Resonance Raman Spectroelectrochemical Study of (μ-3,3',4,4'-Tetraimino-3,3',4,4'-tetrahydrobiphenyl)bis[bis(bipyridine)ruthenium(II)](4+) and Its One-, Two-, and Four-Electron-Reduction Products

F. Hartl,* T. L. Snoeck, and D. J. Stufkens

Anorganisch Chemisch Laboratorium, J. H. van't Hoff Instituut, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

A. B. P. Lever*

Department of Chemistry, York University, North York, Ontario, Canada M3J 1P3

We report resonance Raman data over a range of excitation wavelengths for the title complex and its one-, two-, and four-electron-reduced products. Assignments previously reported are generally supported by these observations. The nature of the various excited states is discussed on the basis of the enhanced, coupled vibrations.

Introduction

The last two decades have seen rapid growth of interest in the application of thin-layer transmission spectroelectrochemistry for simultaneous in-situ generation and spectroscopic (UV−vis, IR, ESR) characterization of transition metal complexes with metal atoms or ligands in different oxidation states.[1] This approach is a very effective method of electrolysis, requiring relatively small amounts of redox-active compound and allowing the spectroscopic detection, as a function of time or temperature, of redox products which cannot otherwise be isolated due to their instability.[2] Considerably less attention has been devoted to resonance Raman (rR) spectroelectrochemical studies.[1a,b,3,4] This is the more surprising since resonance Raman spectroscopy is especially well suited for the description of changes in molecular and electronic structure within a redox series of complexes.[5]

Resonance Raman spectra of the redox series based on the complex {[Ru(bpy)₂]₂(μ-3,3',4,4'-tetraimino-3,3',4,4'-tetrahydrobiphenyl)}(PF₆)₄ (denoted below as RuQ.QRu[6]) were

Chart 1

RuQ.QRu   **RuQ'.Q'Ru**
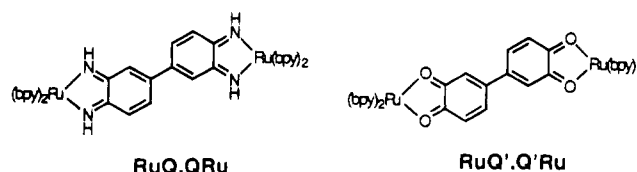
measured to provide proof for previous[7] spectroscopic assignments and to investigate in more detail the electronic structures of the various species. The rR technique was successfully applied in the past to demonstrate delocalized bonding in some related stable o-quinone complexes of Ru(II),[5] Mn(I),[1a] and Re(I).[1b]

The complex RuQ.QRu and products of its one-, two-, and four-electron Q.Q-localized reductions, RuQ.SQRu, RuSQ.SQRu, and RuCat.CatRu,[6] were chosen for study using rR spectroelectrochemistry for the following reasons:

First, the various members of the Q.Q-based redox series possess many electronic transitions[7] in the spectral region covered by the laser lines used. Second, they display[7] a variable degree of electronic interaction between the termini of the bridging ligand and the Ru centers and between the termini themselves, strongly depending on the oxidation state of both the metal and the ligand. This class of complexes, containing redox-active, or so-called noninnocent, ligands has also been systematically studied[1i,8−11] because of their potential as building blocks in molecular wires and switches[7] capable of chanelling electronic energy along a desired direction (vectorial electron transfer).

* To whom correspondence should be addressed.
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Experimental Section

Acetonitrile (CH₃CN) was distilled from P_2O_5 and degassed on a vacuum line prior to use. The supporting electrolyte Bu_4NPF_6 was dried in vacuo at 350 K overnight. The complex {[Ru(bpy)₂]₂(μ-3,3′,4,4′-tetraimino-3,3′,4,4′-tetrahydrobiphenyl)}(PF₆)₄ (RuQ.QRu[6]) was synthesized according to the literature procedure.[7]

The controlled-potential electrolyses and thin-layer cyclic voltammetry at a scan rate of 2 mV/s were carried out within a gastight optically transparent thin-layer spectroelectrochemical (OTTLE) cell[12] (optical path of ~0.2 mm, Pt minigrid (32 wires/cm) working and auxiliary electrodes, Ag wire pseudoreference electrode) equipped with NaCl and quartz windows for resonance Raman measurements and collection of UV–vis spectra of the electrogenerated species, respectively. All the spectroelectrochemical experiments were performed with a PAR Model 174 potentiostat under the following conditions: 6 × 10^{-3} M RuQ.QRu and 5 × 10^{-1} M Bu_4NPF_6 in CH₃CN saturated with dry nitrogen gas. UV–vis spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer equipped with a 3600 data station and attached to a MS-DOS PC. Resonance Raman measurements were performed using a Dilor Modular XY spectrometer with a multichannel diode array detection system. The samples were excited by a Spectra Physics Model 2016 Ar⁺ laser or by a Coherent CR-590 dye laser with Coumarine 6 and Rhodamine 6G dyes.

Results and Discussion

Electrochemistry and Spectroelectrochemistry. As reported by Auburn and Lever,[7] the Q.Q ligand in RuQ.QRu is reduced in an one-electron step at -0.27 V vs AgCl/Ag. The subsequent one-electron reduction of the RuQ.SQRu product was found at -0.49 V. The potential difference of $\Delta E^{\circ\prime} = 220$ mV still allows electrochemical generation of the RuQ.SQRu species in the pure form by having carefully imposed small (5–15 mV) negative potential shifts on the Pt minigrid working electrode until the minimum between the two reduction peaks in the thin-layer cyclic voltammogram (TL CV) was reached. The first reduction step was parallelly followed by UV–vis spectroscopy, which showed a clean isosbestic conversion of RuQ.QRu into RuQ.SQRu. The successive one-electron reduction of RuQ.SQRu to RuSQ.SQRu also proceeded isosbestically. The UV–vis spectra of both electrochemically generated complexes RuQ.SQRu and RuSQ.SQRu were identical with those depicted by Auburn and Lever[7] (see Figure 1B herein). However, they noted[7] that RuSQ.SQRu, obtained by controlled-potential reduction at 293 K, decomposed slowly regardless of the solvent used. However, in our hands, RuSQ.SQRu appeared to be stable in the course of the UV–vis spectroelectrochemical experiment and could easily be reoxidized to give pure RuQ.SQRu and RuQ.QRu in effectively 100% yields. The potential difference between the anodic peaks of the RuQ.QRu/RuQ.SQRu and RuQ.SQRu/RuSQ.SQRu redox couples in the TL CV was found to be more than 80 mV larger than that between the corresponding cathodic peaks. Hence, pure RuQ.SQRu could more easily be generated electrochemically by oxidation of RuSQ.SQRu than by reduction of RuQ.QRu. However, both procedures proved equally convenient for the resonance Raman OTTLE experiments (see below).

Upon further reduction of the bridging ligand at -1.11 and -1.25 V vs AgCl/Ag, the RuSQ.SQRu complex was converted into RuSQ.CatRu and RuCat.CatRu, respectively. The rather small value of $\Delta E^{\circ\prime} = 140$ mV, which predicts[13] disproportionation of about 11% of RuSQ.CatRu into RuSQ.SQRu and RuCat.CatRu, prevented generation of the RuSQ.CatRu mixed-valence complex as a pure product. In accordance with the
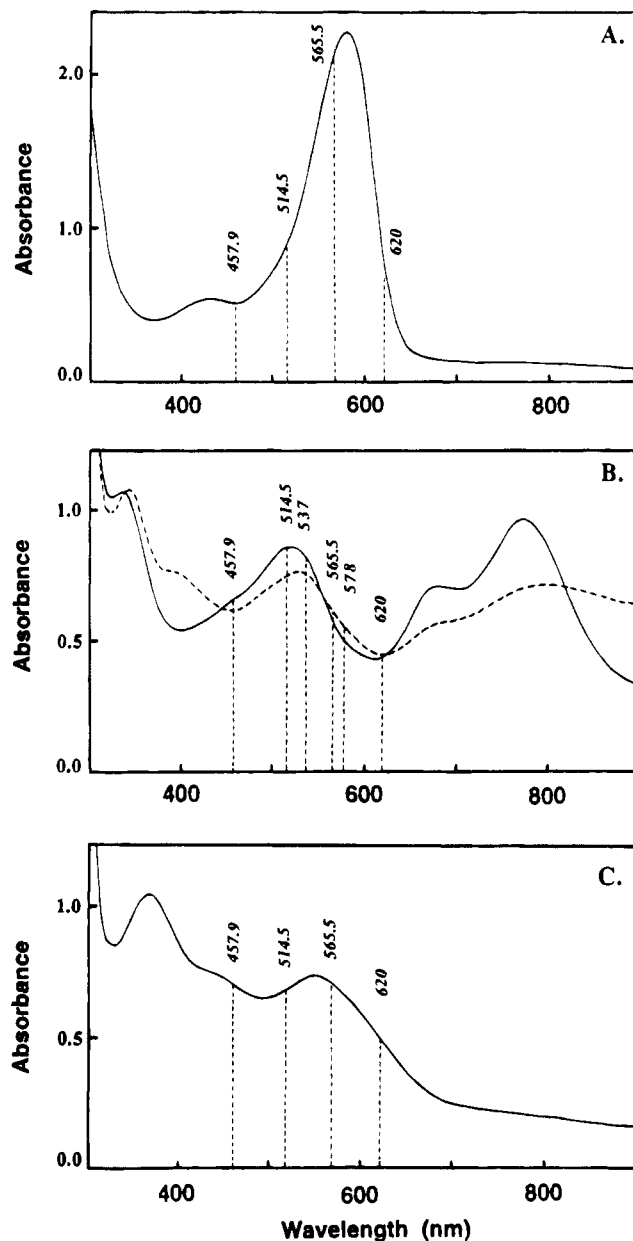

Figure 1. UV–vis spectra of the complexes (A) RuQ.QRu, (B) RuQ.SQRu (full line) and RuSQ.SQRu (dashed line), and (C) RuCat.CatRu.[6] The spectra were obtained in the course of successive OTTLE reduction of 1.95 × 10^{-3} M RuQ.QRu in CH₃CN (saturated solution at 293 K) containing 0.3 M Bu_4NPF_6. The dashed vertical lines denote the excitation laser lines used to carry out the rR experiments.

disproportionation of RuSQ.CatRu, no isosbestic points were observed in the UV–vis spectra measured during the one-electron oxidation of RuSQ.SQRu to RuSQ.CatRu. The UV–vis OTTLE experiment also showed that the absorption bands of RuSQ.CatRu in the visible spectroscopic region, covered by the laser lines, overlap significantly with those of RuCat.CatRu and RuSQ.SQRu. Therefore, RuSQ.CatRu could not be examined by resonance Raman spectroscopy. On the other hand, the electrochemically accessible complex RuCat.CatRu (the first reduction of the bpy ligands occurs[7] at -1.56 V) appeared to be stable enough for the resonance Raman OTTLE study, as indicated by the full reproducibility of the UV–vis spectrum of RuQ.QRu after complete reoxidation of the Cat.Cat bridging ligand to the initial Q.Q redox state. The UV–vis spectrum of RuCat.CatRu, which has not been reported[7] before, is depicted in Figure 1C.

Resonance Raman Spectroscopy. For each exciting laser

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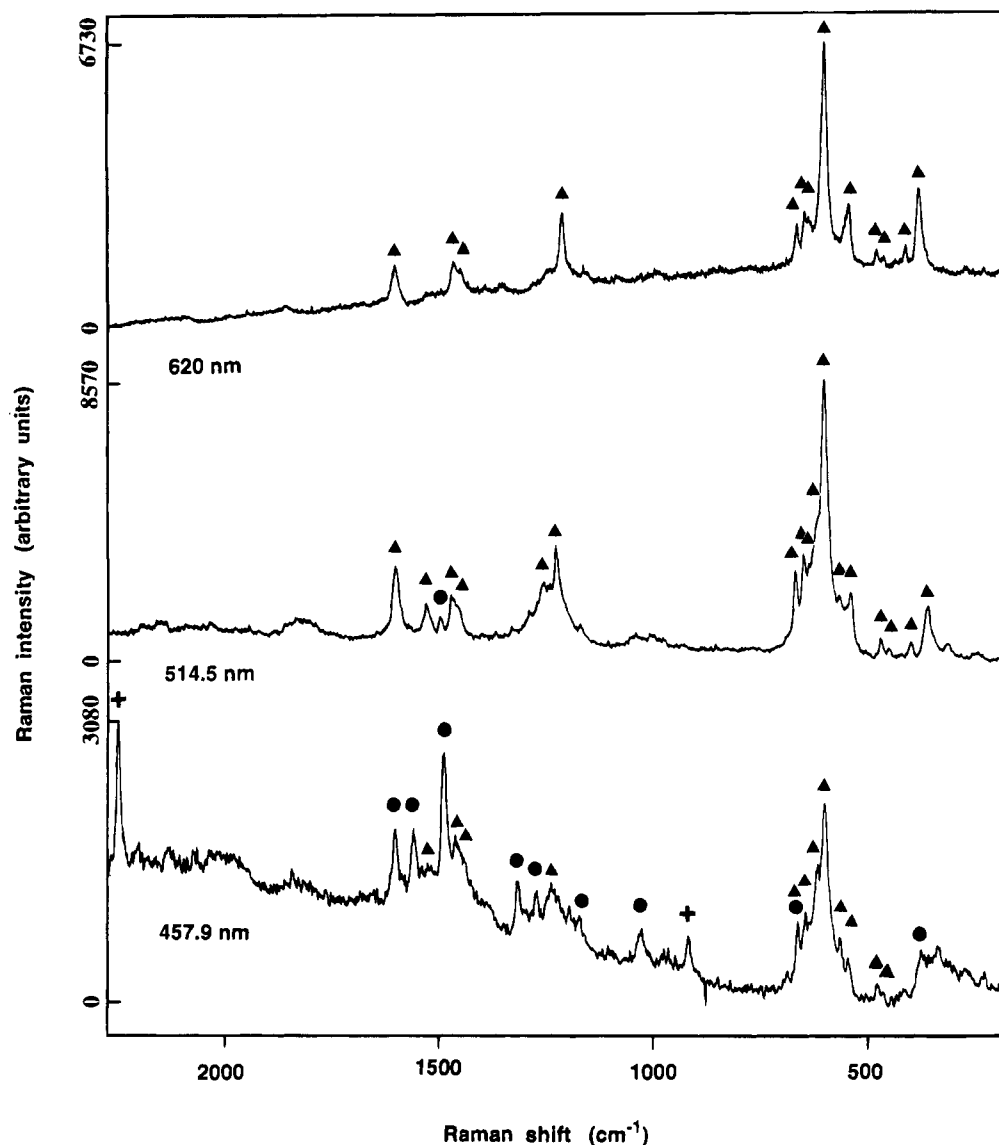
Figure 2. Resonance Raman spectra of RuQ.QRu in acetonitrile solution. Excitation wavelength from top to bottom: 620, 514.5, 457.9 nm. Data correspond to the UV—vis spectrum and excitation wavelengths shown in Figure 1A. The spectra were recorded in an OTTLE cell (NaCl windows). Assignment of the Raman bands: ▲, RuQ fragment (top spectrum—382, 416, 464, 481, 545, 602, 639, 647, 665, 1209, 1445, 1460, 1598 cm^{-1}; middle and bottom spectra—extra bands at 570, 613, 1239, 1523 cm^{-1}); ●, Ru(bpy) fragment (665, 1029, 1172, 1272, 1316, 1487, 1558, 1602 cm^{-1}); +, solvent.

line used, the OTTLE cell was refilled with a fresh solution of RuQ.QRu in acetonitrile. Acetonitrile was used in preference to dichloromethane since RuQ.QRu is much more soluble in this solvent. The resonance Raman (rR) spectra of RuQ.QRu were collected both prior to its reduction and after complete reoxidation of RuCat.CatRu. For each particular laser line, these two rR spectra did not display any apparent difference, not even in the intensity pattern of the resonantly enhanced Raman bands (see below). This is again direct proof of the inherent stability of both RuSQ.SQRu and RuCat.CatRu under the experimental conditions applied. The rR OTTLE experiment then continued with the generation of RuQ.SQRu by careful reduction of RuQ.QRu (see above) or by reoxidation of RuSQ.SQRu. Again, the rR spectra of RuQ.SQRu were identical in both cases (see below). Finally, the rR spectra of RuCat.CatRu were measured with the potential of the minigrid working electrode kept just positive of the onset of the first reduction of the bipyridine ligands.

RuQ.QRu. The UV—vis spectrum of the parent complex RuQ.QRu in acetonitrile shows an intense absorption band at 585 nm ($\epsilon = 6.02 \times 10^4$ M^{-1} cm^{-1}) and a weaker band at 434

nm ($\epsilon = 1.17 \times 10^{-4}$ M^{-1} cm^{-1}) (Figure 1A). In analogy with those for related mononuclear ruthenium dioxolene and quinone diimine complexes,[5,14] these bands are assigned[7] to Ru (d_π) → Q (π^*) and Ru (d_π) → bpy (π_1^*) transitions, respectively. The second Ru (d_π) → bpy (π_2^*) charge transfer (CT) transition is a shoulder at ~320 nm.[7] Similar transitions were indeed recently also reported for the related ligand-bridged complex {[Ru-(bpy)$_2$]$_2$(μ-Q′.Q′)}$^{4+}$ (Q′.Q′ = 3,3′,4,4′-tetraoxobiphenyl).[8]

The resonance Raman spectra of RuQ.QRu were obtained with 457.9, 514.5, 565.5, and 620 nm excitation, and representative rR spectra are shown in Figure 2.

The rR spectrum of RuQ.QRu obtained with 457.9 nm excitation, in preresonance with the 434 nm absorption band, exhibits pronounced features at 1602, 1558, 1487, 1316, 1272, 1172, 1029, and 665 cm^{-1} which are clearly ascribable[5,14–16] to the internal modes of the coordinated bipyridine ligands (see Figure 2). The 434 nm band is therefore assigned to the Ru

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$(d_\pi) \rightarrow$ bpy (π_1^*) MLCT transition,[5,14,15] which is in full accord with the assignment of Auburn and Lever.[7] The other features in the 457.9 nm resonance Raman spectrum (see Figure 2, bottom) have origin in postresonance excitation into the electronic transition(s) involved in the 585 nm band. Their assignment is discussed below.

The rR spectrum obtained by 620 nm excitation into the 585 nm band is dominated by a strong band at 602 cm^{-1} and by a group of less intense bands at 545, 639, 647, and 665 cm^{-1}. The corresponding vibrations might best be considered as the ν(Ru$-$NH(Q)) mode and skeletal modes of the two Ru(Q)$^{2+}$ chelate rings, respectively. Similarly, the resonance Raman spectrum of the related complex Ru(bpy)$_2$(Cl$_2$Q)$^{2+}$ (Cl$_2$Q = 4,5-dichlorobenzoquinone diimine) showed a very intense band of the ν(Ru$-$NH(Q)) vibration at 603 cm^{-1}.[17] A strong Raman band is also present at 382 cm^{-1}. This band cannot be assigned in this case to the stretching Ru$-$N(bpy) vibration (see below) as no intraligand bipyridine modes were found in the 620 nm spectrum. Instead, the 382 cm^{-1} feature is tentatively ascribed to a Q-deformation mode. Another group of Raman bands at 1209, 1445, 1460, and 1598 cm^{-1} corresponds reasonably well with intraligand vibrations of Q.Q.

The scattered Raman intensities I_k and $I_{k'}$ from vibrational modes k and k', respectively, are related to the changes in equilibrium distances Δ_k and $\Delta_{k'}$ between the ground and excited state potential energy curves along the normal coordinates of the vibrations k and k' and to the wavenumbers of the Raman bands ν_k and $\nu_{k'}$, respectively, via

$$\frac{I_k}{I_{k'}} = \frac{\Delta_k^2 (2\pi\nu_k)^2}{\Delta_{k'}^2 (2\pi\nu_{k'})^2} \quad (1)$$

where $2\pi\nu_k = \omega_k$ and $2\pi\nu_{k'} = \omega_{k'}$ are the ground-state radial frequencies of the vibrational modes k and k'.[16] The high intensity of the dominating low-frequency ν(Ru$-$NH(Q)) mode in the 620 nm excited spectrum of the RuQ.QRu complex therefore implies a very strong resonance Raman effect on the Ru$-$NH(Q) bonds, thus a very weak MLCT character of the electronic transition involved in the 585 nm band.[18] Instead, this band may best be assigned to a delocalized $\pi_{Ru-Q} \rightarrow \pi^*_{Ru-Q}$ transition. Such electronic transition originates[1a,b,5] between the π HOMO ($= \pi_{Ru-Q}$) and π^* LUMO ($= \pi^*_{Ru-Q}$) of the Ru(Q)$^{2+}$ chelate ring, which have a mixed d$_\pi$(Ru) $+ \pi^*$(Q) and π^*(Q) $-$ d$_\pi$(Ru) character, respectively. The appearance of the enhanced intraligand modes of the Q.Q ligand nevertheless shows that the mixing is not complete and that the π_{Ru-Q} HOMO may still have a significant d$_\pi$(Ru) contribution while the π^*_{Ru-Q} LUMO possesses a partial π^*(Q) character.

The asymmetric absorption band at 585 nm apparently encompasses at least two electronic transitions (see Figure 1A) which may originate from different close-lying occupied Ru (d$_\pi$) orbitals of RuQ.QRu.[17,18] It can reasonably be excluded[7] that they arise from the two RuQ termini which are electronically nonequivalent in the excited state. Similar asymmetric, intense metal $\rightarrow$ quinone transitions are typically found in the electronic spectra of all mononuclear complexes of Ru(II), Mn(I), and Re(I), with a single o-quinone ligand so far studied.[1a,b,5,17,18]

Upon going from 620 to 565.5, 514.5, and 457.9 nm excitation, certain changes in the rR spectra were observed

which are indeed in favor of the assignment of the 585 nm band to more than one $\pi_{Ru-Q} \rightarrow \pi^*_{Ru-Q}$ transition. The 620 and 565.5 nm excited spectra showed hardly any difference, with the only exception that the vibrations of the Q.Q ligand at 1598 and 1209 cm^{-1} became equally resonantly enhanced in the latter case. Contrary to this, new bands appeared at 570, 613, 1239, and 1523 cm^{-1} in the rR spectrum of RuQ.QRu upon excitation at 514.5 and 457.9 nm (see Figure 2), i.e. into the possible higher energy $\pi_{Ru-Q} \rightarrow \pi^*_{Ru-Q}$ transition which seems to lie at about 510 nm. Interpretation of these rR effects would require separate normal-mode and MO calculations which have not yet been attempted.

RuQ.SQRu. UV$-$vis spectroelectrochemical measurements have indicated[8] that the one-electron-reduced complex Ru-Q.SQRu differs considerably in structure from the corresponding species RuQ'.SQ'Ru. Previously, one of us[7] has argued that the spectroscopic data for RuQ.SQRu are best understood in terms of the N,N-chelated Q.SQ ligand possessing a twist at the central C$-$C bond which implies that both RuQ and RuSQ components remain electronically distinct. Consequently, absorption bands of separate Ru $\rightarrow$ Q and Ru $\rightarrow$ SQ CT and SQ $\rightarrow$ Q intervalence CT transitions have been found[7] in the electronic spectrum of the Robin$-$Day class II[18] valence-localized RuQ.SQRu compound. In contrast, the UV$-$vis spectrum of the complex RuQ'.SQ'Ru leads to the conclusion[8] that the O,O-chelated Q'.SQ' ligand is planar and electronically equivalent (a Robin$-$Day class III[19] delocalized molecule) and lacks spectroscopic signatures to separate the RuQ' and RuSQ' chromophores.

The UV$-$vis spectrum and rR spectra of electrochemically generated RuQ.SQRu are presented in Figures 1B and 3, respectively. Because of the restricted wavelength region of the laser source, rR spectra could only be measured in resonance with three absorption bands:[7] (i) the band at 522 nm (in CH$_3$CN; $\epsilon = 21\,500$ M^{-1} cm^{-1}) which belongs to the Ru (d$_\pi$) $\rightarrow$ Q (π^*) transition; (ii) the Ru (d$_\pi$) $\rightarrow$ bpy (π_1^*) CT band at $\sim$465 nm (sh); (iii) onset of the absorption band at 680 nm ($\epsilon = 17\,000$ M^{-1} cm^{-1}) which was tentatively assigned to an intraligand (SQ) transition. The very interesting SQ $\rightarrow$ Q LLCT transition at 12 900 nm and the Ru (d$_\pi$) $\rightarrow$ SQ (π^*) transition at 775 nm (see Figure 1B) were unfortunately not covered by the laser lines.

The correctness of the assignment of the Ru (d$_\pi$) $\rightarrow$ bpy (π_1^*) CT transition (see above) became apparent upon 457.9 nm excitation. As with RuQ.QRu, the corresponding rR spectrum (see Figure 3) showed a strong rR effect for the bipyridine bands[16] at 1602, 1557 (both ν(C=C)), 1483 (the most intense one), 1317 (both ν(C=N)), 1271 (ν(C$-$C) inter-ring), 1173 (δ(CCH) in plane), 1025 (ring breathing), and 667 (δ(CCC) inter-ring) cm^{-1}. These bands were still observable, although much less intense, upon 514.5 and 537 nm excitation. The presence of only one set of the bipyridine modes is surprising since the bipyridine ligands bound to the RuQ and RuSQ parts should be inequivalent. The similar frequencies of the internal bipyridine modes with respect to RuQ.QRu suggest that the Ru $\rightarrow$ bpy π-back-donation is not much affected by the presence of one RuSQ chromophore, probably due to strong π-acceptor properties of the Q terminus, which can compensate for a weak π-donor character of SQ. All the frequencies of the internal bipyridine modes are apparently lower in both RuSQ.SQRu and RuCat.CatRu relative to RuQ.SQRu (see below). These observations may reflect some electronic coupling between the Q and SQ termini which is strong enough to prevent a charge "leakage" to the bipyridine ligands coordinated to RuSQ.

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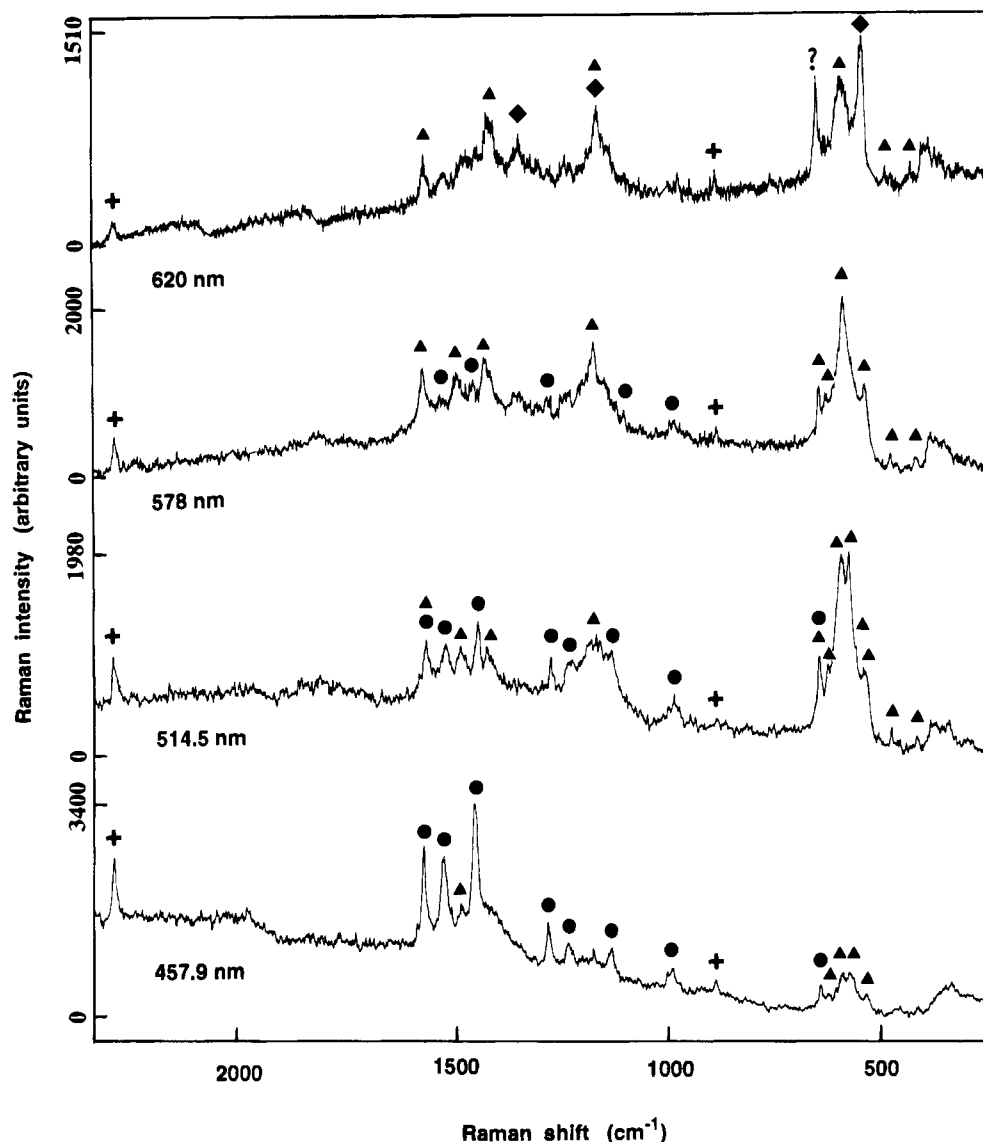(19) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

Figure 3. Resonance Raman spectra of RuQ.SQRu in acetonitrile solution. Excitation wavelength from top to bottom: 620, 578, 514.5, and 457.9 nm. Data correspond to the UV−vis spectrum and excitation wavelengths shown in Figure 1B. The spectra were recorded in an OTTLE cell (NaCl windows). Assignment of the Raman bands: ▲, RuQ fragment (417, 485, 550, 570, 597, 613, 649, 667, 1210, 1457, 1521, 1597 cm⁻¹); ◆, RuSQ fragment (550, 1204, 1366 cm⁻¹); ●, Ru(bpy) fragment (667, 1025, 1173, 1271, 1317, 1483, 1557, 1602 cm⁻¹); +, solvent.

The 514.5 nm excited rR spectrum (Figure 3), obtained upon irradiation into the 522 nm absorption band (Figure 1B), shows enhancement for bands at 1597 (with contribution of a bipyridine mode), 1521, 1457, 1210, 667 (also identical frequency with a bipyridine mode), 649, 613, 597, 570, 550, 485, and 417 cm⁻¹. Evidently, the above frequencies are very similar to those seen with the RuQ.QRu complex (see above) and may therefore be assigned, accordingly, to the skeletal Ru−Q and intraligand Q modes of the RuQ part of RuQ.SQRu. The intense bands at 613 and 597 cm⁻¹ may reasonably be assigned to two stretching Ru−NH(Q) modes, mixed with Q skeletal vibrations. These ν(Ru−NH(Q)) modes are associated with two chemically different NH= groups of the Q terminus. A similar observation has been made for the complex Ru(bpy)₂(dadib)²⁺ (dadib = 3,4-diamino-3′,4′-diimino-3′,4′-dihydrobiphenyl).[17] Its resonance Raman spectrum also shows two ν(Ru−Q) vibrations at 618 and 575 cm⁻¹.[17b]

Similar to that of RuQ.QRu, the intensity pattern of the Raman bands (see Figure 3) is again in favor of a delocalized $\pi_{Ru-Q} \rightarrow \pi^*_{Ru-Q}$ transition. A gradual decrease in the intensities of the above Q and Ru−NH(Q) modes was observed when the wavelength of the exciting laser was varied from 514.5 nm either

to 457.9 nm or to 565.5 nm, using the 2251 cm⁻¹ band of CH₃CN as an internal standard. However, the intensities again increased considerably upon 578 and 620 nm excitation. In this case, the bands at 613 and 597 cm⁻¹ were no longer defined and, instead, only one ill-resolved band at 605 cm⁻¹ was observed in the latter rR spectra (see Figure 3). More evidence must be obtained to determine whether the aforementioned rR properties correspond to two $\pi_{Ru-Q} \rightarrow \pi^*_{Ru-Q}$ transitions.

Finally, the 620 nm excitation of RuQ.SQRu in postresonance with the transition at 680 nm (see Figure 1B) gave rise to resonant enhancement also for bands at 1366, 1204, and 550 (strong) cm⁻¹ (see Figure 3). The presence of the prominent 550 cm⁻¹ band is especially indicative. This band certainly cannot be attributed to the Q terminus as it is also dominant in the rR spectrum of RuSQ.SQRu upon similar excitation (see below). The corresponding vibration is apparently in resonance with an electronic transition associated with the SQ terminus of the Q.SQ bridging ligand. Auburn and Lever briefly noted[7] two possibilities for its assignment. The first one considers the 680 nm transition as another Ru (d$_\pi$) $\rightarrow$ SQ (π^*) CT process whereas the second interpretation suggests its internal-ligand origin.
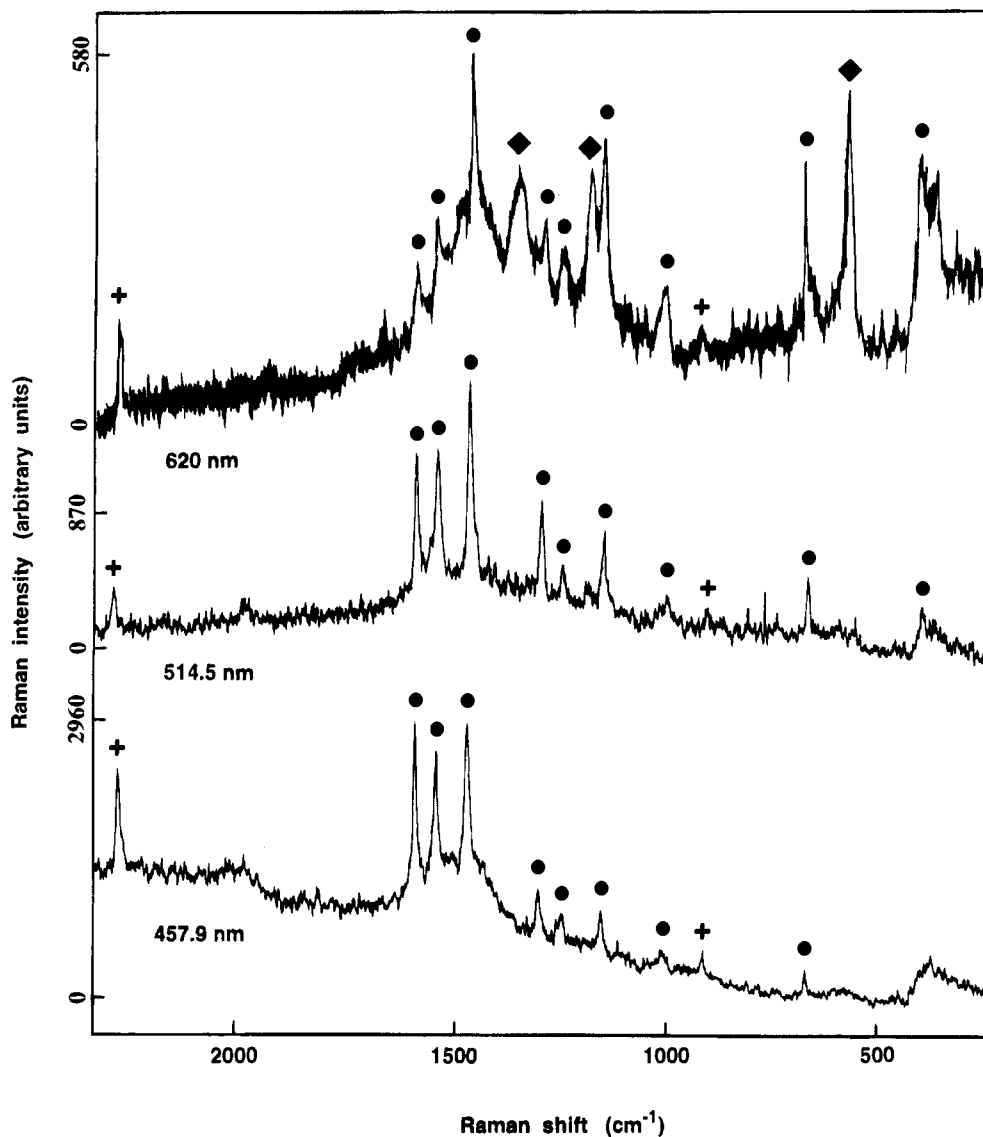
Figure 4. Resonance Raman spectra of RuSQ.SQRu in acetonitrile solution. Excitation wavelength from top to bottom: 620, 514.5, 457.9 nm. Data correspond to the UV−vis spectrum and excitation wavelengths shown in Figure 1B. The spectra were recorded in an OTTLE cell (NaCl windows). Assignment of the Raman bands: ◆, RuSQ fragment (550, 1204, 1366 cm^{-1}); ●, Ru(bpy) fragment (371, 664, 1015, 1167, 1265, 1314, 1480, 1551, 1600 cm^{-1}); +, solvent.

It is well-known from the literature on the mononuclear complexes [Ru(bpy)$_2$(L)]$^+$ (L = o-semiquinone-related ligands derived from 1,2-dihydroxybenzene, 2-aminophenol, and 1,2-diaminobenzene)[1b,18] that the unpaired electron remains generally localized on the radical ligand L instead of being considerably delocalized over the metal-L chelate bond. Similarly, the ESR spectrum of RuQ.SQRu also points to a SQ-centered radical.[7] The Ru (d$_\pi$) → SQ (π^*) transition is henceforth expected to have strong MLCT character. Upon excitation to the Ru (d$_\pi$) → SQ (π^*) MLCT transition, the rR spectrum of RuQ.SQRu should thus exhibit only a weakly enhanced ν(Ru−NH(SQ)) mode at a lower Raman frequency relative to ν(Ru−NH(Q)) but strongly enhanced internal SQ vibrations. This spectroscopic pattern has indeed been found in the rR spectra of the complexes [Re(CO)$_{4-n}$(PPh$_3$)$_n$(DBSQ)] (n = 0−2; DBSQ = 3,5-di-$tert$-butyl-1,2-benzosemiquinone)[1b,20] excited into the Re (d$_\pi$) → DBSQ (π^*) MLCT transitions. For RuQ.SQRu, however, the intensity of the 550 cm^{-1} band in the 620 nm excited spectrum is evidently too high (see Figure 3) to support the Ru (d$_\pi$) → SQ (π^*) MLCT assignment of the 680 nm

absorption band. Better, the 550 cm^{-1} Raman band might belong to a ν(Ru−NH(SQ)) vibration which is then strongly coupled to an electronic transition between orbitals of mixed Ru-SQ character. This interpretation requires further analysis when rR spectra of RuQ.SQRu, obtained with different laser lines throughout the whole 680 nm absorption band and the 775 nm band become available.

In summary, the observation of two independent sets of skeletal vibrations of the bridging ligand when exciting into the shorter and longer wavelength components of the spectrum of RuQ.SQRu argues convincingly for the existence of the electronically and structurally independent Q and SQ termini. This is fully consistent with the interpretation of Auburn and Lever[7] based on analysis of the corresponding UV−vis spectrum. The RuQ.SQRu complex must then exhibit a twisted configuration which limits an electronic coupling between the Q and SQ termini. As reported by Joulié et al.,[8] this is in sharp contrast with the apparently planar geometry of the related, but strongly coupled, RuQ′.SQ′Ru complex.

RuSQ.SQRu. The RuSQ.SQRu complex contains only two types of chelated ligands, bipyridine and SQ, which are responsible for the absorptions in the visible spectroscopic region

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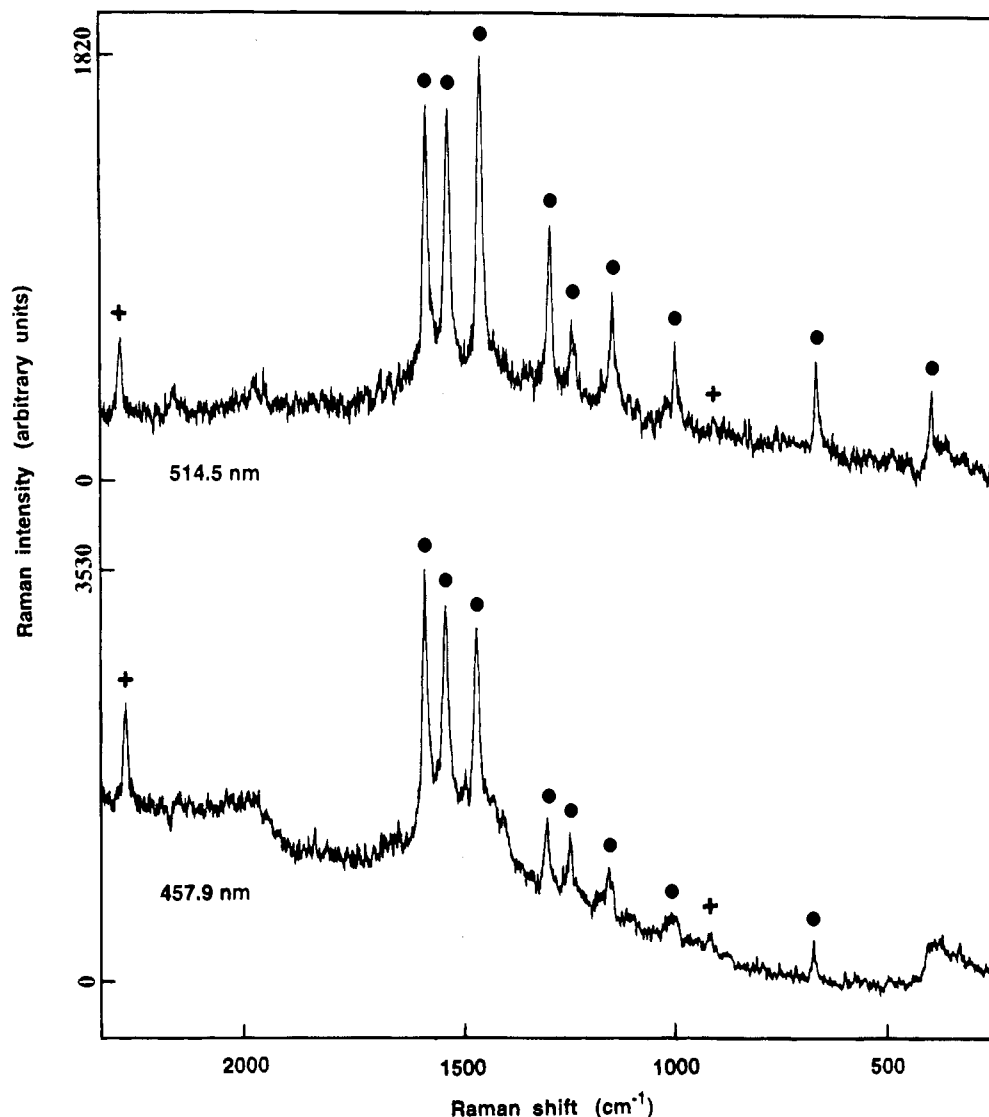
Figure 5. Resonance Raman spectra of RuCat.CatRu in acetonitrile solution. Excitation wavelength from top to bottom: 514.5, 457.9 nm. Data correspond to the UV—vis spectrum and excitation wavelengths in Figure 1C. Spectra were recorded in an OTTLE cell (NaCl windows). Assignment of the Raman bands: ●, Ru(bpy) fragment (371, 664, 1015, 1165, 1261, 1316, 1478, 1550, 1599 cm^{-1}); +, solvent.

(see Figure 1B). The bands at 393 nm (sh) and 538 nm (ϵ = 17 000 M^{-1} cm^{-1}) were tentatively assigned[7] to the Ru (d$_\pi$) → bpy (π_2*) and Ru (d$_\pi$) → bpy (π_1*) transitions, respectively. Both bands are considerably red-shifted due to an increased electron density on the d$_\pi$(Ru) orbitals in comparison with the cases of RuQ.QRu and RuQ.SQRu. Hence, both electronic transitions were in this case available for the rR study. Excitation at 457.9 nm, in preresonance with the band at 393 nm, led to appearance of resonantly enhanced modes in the rR spectrum at 1600, 1551, 1480, 1314, 1265, 1167, 1015, and 664 cm^{-1} (Figure 4), which all belong to the internal bipyridine vibrations (see above). Importantly, the intensity of the 1600 cm^{-1} band is comparable with that of the 1480 cm^{-1} band. This spectroscopic feature has been ascribed[5,15,17] to a preresonace Raman effect of the Ru (d$_\pi$) → bpy (π_2*) transition which is then in agreement with the assignment of the 393 nm band by Auburn and Lever.[7] Noteworthy, all the above modes have slightly lower frequencies than those measured for the complexes RuQ.QRu and RuQ.SQRu (see above). Evidently, increased Ru → bpy π-back-donation due to the absence of the strong π-acceptor Q terminus is responsible for the observed shift of the bipyridine modes. Subsequent variation of the laser-line wavelength from 457.9 to 514.5, 537, and 565.5 nm did not change the character of the rR spectra significantly. In all

cases, only the bipyridine modes were present, accompanied by a more apparent band of the ν(Ru—N(bpy)) vibration at 371 cm^{-1} (Figure 4). The intensity of the 1600 cm^{-1} band gradually decreased as the excitation shifted to lower energy, which then apparently led to population of the π_1*(bipyridine) orbital, in accordance with the literature data on rR spectra of several bipyridine complexes.[5,14,15] The relative intensities of the intraligand bipyridine and ν(Ru—N(bpy)) modes with respect to the standard band of CH$_3$CN at 2251 cm^{-1} paralleled the changes in absorbance of the 538 nm band for the particular laser lines employed, indicating their resonant enhancement. The assignment of the 538 nm band to the Ru (d$_\pi$) → bpy (π_1*) transition[7] was thus unambiguously confirmed.

The last band in the visible spectrum of RuSQ.SQRu which could partially be covered by the laser lines was the ~685 nm shoulder on the high-energy side of the Ru (d$_\pi$) → SQ (π*) transition[7] at 781 nm (Figure 1B). Similar to that of RuQ.SQRu, also in this case the 578 and 620 nm excitation in postresonance with the, as yet unassigned,[7] transition, gave rise to the appearance of a new intense Raman band ((?) ν(Ru—NH(SQ)) at 550 cm^{-1} (see Figure 4). It was accompanied by some other, probably internal, SQ modes at 1366 (the C—C inter-ring stretch[21] of SQ—SQ(?)) and at 1204 cm^{-1}. Using the same reasoning as for RuQ.SQRu (see above), the weak 585 nm band

of RuSQ.SQRu is tentatively attributed to an electronic transition of mixed Ru–SQ character.

RuCat.CatRu. The UV–vis spectrum of RuCat.CatRu (Figure 1C) closely resembles that of RuCat'.Cat'Ru (Cat' = the O,O-derivative of Cat).[8] Both spectra show in the visible region two bands belonging to the Ru → bpy transitions. In the UV–vis spectrum of RuCat.CatRu, the Ru (d_π) → bpy ($\pi_2{}^*$) transition is a shoulder at ∼440 nm, and the band of the Ru (d_π) → bpy ($\pi_1{}^*$) transition is found at 550 nm (ϵ = 16 900 M^{-1} cm^{-1}). Analogous to the case of RuCat'.Cat'Ru,[8] the broad ill-resolved low-energy band at ∼740 nm can be attributed to a Cat → bpy (π^*) interligand charge-transfer (LLCT) transition. However, no evidence for this assignment could be obtained from our resonance Raman measurements which covered only the 457.9–620 nm range.

The red shift of both Ru (d_π) → bpy (π^*) bands with respect to those of RuSQ.SQRu made the Ru (d_π) → bpy ($\pi_2{}^*$) transition more accessible for Raman excitation with the 457.9 nm laser line. The corresponding rR spectrum showed rR effects for the internal bipyridine modes at 1599, 1550, 1478, 1316, 1261, 1165, 1015, and 664 cm^{-1} (see Figure 5). These frequencies are only slightly lower than those found for RuSQ.SQRu, indicating thus a similar Ru → bpy π-back-donation in both complexes. As expected, the most intense Raman band in the spectrum is that at 1559 cm^{-1} which is the typical rR feature for the Ru (d_π) → bpy ($\pi_2{}^*$) MLCT transition.[5,14,15]

Upon excitation into the Ru (d_π) → bpy ($\pi_1{}^*$) MLCT transition with laser lines of 514.5 (Figure 5), 565.5, and 620 nm, the same set of bipyridine Raman bands was observed, accompanied now by the more apparent ν(Ru–N(bpy)) band at 371 cm^{-1}. The relative intensities of the bipyridine bands varied upon going from 514.5 to 620 nm excitation. The intensities of the bands at 1599, 1550, 1478, and 1261 cm^{-1} tend to decrease more rapidly than the intensities of those at 1361, 1265, and 1015 cm^{-1}. The intensity of the 1599 cm^{-1} band was, in all cases, lower than that of the 1478 cm^{-1} band, which confirmed the Ru (d_π) → bpy ($\pi_1{}^*$) MLCT character of the electronic transition at 550 nm. On the other hand, the Raman bands at 664 and 371 cm^{-1} slightly increased in intensity

upon low-energy excitation. These variations imply the presence of two allowed Ru (d_π) → bpy ($\pi_1{}^*$) transitions encompassed within the 550 nm absorption band, as could indeed be expected from its irregular shape (see Figure 1C), and probably arising from two different d orbitals.

The above described resonance Raman spectra prove that the reduction of RuSQ.SQRu and RuSQ.CatRu is localized on the SQ termini and not on the bipyridine ligands. For, the resonance Raman spectrum of the radical anion [bpy]$^-$ in dioxane-d_8 exhibits bands at 1555, 1488, 1353, 1276, 1205, 1164, and 995 cm^{-1}.[22] A similar result was obtained in THF.[23] The resonance Raman spectra of the reduced complexes [Ru(bpy)$_2$(bpy$^-$)]$^+$ and [Ru(bpy)(bpy$^-$)$_2$] then reveal a combined spectroscopic pattern of the bipyridine and [bpy]$^-$ ligands.[24]

The redox series investigated here provides a unique data set showing how the electronic structure changes with successive addition of electrons to a redox-active ligand. Of interest in this context, the Ru (d_π) → bpy ($\pi_1{}^*$) CT transition is an internal marker of the net electron density residing on the ruthenium center. By application of eq 2,[25] the energies of the Ru (d_π) →

$$E_{op} = 0.65E[Ru^{III}/Ru^{II}] + 2.0 \quad [eV] \qquad (2)$$

bpy ($\pi_1{}^*$) transition, E_{op}, can be used to extract the apparent Ru^{III}/Ru^{II} redox potentials, $E[Ru^{III}/Ru^{II}]$, for ruthenium attached to the variously reduced ligands (vs SCE): RuQ.QRu, 1.32 V; RuQ.SQRu, 1.02 V; RuSQ.SQRu, 0.47 V; RuCat.CatRu, 0.39 V. The dramatic change of almost 1 V testifies to the enormous increase in electron richness on ruthenium which occurs as the bridging ligand is reduced from Q.Q to Cat.Cat.

In conclusion, the present rR study of the RuQ.QRu complex and its reduction products, RuQ.SQRu, RuSQ.SQRu, and RuCat.CatRu, has valuably contributed to the description of the bonding picture in these complexes. Importantly, the study has confirmed the previous[7] assignments of the electronic transitions and arguments for twisting, especially in the complex Ru-Q.SQRu. New insight has also been gained into the electronic structures of the various excited states.

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