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Characterization of Multiple Charge-Transfer Excited States of Tris(2,2′-bipyrimidine)ruthenium(II) by Resonance Raman Spectroscopy

Sir:

Resonance Raman scattering can be used effectively to characterize excited electronic states since the nature of the upper state is reflected in those ground-state vibrational modes that display intensity enhancement.[1] The technique is particularly useful for large molecules, which often show broad, featureless electronic absorption. In addition, under favorable lifetime conditions electronic and vibrational information about an excited state itself may be obtained by resonance Raman spectroscopy.[2] We report here Raman scattering in resonance with several partially resolved transitions in the complex ground-state absorption spectrum of tris(2,2′-bipyrimidine)ruthenium(II) [$\mathrm{Ru(bpym)_3}^{2+}$]; Raman scattering from the lowest metal-to-ligand charge-transfer (MLCT) excited state—which may be represented as $\mathrm{Ru^{III}(bpym)_2(bpym^{-}\cdot)^{2+}}$—in resonance with different excited states of the complexed anion radical is also presented.

$\mathrm{Ru(bpym)_3Cl_2}$ was synthesized from anhydrous $\mathrm{RuCl_3}$ and excess 2,2′-bipyrimidine by a modification of the method reported by Hunziker and Ludi.[3] Structural confirmation of the recrystallized product was obtained by UV–visible, emission, and NMR spectroscopy. Raman spectra of $\sim 10^{-3}$ M nitrogen-purged aqueous samples were obtained by dispersing the 90° scattered light through a Spex Triplemate polychromator onto an EGG/PARC Model 1420 Reticon multichannel detector that was coupled to an OMA-II signal processing system. Ground-state resonance Raman spectra were excited by CW radiation at 441.6 nm (Liconix Model 4240 He:Cd laser, 50 mW) or 363.8 nm (Coherent Model 90-5 $\mathrm{Ar^+}$ laser, 60 mW). Excited-state Raman spectra were generated by high-power pulses of the 354.7-nm third harmonic of a Nd:YAG laser (Quanta-Ray Model DCR-1A, 10 Hz, $\sim$10-ns fwhm, $\sim$5 mJ/pulse) or a dye laser pumped by that source. Photons from the same pulse served both to pump the sample and to probe the excited electronic state. Toluene, *o*-chlorotoluene, cyclohexene, and fenchone were utilized for wavenumber calibration. Under typical operating conditions of the Triplemate/OMA system (1800 or 2400 groove/mm grating, 20 scans), wavenumber accuracy of the peak positions is ± 2 $\mathrm{cm^{-1}}$.

Typical d^6-transition-metal polypyridine complexes display absorption spectra showing a broad peak with a subsidiary higher energy shoulder in the 400–550-nm range—attributed to MLCT transitions—and stronger band systems below 300 nm—due to internal ligand excitations and higher energy MLCT transitions.[4] The absorption spectrum of $\mathrm{Ru(bpym)_3}^{2+}$, shown in the inset of Figure 1, is more complex, suggesting the presence of several excited electronic states in the 300–500-nm range. The ground-state resonance Raman spectrum in the $\Delta\tilde{\nu}$ = 1000–1600-$\mathrm{cm^{-1}}$ region excited by CW radiation at 442 nm is traced in the top frame of Figure 1. Seven distinct peaks are observed; their wavenumber shifts correlate well with ring-stretching modes of the 2,2′-bipyrimidine group.[5] The same bands are observed

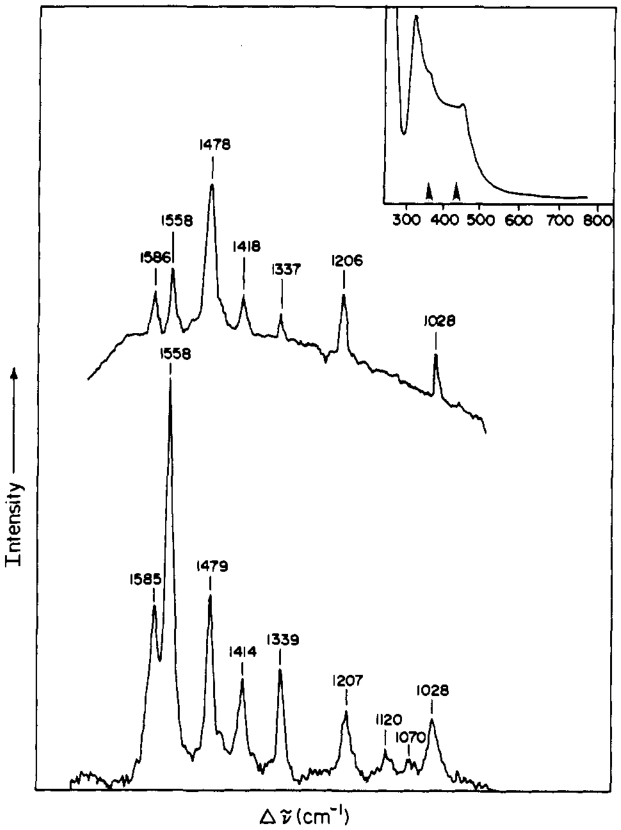

Figure 1. Resonance Raman spectra of deoxygenated 10^{-3} M aqueous solutions of $\mathrm{Ru^{II}(bpym)_3Cl_2}$: top frame, under CW excitation at 441.6 nm; bottom frame, under CW excitation at 363.8 nm. Wavenumber shifts are given above the peaks. [Inset: absorption spectrum in the 250–700-nm region, with excitation wavelengths marked by arrows.]

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(4) See for example the absorption spectrum of tris(2,2′-bipyridine)ruthenium(II): Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441.

(5) The vibrational spectrum is similar to, but somewhat different from, that of uncomplexed bipyrimidine. See for example: Overton, C.; Connor, J. A. *Polyhedron* **1982**, *1*, 53.

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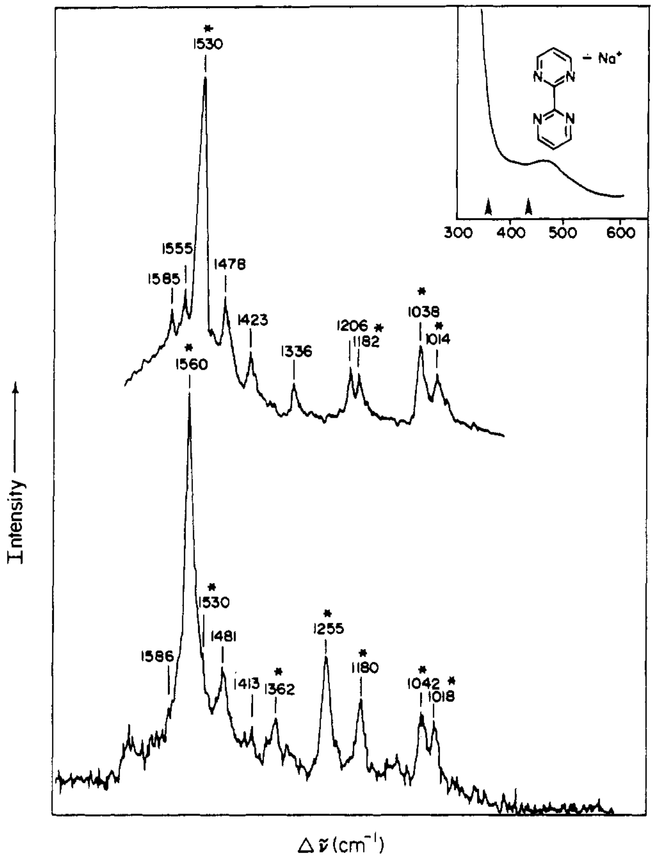

Figure 2. Resonance Raman spectra of deoxygenated 10^{-3} M aqueous solutions of $Ru^{II}(bpym)_3Cl_2$: top frame, under pulsed excitation at 440.0 nm; bottom frame, under pulsed excitation at 354.7 nm. Wavenumber shifts are given above the peaks. Bands attributed to (MLCT) excited-state scattering are marked with asterisks. [Inset: Absorption spectrum (300–600 nm) of Na^+bpym^- in THF, with $Ru(bpym)_3^{2+}$ pulsed excitation wavelengths denoted by arrows.]

under 364-nm CW excitation (Figure 1, bottom frame); however, their relative intensities are markedly different—note the three highest frequency peaks in particular—and two weak new bands are observed, at 1070 and 1120 cm^{-1}. The enhancement pattern has changed, which shows that two (or more) excited states are differently in resonance at the two excitation wavelengths.

Raman spectra of $Ru(bpym)_3^{2+}$ excited by relatively high-power pulses at approximately the same wavelengths as the CW experiments are reproduced in Figure 2. Scattering from an excited electronic state is clearly evident in both cases. Consider first the blue excitation (top frames). Ground-state peaks are still evident in Figure 2 with the same relative intensities shown in Figure 1, but the pulse-excited spectrum is dominated by new peaks at 1014, 1038, 1182, and 1530 cm^{-1}, which are denoted by asterisks in Figure 2. These new bands are also observed under pulsed UV excitation (Figure 2, lower frame). However their relative intensities differ somewhat from those observed under 440-nm irradiation, and there are three new excited-state peaks, at 1255, 1362, and 1560 cm^{-1}. (Some ground-state scattering also contributes to the peak at 1560 cm^{-1}; see relative intensities in bottom frame of Figure 1.) We attribute the excited-state scattering to complexes having one of the bidentate ligands in the MLCT state: $Ru^{III}(bpym)_2(bpym^{-}\cdot)^{2+}$. This model, in which on the vibrational time scale the excitation is localized on one of the ligands, is well established for 2,2′-bipyridine (bpy) complexes of Ru and Os.[6] Our Raman data indicate that different upper electronic states are in resonance with the MLCT-excited tris(bipyrimidine)ruthenium complex at the two excitation wavelengths employed. This is consistent with the electronic absorption spectrum of Na^+bpym^- in THF (Figure 2, inset), which shows two well-separated transitions.

A complete excitation profile of the $Ru(bpym)_3^{2+}$ ground state and additional resonance Raman spectra of the MLCT-excited state, as well as resonance Raman spectra of the mixed-ligand complex $Ru(bpym)_2(bpy)^{2+}$, will be given in a subsequent publication. The photophysical and photochemical properties of such d^6-transition-metal polypyridine complexes are of great interest because of their potential photosensitization applicability;[7] we have demonstrated here that resonance Raman spectroscopy provides a powerful probe of the relevant excited states.

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Registry No. $Ru(bpym)_3^{2+}$, 80263-32-7.

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Energy-Transfer Quenching of Excited States of Polypyridine Complexes of Ruthenium(II) by Hexaamminecobalt(III) or Tris(ethylenediamine)cobalt(III)

Sir:

Electron transfer and energy transfer are established pathways for the deactivation of luminescent states of (polypyridine)ruthenium(II) complexes.[1] For cobalt(III) complexes both mechanisms were postulated,[2,3] but following Navon and Sutin's demonstration[4] of electron-transfer quenching for pentaamminecobalt(III) complexes, this mechanism was tacitly assumed to be operative for all cobalt(III) complexes.[1,5] However, each system must be investigated in detail in order to reach a sound mechanistic assignment. As an illustration, we cite the identification of both energy- and electron-transfer pathways from quenching and quantum yield studies with cobalt(III) cage complexes.[6,7]

Recently,[8] the quenching of the luminescence of ruthenium and osmium polypyridine complexes by several cobalt(III) complexes was reported and interpreted as electron transfer. We have carried out similar studies with three of the complexes studied[8] ($Co(NH_3)_6^{3+}$, $Co(NH_3)_5Cl^{2+}$, and $Co(en)_3^{3+}$), but we have also measured quantum yields for Co(II) production. Our results

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