Characterizations of the Redox Orbitals of Mixed-ligand 2,2′-Bipyridine–2-(2′-Pyridyl)quinoline Ruthenium(II) Complexes[†]

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Electronic absorption spectra from the u.v. to the near-i.r. region, as well as e.s.r. spectra, of the mixed-ligand complexes $[Ru(pquin)_x(bipy)_{3-x}]^{2-n}$ (where $x = 1$—3, $n = 0$—3, pquin = 2-(2′-pyridyl)quinoline, and bipy = 2,2′-bipyridine) are reported. Besides indicating localization of the electrochemically added electrons into separate ligands, the electronic spectra suggest the existence of π orbitals centred primarily on a quinoline portion of the pquin ligand. The absorption in the 4 000 cm^{-1} region has been assigned to an interligand charge transfer which has the net effect of optically transferring a redox electron between the ligands. The e.s.r. spectra are characterized by a lack of spin interaction between the redox electrons, consistent with the localization of these electrons on separate ligands, and by a lack of hyperfine splitting. Furthermore, absence of general temperature-dependent e.s.r. line broadening, associated with a thermal electron hop from a reduced ligand to an unreduced ligand, is rationalized on the basis of donor π^*–acceptor π^* orbital mismatch.

Localization of the redox orbitals onto single ligands has been established for di-imine complexes of iron, ruthenium, and osmium;[1–13] moreover, electron localization within portions of the ligands for the series $[Ru(pquin)_3]^{2-n}$ and $[Ru(bquin)_3]^{2-n}$ [where n is the number of redox electrons, pquin is 2-(2′-pyridyl)quinoline (see Figure 1) and bquin is 2,2′-biquinoline] has been proposed.[14] The spectroscopy of the reduction series of the tris(pquin) complex leading to this proposal will be reviewed here because of its importance in discussing the redox orbitals on the pquin ligand.

The unreduced tris(pquin) complex has two u.v. peaks[‡] at *ca.* 37 000 and 32 000 cm^{-1}, while the tris(bquin) complex also has two peaks in the u.v. region at *ca.* 37 000 and 30 000 cm^{-1}. The peak at *ca.* 37 000 cm^{-1} is twice as intense for the bquin complex as for the pquin complex, and was assigned to a transition between orbitals primarily associated with a quinoline fragment. Such quinoline-localized orbitals have been reported previously for the bquin free ligand,[15,16] and this set of orbitals will be referred to as 'quin' orbitals. Since the intensity and energy of the peaks at *ca.* 32 000 cm^{-1} are similar in both the bquin and pquin complexes, it was suggested that the lower energy $\pi \longrightarrow \pi^*$ transition is between typical π orbitals containing contributions from both imine portions of the di-imine ligand; the similarity of the u.v. spectra of these species argues against a lone pyridine in pquin as a separate chromophore since there is no lone pyridine present in bquin. This set of di-imine orbitals in the ruthenium bound pquin ligand will be referred to as 'pquin' orbitals.

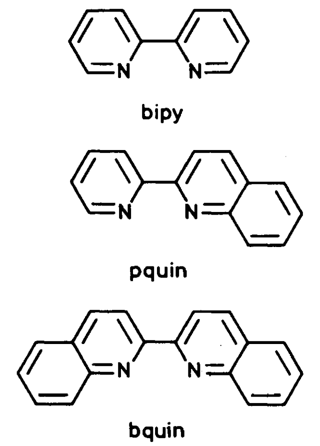

Figure 1. Chemical structures of the ligands discussed: bipy = 2,2′-bipyridine, pquin = 2-(2′-pyridyl)quinoline, bquin = 2,2′-biquinoline

The peak at *ca.* 37 000 cm^{-1} loses intensity as the first two redox electrons are added while that at *ca.* 32 000 cm^{-1} red shifts without appreciable intensity loss, implying that the initial redox orbital is a 'quin' orbital. The remaining peak at *ca.* 38 000 cm^{-1} in the $n = 2$ product was observed to shift to *ca.* 35 000 cm^{-1} upon addition of the third redox electron, and the low-energy peak red shifted further and broadened. It was postulated that the lowest unoccupied 'pquin' orbital on the remaining unreduced ligand received the third electron to generate a 'pquin' chromophore with a broad absorption at *ca.* 30 000 cm^{-1}, similar to the bipy$^-$ (bipy = 2,2′-bipyridine) chromophore generated in the redox series of $[Ru(bipy)_3]^{2-n}$.[5] This switching of lowest energy π^* orbital on the third ligand from 'quin' to 'pquin' would indicate that these π^* orbitals are nearly isoenergetic, and the mechanism for this redox orbital change was postulated to be electrostatic in nature, since the placement of the third electron into the 'quin' orbital of the remaining bquin or pquin ligand would lead to a very unsymmetrical arrangement of redox electrons, with two of them placed adjacent to one another, leading to strong repulsion.

For the unreduced species, the visible region of the spectrum is dominated by a metal to ligand charge transfer (m.l.c.t.) absorption. The resonance-Raman (r.R.) spectrum obtained from excitation into this band was remarkably similar to that found for $[Ru(bipy)_3]^{2+}$,[14] implying that the optical orbitals (*i.e.* the final ligand orbital in the m.l.c.t.) in $[Ru(pquin)_3]^{2+}$ and $[Ru(bipy)_3]^{2+}$ are very similar and that the optical orbital for $[Ru(pquin)_3]^{2+}$ is best described by the lowest unoccupied molecular orbital (l.u.m.o.) of the 'pquin' system. Furthermore, it implies that for this particular

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[†] *Non-S.I. unit employed:* G = 10^{-4} T.

[‡] The u.v. transitions in tris(di-imine) metal complexes are best described as due to three separate ligand chromophores with exciton coupling. See: J. Ferguson, F. Herren, E. R. Krausz, M. Maeder, and J. Vrbancich, *Coord. Chem. Rev.*, 1985, **64**, 21; A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc. A*, 1969, 1428; P. S. Braterman, B. C. Noble, and R. D. Peacock, *J. Phys. Chem.*, 1986, **90**, 4913.

Table 1. U.v.–visible absorption maxima (10^3 cm^{-1}) with absorption coefficients (dm^3 mol^{-1} cm^{-1}) in parentheses, for the series $[Ru(pquin)_x(bipy)_{3-x}]^{2-n}$*

n	*x* = 0	*x* = 1	*x* = 2	*x* = 3	Chromophore
0		37.0 (45 000)	37.2 (41 000)	37.3 (55 000)	'quin'
	35.3 (60 000)	34.8 (56 000)	34.5 (38 000)		bipy
		Shoulder	32.5 (36 000)	32.5 (50 000)	'pquin'
1			37.2 (32 000)	38.1 (46 000)	'quin'
	35.1 (44 000)	34.4 (52 000)	34.5 (38 000)		bipy
		30.5 (20 000)	31.0 (32 000)	31.2 (52 000)	'pquin'
	29.4 (15 000)				bipy$^-$
		26.5 (sh)			'quin$^-$'
2				38.1 (41 000)	'quin'
	33.9 (34 000)	34.5 (36 000)	34.5 (36 000)		bipy
				30.3 (45 000)	'pquin'
			29.7 (31 000)		'pquin$^-$'
	29.2 (23 000)	29.5 (32 000)			bipy$^-$
3			34.2 (29 000)	34.7 (38 000)	'quin'
	30.5 (37 000)	29.6 (43 000)	29.6 (40 000)		bipy$^-$
			29.6 (40 000)	29.4 (48 000)	'pquin$^-$'

* *x* Is the number of 2-(2′-pyridyl)quinoline ligands and *n* is the number of electrons added.

orbital there is a major contribution from the atomic orbitals common to both pquin and bipy.[14] Because there would be at least two unoccupied 'pquin' l.u.m.o.s throughout the reduction series (n = 0—3) in the postulated reduction scheme, this m.l.c.t. band would not be totally replaced in the absorption spectra by ligand-based $\pi^* \longrightarrow \pi^*$ absorption bands as in the tris(bipy) complex,[5] and the similarity of the r.R. spectrum throughout the reduction series was attributed to the continued presence of m.l.c.t. bands.[14] Since the optical orbital, as shown by similar vibrational spectra, remains relatively unchanged with the addition of electrons to the redox orbital, the redox electron density may be isolated from the optical orbital suggesting[14] that, for the particular case of the redox orbital (lowest unoccupied orbital of the 'quin' π system) in the complex, major contributions are made from the atomic orbitals at the periphery of the ligand, *i.e.* the benzene ring.

In these complexes, then, the redox orbital for the first and second electron was postulated to be localized on a quinoline portion of the ligand while that of the third electron is more centrally located over the nitrogen–metal–nitrogen portion of the remaining pquin or bquin ligand. If indeed the third electron does enter a different type of orbital then there is some communication between the ligands, presumably through an avoidance of electrostatic repulsion between electrons on the quinoline portions of adjacent ligands. In the case of the tris(bipy) complexes, however, the redox and optical orbitals are the same,[9] and in this respect, the tris(bipy) metal complexes are model systems to which perturbations can be made to understand more complicated systems. The extent of communication remaining in mixed pquin–bipy ligand complexes could be systematically examined by progressively replacing bipy ligands with pquin ligands to form tris(di-imine) complexes approaching the complexity of the tris(pquin) species. Furthermore, the previously reported unusual nature of the redox orbital on pquin ligands[14] could be investigated with more data from other systems with possibly more conventional behaviour.

Experimental

Materials.—The compound 2,2′-bipyridine (bipy) was purchased from Aldrich and purified by recrystallization from light petroleum (b.p. 38—58 °C) or methanol, while 2-(2′-pyridyl)quinoline (pquin) was prepared as described earlier[17] and purified by recrystallization from ethanol. Tetraethylammonium hexafluorophosphate and tetrabutylammonium hexafluorophosphate were prepared by metathesis of the corresponding perchlorates with ammonium hexafluorophosphate and subsequent recrystallization from water (four times) and methanol (once). Certified A.C.S. grade *N,N*-dimethylformamide (dmf) (Fisher Scientific) was purified by storing over AW-500 molecular sieves (Alfa Products) under dry nitrogen. Subsequent vacuum distillation yielded an electrochemically pure solvent which was stored in a dry-box until needed.

The tris(pquin) ruthenium complex was synthesized as described in the literature,[18] while the mixed-ligand complexes were made by first preparing the bis(ligand) ruthenium dichloride intermediate.[19] This intermediate was purified by recrystallization from $EtOH-H_2O$ (6:1) saturated with LiCl[19,20] before being treated with the appropriate ligand. The complex was precipitated as the $[PF_6]^-$ salt using NH_4PF_6. All complexes were washed with diethyl ether to remove free ligand and recrystallized from either methanol or acetone–isopropanol and dried under vacuum.

Electrochemistry.—Electrochemical reductions were carried out using a standard three-compartment H-cell under dry nitrogen in a Vacuum Atmospheres model 493 glove-box equipped with a model HE-63P Dri-train. The electrochemical apparatus and procedure have been described previously.[21] Sample stability was checked after each bulk electrolysis by re-measuring the cyclic voltammogram and comparing it to that of the starting material.

Spectroscopy.—U.v.–visible spectra were obtained on a Hitachi 110 spectrophotometer using 1-mm pathlength quartz cells equipped with ground-glass stoppers. For the near-i.r. region, either a Cary 14 or a Cary 2300 spectrometer was used. All spectra were corrected for baseline. Resonance-Raman spectra were collected as described previously.[11,14]

Electron spin resonance (e.s.r.) spectra were obtained with a JEOLCO model JM-ME3 e.s.r. spectrometer as described previously.[4,8] The g values were determined using diphenylpicrylhydrazine as an external standard (g = 2.0037).

Results and Discussion

U.v.–Visible Absorption Spectra.—The absorption wavenumbers are given in Table 1 and orbital assignments are based

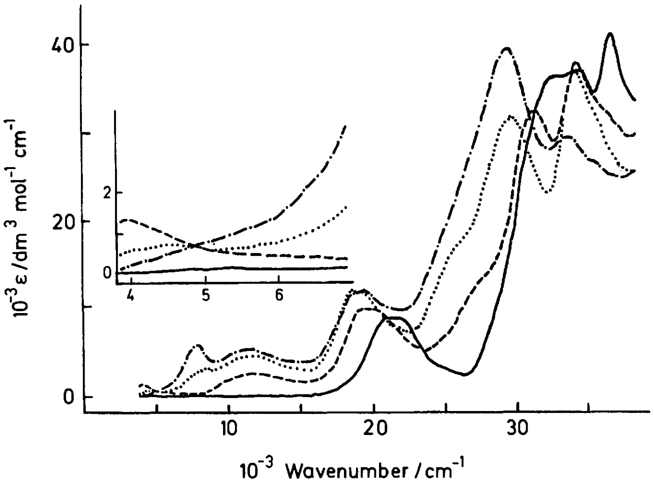

Figure 2. U.v.–visible and near-i.r. (inset) absorption spectra for $[\mathrm{Ru(pquin)_2(bipy)}]^{2-n}$ in dmf, for n = 0 (——), 1 (– – – –), 2 (· · · ·), and 3 (– • – • –)

Table 2. Near-i.r. absorption maxima (10^3 cm^{-1}), with absorption coefficients (dm^3 mol^{-1} cm^{-1}) in parentheses, for the series $[\mathrm{Ru(pquin)}_x\mathrm{(bipy)}_{3-x}]^{2-n}$

n	$x = 0$	$x = 1$	$x = 2$	$x = 3$
1	11.36 (1 050)	11.24 (3 000)	11.24 (3 000)	11.49 (2 800)
	10.00 (900)	5.70 (250)	3.91 (1 100)	3.85 (1 250)
2	11.30 (2 100)	11.30 (4 370)	11.17 (5 500)	11.63 (3 900)
	10.05 (1 250)	5.49 (200)	8.55 (3 400)	3.91 (1 400)
			4.41 (500)	
3	11.36 (2 800)	11.36 (7 800)	11.43 (4 400)	11.24 (8 000)
	10.00 (1 700)	8.00 (5 200)	7.81 (5 600)	7.69 (6 000)

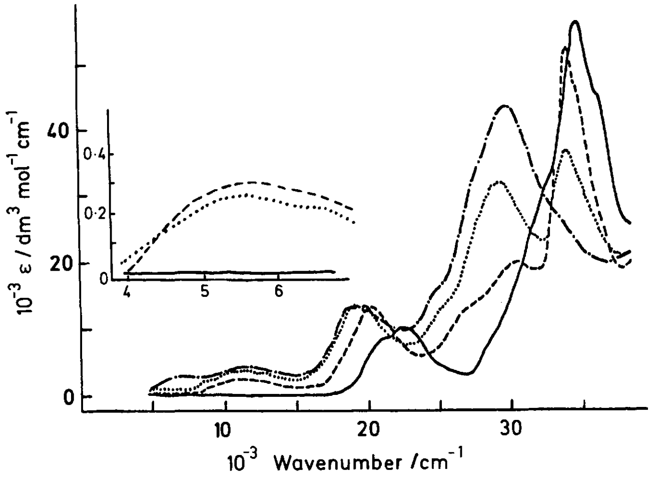

Figure 3. U.v.–visible and near-i.r. (inset) absorption spectra for $[\mathrm{Ru(pquin)(bipy)_2}]^{2-n}$ in dmf, for n = 0 (——), 1 (– – – –), 2 (· · · ·), and 3 (– • – • –)

Table 3. Electron spin resonance linewidths and g values at selected temperatures (given in parentheses) for $[\mathrm{Ru(pquin)}_x\mathrm{(bipy)}_{3-x}]^{2-n}$ in dmf

x	n	$H_{\text{p-p}}$/G	g	$H_{\text{p-p}}$/G	g
1	1	15.7 (27)	1.992	15.3 (−56)	1.996
	2	15.7 (38)	1.995	16.8 (−54)	1.998
	3	15.8 (36)	1.991	20.3 (−54)	1.996
2	1	15.3 (23)	1.992*	14.9 (−48)	1.992*
	2	16.8 (28)	1.994	15.9 (−43)	1.994
	3	17.1 (18)	1.991	15.9 (−45)	1.995
3	1	75.3 (−9)	1.993	23.6 (−48)	1.995
	2	17.4 (−20)	1.991	18.5 (−50)	1.990
	3	asymmetric signal			

* This moiety was also examined in acetonitrile: at −13 °C, $H_{\text{p-p}}$ = 23.5 G and g = 1.993; at −38 °C, $H_{\text{p-p}}$ = 23.2 G and g = 1.994.

on the spectral assignments for the two series $[\mathrm{Ru(bipy)_3}]^{2-n}$ and $[\mathrm{Ru(pquin)_3}]^{2-n}$.

(*i*) $[\mathrm{Ru(pquin)_2(bipy)}]^{2-n}$ (n = 0—3). Examination of Figure 2 reveals loss of much of the 'quin' absorption with addition of the first electron, implying a 'quin' redox orbital. Neither the first nor second redox electrons affects the *ca.* 35 000 cm^{-1} band (bipy), which is consistent with the reduction of the pquin ligands prior to the bipy ligand. The third redox electron, however, does enter the bipy orbital as evidenced by the disappearance of this band and the appearance of a band at *ca.* 30 000 cm^{-1}. Furthermore, the presence of an absorption in the three-electron reduction species at 34 200 cm^{-1} may imply, as in the tris compound, that a 'quin' orbital remains unreduced (*i.e.* reduction into a 'pquin' orbital for one of the ligands), consistent with strong electrostatic repulsion ensuing from two fused rings adjacent to one another.

(*ii*) $[\mathrm{Ru(pquin)(bipy)_2}]^{2-n}$ (n = 0—3). The major features in the u.v. spectrum of the tris(pquin) complex now appear only as shoulders, obscured by the strong bipy $\pi \longrightarrow \pi^*$ absorption peak at 34 800 cm^{-1} in the unreduced parent complex (Figure 3, Table 1). The first redox electron clearly eliminates the shoulder at 37 000 cm^{-1}, suggesting that the first redox electron goes into the 'quin' l.u.m.o. on the pquin ligand. The second and third electrons each reduce the peak at *ca.* 35 000 cm^{-1} associated with unreduced bipy ligand, and a concomitant absorption increase occurs at *ca.* 30 000 cm^{-1} associated with reduced bipy; both observations are consistent with the consecutive reduction of the bipy ligands. Unlike the previous complexes, no peak is revealed at *ca.* 34 500 cm^{-1} for the fully reduced species, suggesting that the pquin ligand remains reduced at the quinoline portion of the ligand.

The two peaks in the visible spectra of both unreduced complexes are attributed to m.l.c.t.s into the pquin and bipy ligands in the unreduced complexes, and show that the energy difference between the optical orbitals is *ca.* 1 800 cm^{-1} for each of the mixed-ligand complexes (see Table 1). The visible region is too congested to extract much information for the reduced species. In addition to the two m.l.c.t.s present, a bipy$^-$ $\pi^* \longrightarrow \pi^*$ transition occurs in this region.

Near-infrared Spectra.—The weak absorption near 4 000 cm^{-1} in ruthenium–bipy complexes has been attributed to the so-called 'inter-valence charge transfer' (i.v.c.t.) band,[14] in which a redox electron is effectively transferred from a reduced ligand to an unreduced ligand.[7,*] This region of the near-i.r. has been reported previously for the tris(pquin) complex[14] and consists of bands for the one- and two-electron products only. Neither the unreduced nor fully reduced complexes show

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* An i.v.c.t. absorption implies 'class 1' behaviour, characterized by some degree of interligand interaction. However, the i.v.c.t. absorption band is expected only for mixed-valence species and not for a complex in the delocalized limit where the charge is spread across the entire system ('class 3'). See, ref. 22; M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247; S. B. Piepho, E. R. Krausz, and P. N. Schatz, *J. Am. Chem. Soc.*, 1978, **100**, 361.

comparable absorptions. These bands for the $n = 1$ and 2 tris(pquin) species, with absorption coefficients of *ca.* 1 200 dm^3 mol^{-1} cm^{-1} (see Table 2), are more intense than for the corresponding tris(bipy) species[7] and are assigned to charge transfer transitions, 'quin$^-$' ⟶ 'quin', with the closer proximity of one 'quin' orbital to another, compared to simple bipy ligands, yielding the larger absorption coefficient for the pquin complexes.[22,23] The absence of this band in the unreduced and fully reduced species, as well as in the free ligand,[24] is consistent with the interpretation of this absorption as a charge transfer band, since at least one reduced and one unreduced ligand, apparently, must be present for the process.

The $[Ru(pquin)_2(bipy)]^{2-n}$ species, however, reveal a different pattern (see Figure 2 and Table 2). With no electrons added no absorption occurs, as is expected. The one-electron reduction product shows a relatively strong (ε *ca.* 1 100 dm^3 mol^{-1} cm^{-1}) i.v.c.t. absorption near 4 000 cm^{-1}, while the two-electron reduction product shows a considerably weaker one (ε *ca.* 500). The intensity of the absorption for the one-electron reduction product argues for its assignment as a 'quin$^-$' ⟶ 'quin' charge transfer band, and consequently for a configuration of the pquin ligands such that the fused rings are adjacent to one another. The second reduction product no longer has an unreduced pquin ligand into which the electron can be transferred, thus the weaker absorption is attributed to a 'quin$^-$' ⟶ bipy charge transfer. The intensity of this band, intermediate to those assigned to bipy$^-$ ⟶ bipy and 'quin$^-$' ⟶ 'quin' charge transfer bands, is consistent with this picture. Any remaining absorption in the $n = 3$ species is buried under the higher energy near-i.r. absorption (see below).

Finally, $[Ru(pquin)(bipy)_2]^{2-n}$ shows low-energy near-i.r. peaks for the $n = 1$ and $n = 2$ species (see Figure 3 and Table 2). Consistent with the presence of only one pquin ligand and the absorption coefficients of *ca.* 250 dm^3 mol^{-1} cm^{-1} in both cases, these peaks are assigned as 'quin$^-$' ⟶ bipy charge transfer processes analogous to that seen above in the $n = 2$ species of the bis(pquin) complex. Again, however, the spectrum is obscured in the $n = 3$ complex by the stronger absorption in the higher energy region of the near-i.r.

Raman Spectra.—Resonance-Raman (r.R.) spectra were recorded for all of the complexes using excitation lines in resonance with the absorptions in the visible region. Since no absorptions due to the 'quin' chromophore are at energies that can be probed with the system used, enhancements were observed only for modes associated with bipy and 'pquin' (probing the m.l.c.t.) and bipy$^-$ and 'pquin$^-$' (probing $\pi^* \longrightarrow \pi^*$). The resulting spectra consisted of many unresolved, overlapping peaks due to the similarity of the pquin and bipy r.R. spectra,[14] and only limited information concerning the nature of the redox orbitals could be gained. The presence of a vibrational peak at 1 502 cm^{-1} is diagnostic of the bipy$^-$ chromophore,[10] and its appearance (18 900 cm^{-1} excitation) coincided with the disappearance of the band at *ca.* 35 000 cm^{-1} and increase in absorbance at 30 000 cm^{-1} for both mixed-ligand complexes, confirming the assignment of these two u.v. bands to bipy and bipy$^-$ respectively. Furthermore, the highest energy vibration (other than C–H stretches) occurs at 1 600 cm^{-1}, and upon reduction it is expected to shift to the 1 500—1 570 cm^{-1} range,[10] leaving no peaks observable near 1 600 cm^{-1}. The fact that a peak was observed in the $n = 3$ spectra of both the tris(pquin) and bis(pquin) complexes indicates the presence of an unreduced portion of the pquin ligand, thus supporting localization of the redox electron into a remote part of a 'quin' orbital.

E.S.R. Spectra.—As in other d^6 metal di-imine complexes,[4,8] the e.s.r. signals for all of the reduced mixed-ligand complexes consist of unresolved, single-derivative curves with no hyperfine structure apparent. Despite similar findings for other ruthenium–tris(di-imine) systems,[4,8,24] a single line is generally unexpected for multiple-electron reduction products, especially the $n = 2$ product, since $S = 1$ behaviour at low temperature (frozen matrix) has been noted for bis(di-imine) complexes of the alkaline earths and alkali metals.[25] (The triplet state for the frozen e.s.r. signal also collapsed into a single line near the tetrahydrofuran melting point for these complexes.) However, since a triplet state would not be expected to produce an e.s.r. signal much above the freezing point of the solvent (213 K) unless the axial and rhombic zero-field splitting parameters, D and E, are very small,[24,26] the persistence of this single signal throughout a large temperature range (116 to $\geqslant$255 K) for the two- and three-electron reduction products, as well as a lack of signal at half field ($\Delta M = \pm 2$), implies relatively independent, weakly interacting reduced ligands, each of spin $\frac{1}{2}$, with negligible exchange energy. Alternatively, the D term may be approaching zero, which would also make the spectrum appear as a single line as if due to an $S = \frac{1}{2}$ system. Either case would lead to the same conclusion of electron localization within redox orbitals on single ligands.[24,25] The g values for the redox electrons in the ruthenium complexes are very close to 2.000 (Table 3), indicating that the redox orbital is essentially ligand localized. Additionally, the g factors for the species $[Ru(pquin)_3]^0$ and $[Ru(pquin)_2(bipy)]^{+,-}$ demonstrate some temperature dependence, decreasing by $\leqslant$0.4% upon warming from 213 and 273 K. The asymmetry of the e.s.r. signal in frozen matrices indicates some degree of g-value anisotropy, similar to that seen previously for other ruthenium–di-imine systems.[4,8,24]

Since no temperature region of line narrowing has been observed and the peak to peak linewidth has values up to 120 G, the line broadening is a T_1 rather than a T_2 process, with an electron hopping from a reduced to an unreduced ligand on the nanosecond time-scale of the X-band e.s.r. experiment.[4,8,24] Temperature dependence was observed only for the first reduction products of the tris(pquin) complex (233—255 K). A plot of ln (linewidth) *vs.* $1/T$ for the $[Ru(pquin)_3]^+$ complex yielded a line from which an activation energy of *ca.* 850 cm^{-1} was calculated from the slope. Temperature independence in the e.s.r. linewidths observed in the mixed-ligand complexes may be attributed to a lack of electron hopping between ligands (high barrier limit) rather than to very fast hopping (low barrier limit) because the linewidths found for these mixed-ligand complexes (18—24 G) are comparable to the low-temperature limit for species which do exhibit e.s.r. temperature dependence and which presumably correspond to negligible hopping.

Unlike the optical process described above in the near-i.r. results, thermal activation should be an adiabatic process, *i.e.*, one which remains on the lowest energy surface. Since the energy gap between a 'quin' or 'pquin' and a bipy orbital, as measured from the difference in m.l.c.t. energies, is $\geqslant$1 800 cm^{-1}, thermal activation from pquin to bipy was not expected, thus explaining the lack of line broadening for $[Ru(pquin)_2(bipy)]^0$ and $[Ru(pquin)(bipy)_2]^+$. In those cases where the redox orbital (l.u.m.o.) on the acceptor ligand has been postulated to be of a different type to that on the donor (*i.e.* 'quin' and 'pquin'), a pquin$^-$ ⟶ pquin thermal hop is not observed, possibly indicating non-adiabatic behaviour supporting the orbital assignments. The only case remaining is $[Ru(pquin)(bipy)_2]^0$, where a bipy$^-$ ⟶ bipy hop might be expected. However, this is likely to involve the transfer of an electron to a bipy ligand adjacent to a 'quin$^-$' moiety, possibly presenting electrostatic reasons for the observed lack of thermal electron transfer.

Conclusions

Based on the absorption, resonance-Raman, and e.s.r. spectra as well as the electrochemistry, the redox orbitals of these complexes are ligand localized with the pquin orbital being lower in energy. However, there does appear to be some interaction between the pquin ligands, as shown by the red shifting of the 'pquin' u.v. absorption bands on both reduced and unreduced ligands, as electrons are added electrochemically, and the strong i.v.c.t. bands exhibited between pquin ligands. The data are also consistent with the previous formulation of both 'quin' and 'pquin' π systems within the pquin ligand.

Acknowledgements

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