m.l.c.t. transition at 480 nm. Fig. 5(*d*) shows the spectrum obtained for $[Ru(bipy)_2(HL^p)]^+$ excited at 632.8 nm. What is immediately apparent is that this spectrum contains bipy-based features at 1606, 1557 and 1486 cm^{-1} while in addition a number of new features are apparent in the low-frequency region at 551, 486 and 433 cm^{-1}; the latter show no isotopic shifts on bipyridyl deuteriation. Also the band at 374 cm^{-1} has disappeared. This latter feature has always been associated with m.l.c.t. transitions[15] in these compounds and its absence suggests that there is no contribution from such a process. Based on a comparison with other oxygen-bound complexes[13,15] the band at 551 cm^{-1} is assigned to Ru–O stretching vibrations and the last two to coupled Ru–O and ligand modes. These features are distinctly enhanced, suggesting the Ru–O bond is significantly influenced by the transition at 578 nm. These observations in conjunction with the simultaneous presence of bipy-centred modes, suggest that the absorption process we are probing in this experiment, namely the transition centred at 578 nm, is best described as a $L(\pi) \longrightarrow bipy(\pi^*)$ interligand transition. Loss of electron density on the oxygen as the electron is transferred from the oxygen lone pair to bipy π^* should have a significant effect on the Ru–O bond, resulting in enhancement of modes of this bond in line with what is observed.

It is interesting that in the 632.8 nm spectra the intensities of the bipy vibrations around 1500 cm^{-1} have changed with respect to those of the complex excited at 457.4 nm. A very similar effect was reported previously by Lever and co-workers[2] for O,O′-co-ordinated catechol complexes of Ru^{II}. For the latter compounds near-equal intensities of the bands at 1604 and 1557 cm^{-1} were observed upon excitation at 457.9 nm, compared to a 1:3 intensity ratio upon excitation at 540 nm, attributed to the 457.4 nm line being pre-resonant with the $Ru^{II} \rightarrow bipy(\pi_2^*)$ transition near 480 nm. The change in intensity on excitation at wavelengths of $\geqslant$540 nm was ascribed to pre-resonance with the lower-energy $Ru^{II} \rightarrow bipy(\pi_1^*)$ transition. Our results suggest that the intraligand transition centred at 530 nm involves the bipy-based π_1^* orbital rather than the higher-energy π_2^* level. Furthermore the absence of the weak feature at 1342 cm^{-1} seen upon 457.4 nm excitation is notable, and would appear to confirm the fact that this feature is associated with pre-resonance of internal high-energy hydroquinone transitions.

Resonance-Raman studies were also carried out on the oxidized species. Spectra were recorded of solutions electrochemically oxidized by holding the potential at 0.6 V for 20 min or by the addition of Ce^{4+}. The spectra obtained for the L^p compound (*a*) and for its deuteriated analogue (*b*) upon excitation at 780 nm are given in Fig. 6. The spectroscopic features are clearly not associated with bipy, because of the absence of any isotopic effect on the frequency of the bands. The band at 1488 cm^{-1} assigned to bipy in the spectrum in Fig. 5 remains enhanced for the oxidized complex, which might suggest that the spectrum of the latter still derives some intensity from resonance with the m.l.c.t. transition. However, comparison with the spectrum obtained for the deuteriated complex demonstrates that this mode exhibits no isotope effect. It is therefore unlikely that this band is bipy based. Another striking feature is the strong enhancement observed for the vibrational mode at 443 cm^{-1}. For the corresponding L^o complex a similar feature was observed at 445 cm^{-1}. It is likely that this is a Ru–O[15] mode coupled to a L^p (or L^o) deformation. Some further, strongly enhanced features appear in Fig. 6(*a*) at 1647, 879 and 706 cm^{-1}. These bands are not observed in the spectra of the parent compounds and can therefore not be explained as hydroquinone vibrations. By comparison with other similar compounds[13] we propose that these are associated with quinone stretching and deformation modes. This is a direct indication that the first redox process is hydroquinone based and that the product obtained in this oxidation is a ruthenium(II)–quinone complex. It is noteworthy that the resonance-Raman spectra of the oxidized complexes containing L^o and L^p are readily distinguishable. These observations again suggest that the ligand L is strongly involved in the spectroscopic process observed at about 750 nm for the oxidized species. Furthermore, resonance-Raman spectra of the oxidized complexes upon 457.9 nm excitation reveal that the Ru–N and bipy modes are still present. In addition the weak mode at 1342 cm^{-1} present for the parent compound has disappeared (SUP 57224). Consistent with the electrochemical data, this suggests the presence of a ruthenium(II) moiety after oxidation and indicates the band at 700 nm is best described as a $Ru(d_\pi) \rightarrow quinone(\pi^*)$ m.l.c.t. transition. This interpretation is in agreement with observations for similar complexes[2,13] for which the primary electrochemistry occurs at the hydroquinone ligand.

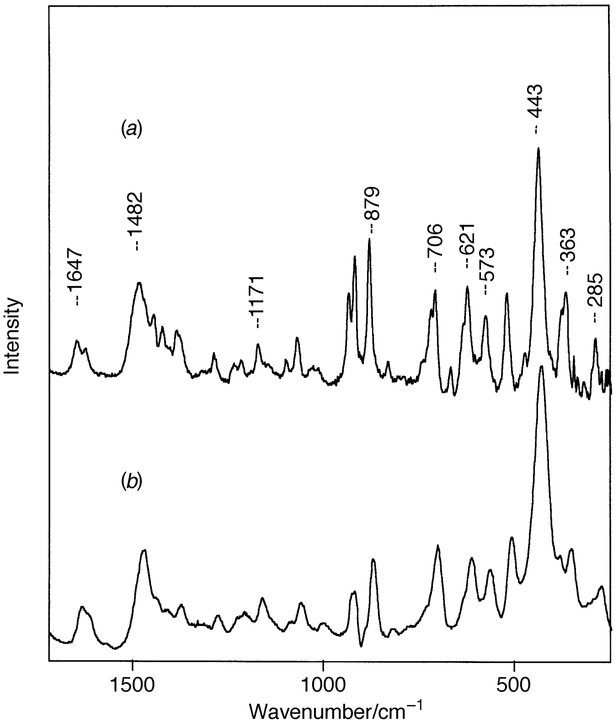

Fig. 6 Resonance-Raman spectra of (*a*) $[Ru(bipy)_2(L^p)]^{2+}$ and (*b*) $[Ru([^2H_8]bipy)_2(L^p)]^{2+}$ at 0.6 V (after the first two-electron oxidation) excited at 780 nm in acetonitrile

Conclusion

The compounds reported in this work show some well defined spectroscopic and electrochemical properties. Electrochemical and spectroelectrochemical experiments show that the first redox process in these compounds is hydroquinone based. Resonance-Raman spectra provide direct evidence for a low-energy hydroquinone to bipy charge-transfer transition. The absorption features of the compounds, far into the visible, make them in principle of interest for application as dyes in solar cells. However, for these particular compounds problems are expected to arise because of the presence of hydroquinone-based redox processes at low potentials. These features make these compounds interesting building blocks for supramolecular structures. We are at present engaged in the study of the dinuclear analogues.

Acknowledgements

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