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Resonance Raman Spectrum of the Phenanthroline Anion: Implications on Electron Delocalization in the MLCT Excited State of Ru(phen)$_3^{2+}$

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Introduction

Time-resolved resonance Raman (TR^3) spectroscopy has been utilized to demonstrate that electronic excitation in the lowest metal-to-ligand charge-transfer (MLCT) excited states of many transition metal tris- or bis(diimine) complexes in solution is localized on just one of the ligands.[1−6] Therefore the MLCT state of Ru(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridine) is often represented as (bpy)$_2$Ru(III)(bpy$^{\bullet-}$)$^{2+}$. As evidence for this localization, the correspondence of the TR^3 spectrum of the excited complex to the ground state resonance Raman (rR) spectrum of 2,2′-bipyridine radical anion (bpy$^{\bullet-}$) in solution is particularly persuasive.[1b,6] This picture is supported by several other types of spectroscopic studies, most notably photoselection[7] and time-resolved absorption polarization,[8] and further evidence is available from the normal coordinate analysis of the ground and MLCT excited states of Ru(bpy)$_3^{2+}$ and of the bpy radical anion.[9]

Despite the strong similarities between the spectroscopic[10] and electrochemical[10,11] characteristics of the 1,10-phenanthroline (phen) complexes with Ru and those of their bpy analogs, definitive TR^3 spectra of the MLCT states of Ru(phen)$_3^{2+}$ and other tris- and bis(phen) complexes have been difficult to obtain.[12] The TR^3 spectrum of Ru(bpy)$_3^{2+}$ is markedly different from ground state scattering and is easily obtained by irradiating $\sim 10^{-4}$ M aqueous solutions with 354.7 nm pulses having a fluence of $\sim 6 \times 10^6$ W/cm^2 (∼2 mJ, 10 ns/pulse, beam waist of ∼1 mm).[1] Hopkins and co-workers recently reported[13] that only the ground state spectrum of Ru(phen)$_3^{2+}$ can be observed under comparably low fluence conditions, in agreement with our own work.[14] However they could observe a TR^3 spectrum of excited Ru(phen)$_3^{2+}$ under the uncommonly large light fluence of 2×10^9 W/cm^2 (100 μJ/pulse, 30 ps/pulse, beam waist 250 μm, 354.7 nm); it appears to be rather similar to the ground state spectrum.[14] Kumar *et al.* earlier reported a very weak TR^3 spectrum of Ru(phen)$_3^{2+}$ obtained with very large fluences (2×10^8 W/cm^2 of highly focused 15 mJ, 10 ns pulses, assuming 0.5 mm beam waist); this spectrum also was similar to the ground state spectrum.[15]

For some time there has existed an obvious question: why should complexes with two such similar ligands produce TR^3 spectra of such different intensities and appearance? In the absence of any spectroscopic measurements on phenanthroline radical anion, it was not possible to dismiss the possibility, however unlikely, that its rR spectrum coincidentally may be nearly identical to that of ground state phen. We report in this paper the electronic and resonance Raman spectra of phen$^{\bullet-}$ in THF solutions. Neither the electronic absorption spectrum of phen$^{\bullet-}$ nor the positions of its Raman bands match those of the ground state or of the lowest MLCT excited electronic state of Ru(phen)$_3^{2+}$. Implications of these results on the electron localization in the MLCT state of the complex will be discussed in a future publication.

Experimental Methods

1,10-Phenanthroline radical anion was synthesized in a specially-designed three-compartment glass apparatus which enables material loading and all manipulations to be performed under purified helium or *in vacuo*. Small pieces of lithium metal (Automergic Chemical Co., 99.99%) with total mass 0.010 g were placed into one chamber and 0.030 g of phen (Aldrich, 99+%), previously sublimed at ∼100 °C under 2×10^{-5} Torr pressure, was added to another. The apparatus was evacuated to 10^{-5} Torr, and 15−20 mL purified[16] tetrahydrofuran (THF) was distilled onto the phen at −78 °C. Upon warming to room temperature the THF dissolved the phen; the solution was poured through a sintered glass frit onto the metal, with instantaneous formation of a dark blue color. After the reaction was complete, the blue solution was poured back through the frit into the neighboring chamber, and a portion was decanted into the third compartment, a 1 cm path length quartz optical cell through which all UV−vis absorption and Raman measurements were made. The phen$^{\bullet-}$ concentration could be controlled by adding or removing THF by distillation. (Similar procedures were employed to generate phen$^{\bullet-}$ with other alkali metal cations.) Os(phen)(py)$_4^{2+}\cdot$2PF$_6^-$, a gift from Professor T. J. Meyer, was examined without any further purification.[17]

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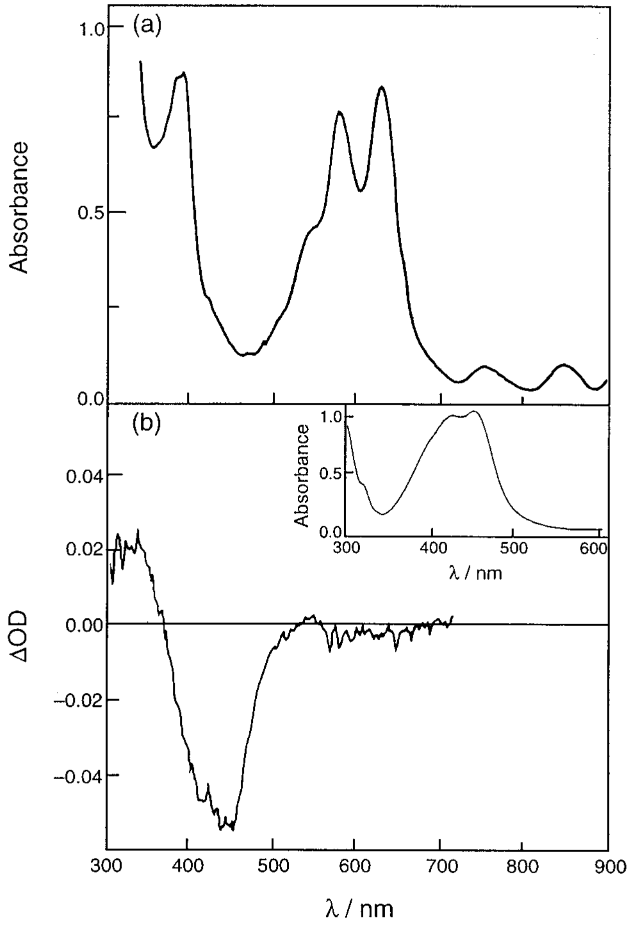

Figure 1. (a) Electronic absorption spectrum of Li$^+$phen$^{\bullet-}$ in THF. (b) Transient absorption spectrum of the MLCT state of Ru(phen)$_3$$^{2+}$ obtained 300 ns after the laser excitation pulse. The inset shows the ground state absorption spectrum of Ru(phen)$_3$$^{2+}$.

All Raman spectra were obtained using 90° scattering geometry, with the laser beam entering through the bottom of the 1 × 1 cm quartz sample cell. Ground state rR spectra were obtained using a water-cooled EG&G Princeton Applied Research (PAR) OMA III Model 1421 detector with a Model 1463 detector controller, mounted on a Spex Model 1877 triple monochromator with filter stage. Gratings with 2400, 1800, or 1200 gr/mm (all blazed at 500 nm) were used for UV, blue, and red excitations, respectively. Excitation radiation from Coherent Innova 200 Ar$^+$ or Innova 90 Kr$^+$ ion lasers was utilized for cw rR measurements, after further beam dispersion through a 60° equilateral prism. The TR^3 spectra were obtained using a Spex Triplemate triple monochromator and filter stage with a cooled EG&G PAR OMA II detector and a Model 1218 detector controller. Pulsed 354.7 nm, ~10 ns excitation was obtained from the third harmonic of a Quanta Ray DCR-1 Nd:YAG laser with HG-1 harmonic generator and PHS-1 prism harmonic separator. Electronic absorption spectra in the UV and visible regions were obtained using a Perkin-Elmer PE-5 diode array spectrometer. The transient absorption spectrum of Ru(phen)$_3$$^{2+}$ was obtained with the help of Dr. J. C. Scaiano at the NRC in Ottawa, using 308 nm excimer laser excitation and OMA detection.[18]

Results

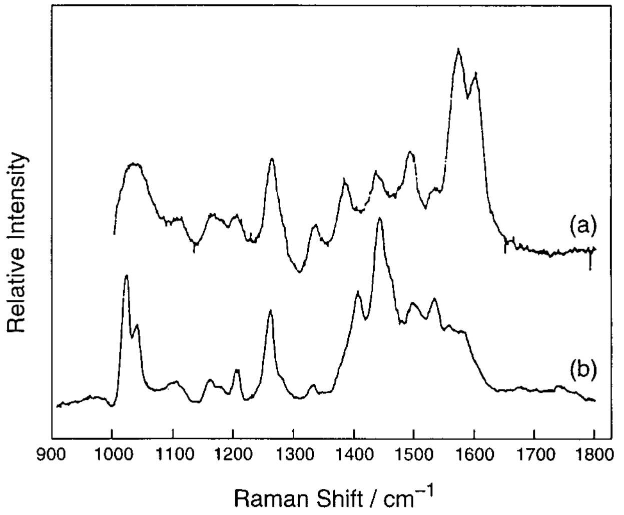

Figure 2. Resonance Raman spectrum of Li$^+$phen$^{\bullet-}$ in THF under (a) 351.1 nm and (b) 406.8 nm excitation.

Table 1. Raman Shifts (1000−1650 cm^{-1}) and Relative Intensities[a] of Phenanthroline Anion (Li$^+$phen$^{\bullet-}$) at Several Excitation Wavelengths

excitation wavelength		
568 and 647 nm	406.8 nm	351.1 and 363.8 nm
	1043 vs	1044 m
1066 ms	1061 m	
1130 m	1122 w	1128 vw
1177 m	1174 w	1178 w
	1221 mw	1217 w
1271 mw	1272 s	1273 s
1340 m	1343 w	1344 w
	1390 m	
1405 ms	1414 w	
1444 s	1449 vs	1442 m
1490 mw	1506 w	1499 m
	1539 w	1539 vw
1570 m	1575 vw	1576 s
		1606 s

[a] vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, and vw = very weak.

The electronic absorption spectrum of Li$^+$phen$^{\bullet-}$ in THF is reproduced in Figure 1a; it shows strong maxima at 387, 585, and 636 nm. This spectrum is consistent with that of phen$^{\bullet-}$ in a solid MTHF (2-methyltetrahydrofuran) matrix[19] and other reports of solution spectra.[20,21] The transient absorption spectrum of Ru(phen)$_3$$^{2+}$ (Figure 1b) closely resembles that previously reported;[22] it shows ground state bleaching in the 380−520 nm region (see inset, Figure 1b) and excited state absorption between 300 and 370 nm, with no phen$^{\bullet-}$-like features in the 520−650 nm region or near 390 nm in the excited state. In contrast, the transient absorption spectrum of Ru(bpy)$_3$$^{2+}$ exhibits strong bpy$^{\bullet-}$-like excited state contributions at 370 nm.[1b,6]

Resonance Raman scattering from THF solutions of phen$^{\bullet-}$ with Li$^+$, Na$^+$, K$^+$, and Cs$^+$ as counterions has been measured at several excitation wavelengths under a variety of experimental conditions. Representative spectra of Li$^+$phen$^{\bullet-}$ observed with 351.1 and 406.7 nm cw excitation are reproduced in Figure 2 and peak positions with their relative intensities at several excitation wavelengths are listed in Table 1. Within the ~2 cm^{-1} experimental uncertainty, the Raman spectra are independent of the countercation. The number of bands and their intensity pattern resemble the bpy$^{\bullet-}$ rR spectra obtained under

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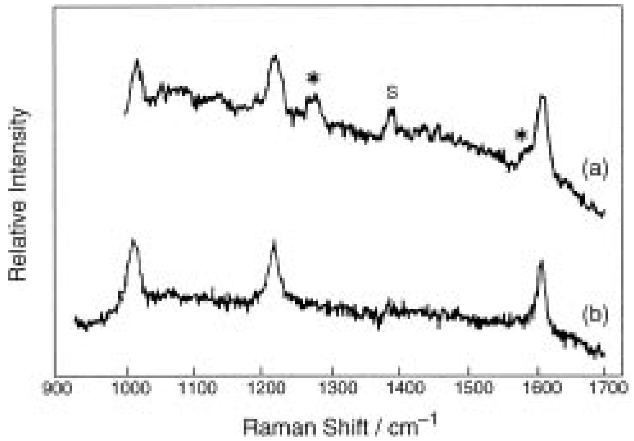

Figure 3. Resonance Raman spectra of $Os(phen)(py)_4^{2+}$ in acetonitrile under (a) 354.7 nm pulsed excitation and (b) 363.8 nm cw excitation. Bands marked with an asterisk are due to the reduced phen ligand in the MLCT excited electronic state. (S denotes a solvent peak which was not fully subtracted from the spectrum.)

similar conditions by Hornberger.[6] For example, the strongest band under 351.1 nm excitation lies near 1275 cm^{-1} for both anions. The strong peak at 1285 cm^{-1} in the TR^3 spectrum of $Ru(bpy)_3^{2+}$ has been attributed to this bpy$^{\bullet-}$ mode in the MLCT excited state.[1b,4,6]

Early in the course of this research we measured TR^3 spectra for $10^{-3}-10^{-4}$ M aqueous solutions of the eight $Ru(II)(bpy)_x(L)_{3-x}{}^{\bullet}(BF_4)_2$ mixed-ligand salts, where L = either 2,2′-bipyrimidine (bpm) or phen. The behavior observed depends on the nature of L. When the second ligand is bpm, the same TR^3 spectra that we have already reported[3a] for $Ru(bpm)_3^{2+}$ are easily observed when $x = 1$ or 2.[3c,14,23] These contain none of the well-known bpy$^{\bullet-}$ features and are presumably characteristic only of bpm$^{\bullet-}$. For L = phen the TR^3 spectra are nearly identical to each other and to those reported by Kumar *et al.*[15] and by Hopkins *et al.*[13] and vary only slightly in intensity when $x = 1-3$. They are readily observable even with defocused excitation and are all characteristic of bpy$^{\bullet-}$, as originally observed for the $x = 3$ ion. However, for $x = 0$, *i.e.* for $Ru(phen)_3^{2+}$, the TR^3 spectrum shows no phen$^{\bullet-}$ peaks but only ground state features even with highly focused excitation. None of the three phen-containing complexes show the peak at 1557 cm^{-1} reported by Kumar *et al.*[15]

Figure 3 shows the ground state rR and TR^3 (excited state) spectra of $\sim 10^{-3}$ M solutions of $Os(phen)(py)_4^{2+}\cdot 2PF_6^-$ in acetonitrile. In this complex the lowest energy transition corresponds to $Os^{II} \rightarrow$ phen MLCT.[24] Therefore the promoted electron would necessarily be localized on phen, since the MLCT transition to the pyridine ligands lies at much higher energies. As in our earlier report on $Ru(bpy)(py)_4^{2+}$,[3b] ground state peaks dominate the Raman scattering; however, weak features near 1275 and 1580 cm^{-1} are observed, which correspond to the strongest bands of phen$^{\bullet-}$ under UV excitation (Figure 2).[25]

Discussion

It is clear that the TR^3 spectrum of $Ru(phen)_3^{2+}$ obtained at high peak powers[13] does not correspond to that of phen$^{\bullet-}$, and therefore does not support a localized model for the MLCT excited state of this complex. The spectrum reported by Kumar *et al.* for $Ru(phen)_3^{2+}$ under nanosecond pulsed excitation is that of the *ground state*, plus an additional band at 1557 cm^{-1} which is an experimental artifact.[15,26] Other published time-resolved Raman spectra of related systems, such as Cu complexes with substituted phen ligands,[27] also differ little from the ground state spectrum, and do not resemble the rR spectrum of phen$^{\bullet-}$. Recently the rR spectra of $[(phen)(CO)_3Re(NC)Ru(phen)_2(CN)]^+$ and related complexes collected under pulsed excitation were reported, and the observed bands were assigned to the spectrum of phen$^{\bullet-}$.[28] However, inspection of the spectral profile and vibrational frequencies reveals that this spectrum is also that of the ground state of the Ru−phen chromophore.[13]

The rR spectrum of the MLCT excited state of $Ru(phen)_3^{2+}$ has vibrational frequencies very close to those of the ground state at similar excitation wavelengths,[13] which indicates little nuclear displacement between the ground and lowest MLCT excited states. Franck−Condon resonance Raman scattering from a molecule with little change in nuclear coordinates between the states in resonance is expected to be very weak,[29,30] in accordance with the observations of TR^3 spectroscopy.

It has been shown that the TR^3 spectrum of $Ru(phen)_3^{2+}$ is not observed at low light fluences,[13] whereas $Ru(bpy)_3^{2+}$ posseses excited state Raman scattering that is easily obtained under low power conditions, even with highly focused cw lasers.[31] This suggests that in $Ru(phen)_3^{2+}$ the electron is either delocalized or hopping among ligands at a rate comparable to that of vibrational frequencies ($\sim 10^{13}$ s^{-1}). In a future paper we explain the localization, on the vibrational time scale, of the transferred electron on a bpy-like ligand and its apparent delocalization over all three ligands in $Ru(phen)_3^{2+}$.

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(25) The similarity of the TR^3 spectra of $Ru(bpy)_3^{2+}$ and $Re(bpy)(CO)_3^{+}$ [2] helped confirm the localized model originally proposed by Woodruff and co-workers.[1]

(26) Kumar *et al.* (ref. 15) utilized a flowing sample in the form of a capillary stream in air. We have simulated this condition by simply measuring the Raman scattering under pulsed excitation from an empty sample compartment following alignment and calibration with toluene in a 1 × 1 cm cuvette. In the 1000−1700 cm^{-1} region, the result is a single peak at 1557 cm^{-1}, which we attribute to the well-known O_2 vibration at 1554.7 cm^{-1} reported by Herzberg. (Herzberg, G. *Spectra of Diatomic Molecules*; D. Van Nostrand Company: New York, NY, 1950, p 62.)

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