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Resonance Raman Spectroscopy for the Investigation of Heteroleptic Ruthenium Polypyridine Complexes

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Resonance Raman (RR) spectroscopy is a very powerful tool for the study of the structural and electronic properties of ruthenium (II) complexes with 2,2'-bipyridine and related ligands, in both the ground and ³MLCT (triplet metal-to-ligand charge transfer) excited states. Resonance Raman spectroscopy is especially very useful for the unambiguous assignment of electronic absorption spectra (Manuel et al. 1997, Danzer and Kincaid 1990, Danzer et al. 1993). In conventional Raman spectroscopy we measure the spectrum of the scattered radiation at some angle (90 degree is very common) with a spectrometer. Intensities of the Raman lines are very weak compared to the intensity of the source, as a result their detection and measurement are somewhat challenging. Raman line intensities can be greatly enhanced by measuring the resonance Raman spectrum. In resonance Raman, the sample is irradiated with a laser line that is close in energy to the electronic transition of a particular chromophoric group in a molecule. The intensities of the Raman bands of this chromophore are selectively enhanced by a factor of 10³ to 10⁵ under this condition (Ferraro and Nakamoto 1994). In systems containing two chromophoric groups having different transition energies, RR can thus be used to assign an absorption band to a particular chromophore by selective enhancement of its characteristic vibrational modes.

Raman spectroscopy is useful in probing the vibrational data similar to infrared spectroscopy, which helps us to obtain structural and electronic information. Although Raman spectroscopy and infrared spectroscopy are considered to be complementary, Raman spectroscopy finds greater applicability because of three factors. First, water (often the preferred solvent) does not pose any problem as it does in infrared spectroscopy. Second, glass and quartz cells can be used instead of alkali halide or other atmospherically unstable window materials. Most importantly, Raman spectroscopy provides information about the totally symmetric vibrational modes that play an important role in photophysical processes. Unlike infrared spectroscopy, Raman spectroscopy can easily probe the excited states.

Complexes of ruthenium (II) with 2,2'-bipyridine (bpy) and related ligands have attracted much attention over the past two decades as potentially useful components of solar energy conversion devices (Meyer 1978 and 1989, Juris et al. 1988). We employ the commonly used bridging ligand, 2,3-bis(2-pyridyl)pyrazine (dpp) to prepare the mixed ligands complex, Ru(bpy)₂(dpp)²⁺ (where bpy = 2,2'-bipyridine and dpp = 2,3-bis(2-pyridyl)pyrazine). The structure of the complex is shown in Figure 1.

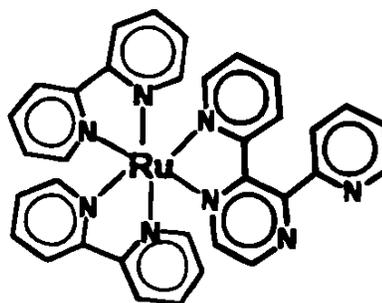
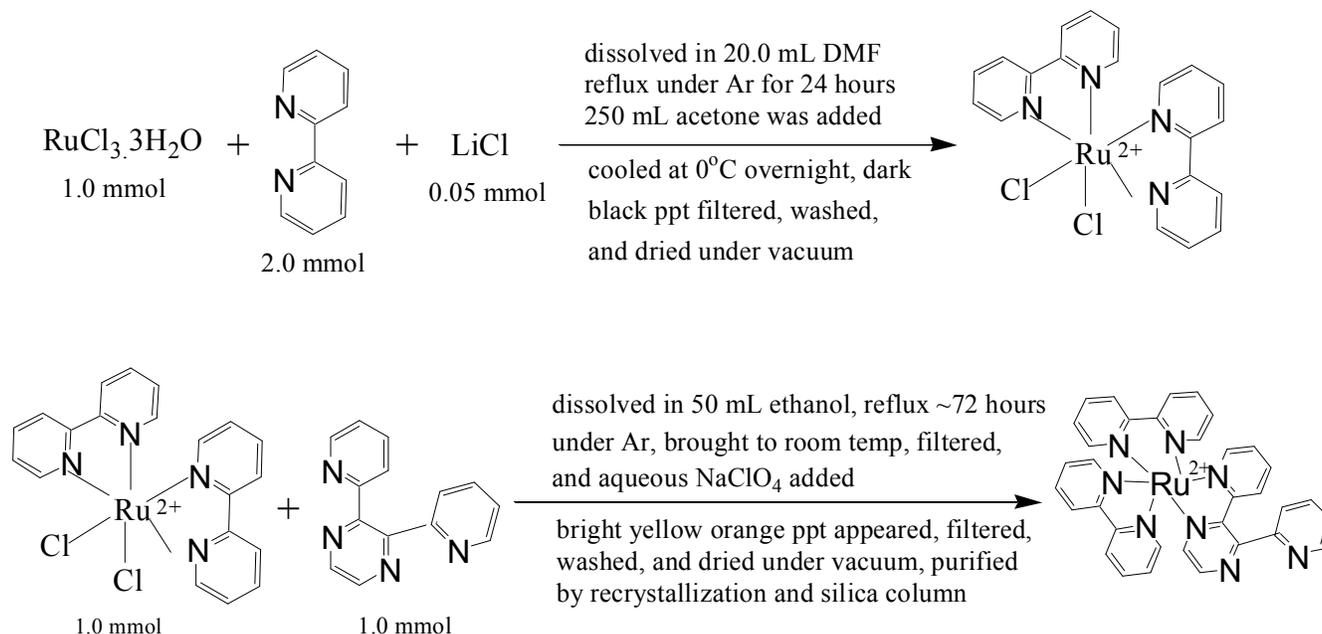


Figure 1. Structure of Ru(bpy)₂(dpp)²⁺ complex (where bpy = 2,2'-bipyridine and dpp = 2,3-bis(2-pyridyl)pyrazine).

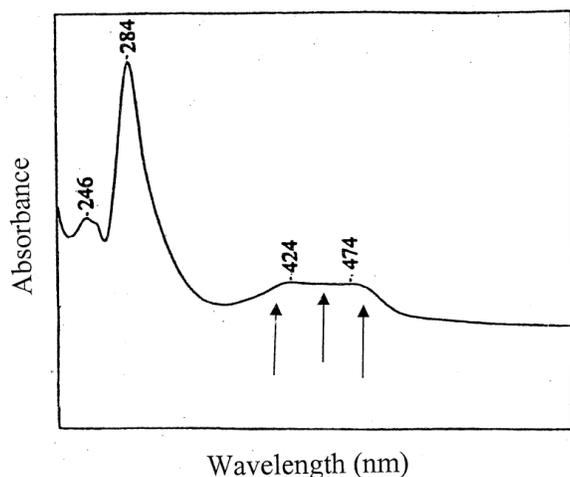
The complex Ru(bpy)₂Cl₂ was prepared from RuCl₃·3H₂O according to the method described by Sprintschnik et al. (1977) and Ru(bpy)₂(dpp)ClO₄ was prepared from Ru(bpy)₂Cl₂ and a stoichiometric amount of dpp ligand, according to the previously described method (Braunstein et al., 1984; Bhuiyan and Kincaid, 1999). The sample was purified by repeated recrystallization from 1:1 water ethanol solution and further purified on a silica gel column, which was eluted with a 0.5 M ethanolic solution of (C₂H₅)₄NBr. The synthetic procedure is shown in Scheme 1. This study reports the resonance Raman spectra of Ru(bpy)₂(dpp)²⁺. The results permit the definitive assignment of the ground state absorption bands of Ru(bpy)₂(dpp)²⁺ complex.

Electronic absorption spectrum was obtained using a Hewlett-Packard Model 8452A diode array spectrometer using a 1-cm quartz cuvette. Spectrum was obtained in the absorbance mode. The absorption

Resonance Raman Spectroscopy for the Investigation of Heteroleptic Ruthenium Polypyridine Complexes

Scheme 1. Synthetic scheme for the preparation of $\text{Ru}(\text{bpy})_2(\text{dpp})^{2+}$ complex.

spectrum of the complex in water solution, shown in Figure 2, matches the absorption spectrum reported by Kalyanasundaram and Nazeeruddin (1990). The absorption spectrum of the complex consists of a series of absorption bands in the uv and visible region. The intense uv bands are ascribable to the ligand centered $\pi-\pi^*$ transitions. The visible spectrum is not well resolved and consists of absorption bands at ~424 nm and ~474 nm. The visible bands are assigned to $d-\pi^*$ MLCT transitions. Resonance Raman spectroscopy can be used for definitive assignment of these visible bands.

Figure 2. Electronic Absorption spectrum of $\text{Ru}(\text{bpy})_2(\text{dpp})^{2+}$ complex. The arrows indicate the excitation wavelengths used in the RR studies.

The resonance Raman spectra of the complex was measured at Marquette University. A block diagram of the instrumentation is shown in Figure 3. The spectra were obtained with a Spex model 1403 double monochromator equipped with a Spex model DM1B controller and Hamamatsu R928 photomultiplier tube. The excitation lines 488.0 and 457.9 nm were obtained from a Spectra-Physics model 2025-05 argon ion laser and the 413.1 nm excitation line was obtained from a Coherent Model Innova 100-K3 krypton ion laser.

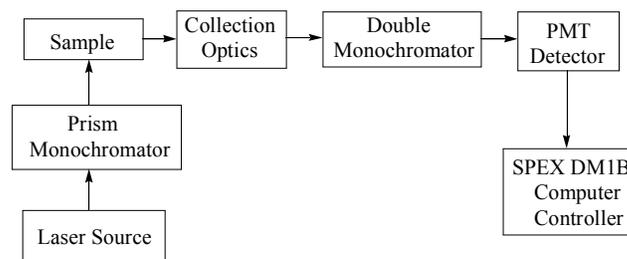


Figure 3. Block diagram of the instrument used for acquisition of ground state resonance Raman spectra.

Spectra of the complex were obtained from aqueous solution in a rotating NMR tube. The RR spectra of the complex at various excitations in aqueous solution are shown in Figure 4.

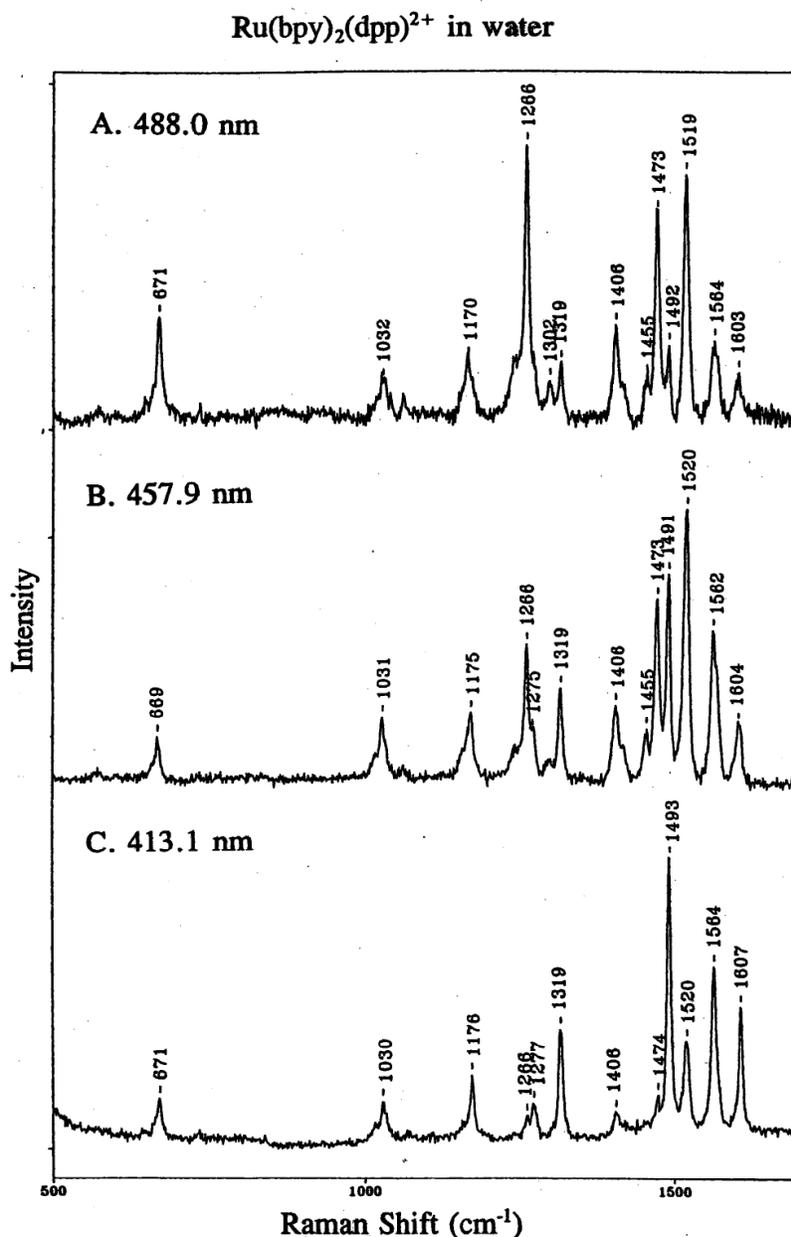


Figure 4. Ground state resonance Raman spectra of aqueous solution of $\text{Ru}(\text{bpy})_2(\text{dpp})^{2+}$ complex taken with excitation at 488 nm (trace A), 457.9 nm (trace B), and 413.1 nm (trace C).

The spinning 5 mm i.d. NMR tube (to prevent local overheating and sample decomposition) was illuminated by a laser beam focused through a glass lens, and the scattered light was collected with a conventional two-lens collection system. The frequencies of the complex are in good agreement with the literature (Braunstein et al. 1984, Bhuiyan and Kincaid 1999).

The spectra of $\text{Ru}(\text{bpy})_2(\text{dpp})^{2+}$ complex consist of bpy vibrations as well as dpp vibrations. The bpy vibrations can easily be identified by comparison with the well documented spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ complex

(Danzer and Kincaid 1990). The additional vibrations at 1266, 1473, and 1519 cm^{-1} were assigned to dpp ligand in a report by Braunstein et al. (1984). In addition to those three bands, there are more dpp bands that overlap with the bpy bands. The dpp vibrations consist of three subsets. One set of bands (such as 1603 and 1170 cm^{-1} in Figure 4) is associated with the pyridine fragment of the dpp ligand which overlaps the bpy bands, the second set (such as 1519 and 1473 cm^{-1} in Figure 4) is associated with the pyrazine fragment of dpp ligand which has frequencies quite similar to those

Resonance Raman Spectroscopy for the Investigation of Heteroleptic Ruthenium Polypyridine Complexes

of coordinated bipyrazine. A third set of vibrations has contributions from both fragments (such as 1319 and 1266 cm^{-1} in Figure 4) and are attributed to the inter-ring and adjacent bond stretching.

Resonance Raman spectra of the $\text{Ru}(\text{bpy})_2(\text{dpp})^{2+}$ complex were measured at 488.0, 457.9 and 413.1 nm excitation wavelengths. These spectra are readily understood on the basis of selective enhancement with the specific MLCT absorption bands. The RR spectra exhibit a revealing dependence on the excitation wavelength. The visible absorption spectrum of $\text{Ru}(\text{bpy})_2(\text{dpp})^{2+}$ consists of bands ~ 424 nm and ~ 474 nm. Excitation (488.0 nm) within the lower energy MLCT transition selectively enhances dpp modes relative to bpy modes (1519 vs 1492 cm^{-1} in trace A, Figure 4). On the other hand, excitation (413.1 nm) near resonance with the higher energy MLCT transition results in strong enhancement of the bpy modes (1493 vs 1520 cm^{-1} in trace C, Figure 4). Excitation with 457.9 nm, which is intermediate between the absorption bands, moderately enhances both bpy and dpp bands (trace B, Figure 4). The results of these studies permit the definitive assignment of the ground state absorption bands. The identities of the observed visible absorption bands are clearly established upon careful comparison of the resonance Raman spectra taken at various excitation wavelengths. From the selective enhancement of the RR experiment, the lower energy band is assigned to a $\text{Ru} \rightarrow \text{dpp}$ electronic transition, and the higher energy band is ascribable to a $\text{Ru} \rightarrow \text{bpy}$ electronic transition. We can exploit this strategy to provide unambiguous assignments of the absorption spectra for many bis-heteroleptic complexes of ruthenium (II), $\text{Ru}(\text{L})_n(\text{L}')_{3-n}^{2+}$, where, $\text{L} = 2,2'$ -bipyridine, $\text{L}' = \text{bpy}$ related ligands. Alternatively, if we know the identity of absorption bands, then we can characterize the vibrational modes certainly from the selective enhancement of RR data.

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