Table I. Binding Energies, Chemical Shifts, and Calculated Charges

compd	C 1s BE, eV	C 1s shift, eV	calcd q_C	Li 1s BE, eV	calcd q_{Li}
C_3H_6	285.0[a]	0.0	−0.03		
CH_3Li	282.6	−2.4	−1.02	54.0	+0.86
CH_2Li_2	280.9	−4.1	−1.55[b]	53.9	+0.71[b]
			(0.07)		(0.04)

[a] Used as reference. [b] Average of monomer, dimer, and trimer structures (see text). Standard deviation in parentheses.

this is to be expected both from the structure[6] and the observation of a single line in the solid state [1]H- and [6]Li-decoupled ^{13}C NMR spectrum for $CH_3{}^6Li$.[7] For CH_2Li_2 the presence of one carbon environment is also supported by a single line in the ^{13}C NMR spectrum of $CH_2({}^6Li)_2$.[7] Furthermore, the direction of the C 1s core level shifts and ^{13}C chemical shifts suggests an increased charge density of the methylene carbon in CH_2Li_2.[7] Our results also indicate the presence of one Li environment, which suggests that CH_2Li_2's solid-state structure will be highly symmetric.

As a comparison, the groups IV, V, and VI interstitial carbides exhibit C 1s chemical shifts in the range of −2.0 to −4.0 eV relative to contaminant hydrocarbon.[13] The C 1s chemical shift for CH_2Li_2 (−4.1 eV) is significantly greater than that for TiC (−3.3 eV) for which APW band structure calculations have indicated charge transfer of nearly one Ti 3d electron to the C 2p band.[14] To our knowledge, the C 1s binding energy of CH_2Li_2 is the lowest ever reported.

Fenske–Hall molecular orbital (MO) calculations[15] were performed on cyclopropane (a hydrocarbon reference) and the CH_3Li tetramer, using geometrical parameters from published electron diffraction[16] and X-ray data,[6b] respectively. As the structure of CH_2Li_2 is unknown, calculations were performed on model monomeric,[17] dimeric,[18] and trimeric[19] structures of CH_2Li_2. The monomeric and dimeric structures are among the lowest energy (ab initio geometry optimization) structures in which C and Li atoms are of one chemical type. The trimeric CH_2Li_2 structure was one suggested by Schleyer et al. in which C and Li atoms are in equivalent environments.[19]

Experimental binding energies, chemical shifts, and gross Mulliken charges are listed in Table I. Average calculated values are reported for all three CH_2Li_2 model structures as similar results were obtained.

As Table I indicates, the presence of one Li in CH_3Li shifts the carbon binding energy by 2.4 eV. The presence of a second Li in CH_2Li_2 shifts the carbon binding energy by an additional 1.7 eV. The carbon charge increases from −1.02 in CH_3Li to −1.55 in CH_2Li_2. This is shown in Figure 2 where the calculated carbon charge is plotted against the C 1s chemical shift. A line has been drawn through points for C_3H_6 and CH_3Li as these represent known structures. The average value of the carbon charge in the CH_2Li_2 models is placed on this curve at the observed chemical shift. The excellent correlation ($r^2 = 0.994$) suggests that the carbon potentials in these compounds are well represented by the calculations.

The calculations also predict that the Li positive charge should decrease slightly on going from CH_3Li to CH_2Li_2 (Table I), but

Figure 2. Fenske–Hall MO charges for C in C_3H_6 (**1**), CH_3Li (**2**), and CH_2Li_2 (**3**) plotted against observed C 1s chemical shift. Vertical bars represent uncertainty of ±0.2 eV in binding energy. The horizontal bar represents the standard deviation in the average charge of three CH_2Li_2 model structures (see text).

the magnitude of these changes is small ($\Delta q_{Li} = -0.15$), and we observe a small decrease in Li 1s binding energy ($\Delta BE = 0.1$ eV). The Li 1s binding energies for CH_3Li (54.0 eV) and CH_2Li_2 (53.9 eV) are closer to those of LiOH and Li_2O[20] than to other lithium salts containing noncoordinating anions like ClO_4^- and PO_4^{3-}.[10] Thus, the overall Li potential in these lithiocarbon compounds is similar to that for lithium in extended oxidic structures.

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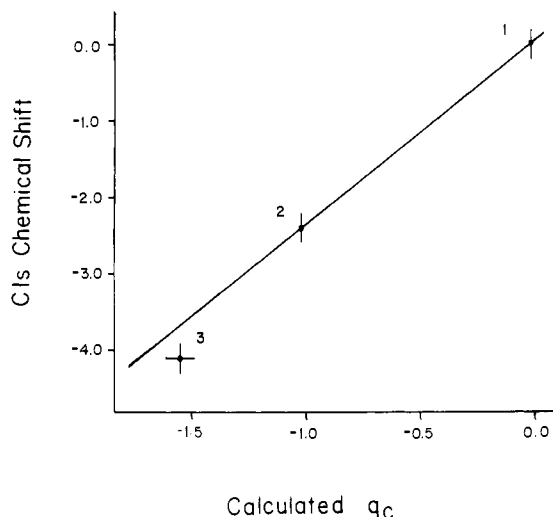(14) Conklin, J. B., Jr.; Silversmith, D. J. *Int. J. Quantum Chem.* **1968**, *2*, 243.

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(19) The D_{3h} structure is best viewed as a trigonal prism of Li atoms with methylene groups bridging rectangular faces (see Structure XIII[18]). Geometrical parameters are as follows: C–C (2.87 Å), C–H (1.10 Å), Li–C (2.10 Å), Li–Li (2.1 Å, triangular faces), Li–Li (2.97 Å, rectangular faces). These parameters are idealized and not the result of geometry optimization.

Resonance Raman Spectra of Ground and Low-Lying Excited States of Ruthenium(II) Pentaammine Pyridine Derivatives

Y. C. Chung, N. Leventis, P. J. Wagner,* and G. E. Leroi*

Department of Chemistry, Michigan State University
East Lansing, Michigan 48824

Received August 27, 1984

Raman spectra of electronically excited molecules have been reported for polypyridine complexes of d[6] transition metals.[1–5] The prototypical case has been tris(2,2'-bipyridine)ruthenium(II) [$Ru(bpy)_3{}^{2+}$], for which it has been demonstrated that the electron promoted by metal-to-ligand charge-transfer (MLCT) absorption is localized (on the Raman time scale) on one of the bipyridine ligands.[1–4] We describe here observations on two pentaammineruthenium(II) pyridine complexes, models of another system for which the photochemistry and photophysics have received considerable recent attention.[6–10] The results are consistent

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Communications to the Editor

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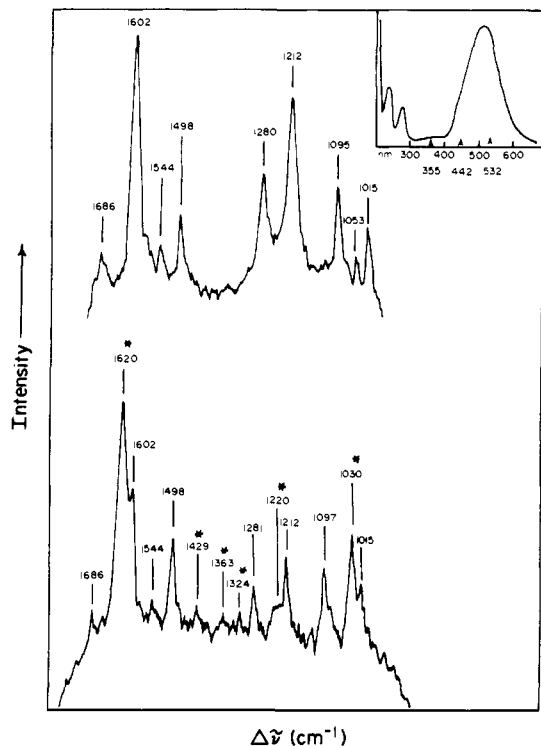
Figure 1. Resonance Raman spectra of deoxygenated 10^{-3} M aqueous solutions of $Ru^{II}(NH_3)_5(acpy)(BF_4)_2$. Top frame: under CW excitation at 441.6 nm. Bottom frame: under pulsed excitation at 354.7 nm. Wavenumber shifts are given above the peaks. Bands attributed to excited-state scattering are marked by asterisks. [Inset: absorption spectrum in the 250–650-nm region, with excitation wavelengths marked by arrows.]

with excited state ordering based on photochemical evidence and provide the first example of an excited-state Raman spectrum involving a monodentate pyridine ligand.

Resonance Raman spectra have been obtained for $\sim 10^{-3}$ M aqueous solutions of $Ru^{II}(NH_3)_5(py)(BF_4)_2$ (py = pyridine) (**1**) and $Ru^{II}(NH_3)_5(acpy)(BF_4)_2$ (acpy = 4-acetylpyridine) (**2**). The complexes were synthesized and characterized by well-established methods.[11-13] Raman spectra were excited by the following sources: He-Cd CW laser (441.6 nm, 50 mW; Liconix Model 4240), Nd:YAG pulsed laser (532.0 and 354.7 nm, variable power up to ~ 8 mJ/pulse, 10 ns fwhm, 10 Hz; Quanta-Ray DCR-1A). Excited-state spectra were observed under high-power illumination of the Nd:YAG laser. Photons from the same laser pulse served both to pump the sample and to interrogate the species present in solution following absorption. Scattering in the range $\Delta\nu = 1000-1700$ cm^{-1} was collected at 90° to the incident laser beam and dispersed by a Spex Triplemate polychromator onto an EGG/PARC Model 1420 Reticon multichannel detector, which was coupled to an OMA-II signal processing system. Toluene, cyclohexene, o-chlorotoluene, and fenchone were utilized for wavenumber calibration. Under typical operating conditions of the Triplemate/OMA system (1800 or 2400 groove/mm grating, 600 delays, 20 scans), wavenumber accuracy of the measured peak positions is ± 2 cm^{-1}.

The near-UV/visible spectrum of aqueous **2** (inset, Figure 1) displays strong MLCT absorption with $\lambda_{max} = 524$ nm. This

$\Delta\tilde{\nu}$ (cm^{-1})
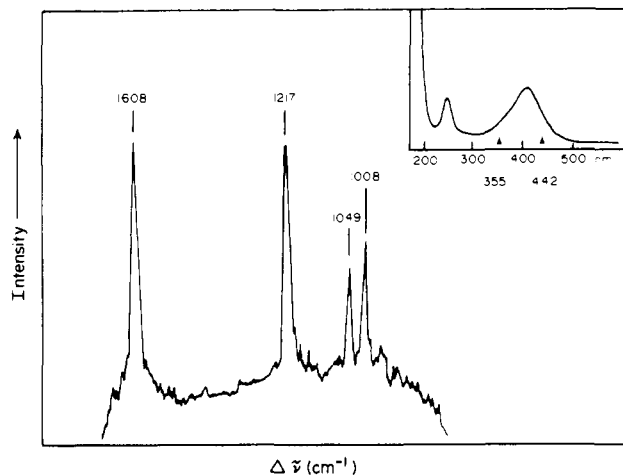
Figure 2. Resonance Raman spectrum of deoxygenated 10^{-3} M aqueous solution of $Ru^{II}(NH_3)_5(py)BF_4)_2$ excited by pulsed 354.7-nm radiation. [Inset: absorption spectrum in the 250–500-nm region.]

complex exemplifies species classified as "unreactive" toward ligand photosolvation, for which MLCT absorption is thought to lie at lower energies than the dissociative ligand field (LF) transitions.[6] The ground-state resonance Raman spectrum of **2** excited at 442 nm is displayed in the top frame of Figure 1. It is dominated by vibrations of the acpy ligand.[14] Attempts to obtain the Raman spectrum of the MLCT excited state by excitation with intense (5–8 mJ) pulses of 532-nm radiation from the Nd:YAG laser were unsuccessful. (Only the ground-state spectrum was observed.) The lifetime of this excited state is extremely short,[15] so only very small concentrations of the excited species, representable as $Ru^{III}(NH_3)_5(acpy^-\cdot)^{2+}$ (**2***), can be generated. Moreover its Raman spectrum is not expected to be resonance enhanced at 532 nm since the lowest energy absorption of the acpy$^-\cdot$ radical anion occurs at ~ 325 nm.[16] Two-color experiments involving 532-nm pump and 355-nm probe wavelengths also failed, probably due to synchronization difficulties with the short-lived excited state.

However, new Raman peaks in addition to ground-state acpy scattering were generated when aqueous solutions of **2** were excited by 5–8-mJ pulses of 354.7-nm radiation; the Raman spectrum in the 1000–1700-cm^{-1} region is shown in the lower frame of Figure 1. Six peaks attributable to excited-state scattering are denoted by asterisks. Three are relatively prominent; the remainder are weak, but quite reproducible. The C=O stretching vibration (1686 cm^{-1}) is conspicuously diminished. The pattern correlates reasonably well with the ground-state resonance Raman spectrum of the free acetylpyridine radical anion.[16] Further support for the assignment of the new peaks to **2*** is provided by several acylpyridine complexes of rhenium carbonyls and tungsten carbonyls, for which there is strong evidence that the lowest excited states are MLCT.[17-19] Preliminary excited-state resonance Raman spectra of these species are dominated by peaks near 1620 and 1030 cm^{-1}.[20] Observation of MLCT excited-state scattering from **2** is thus consistent with Ford's model for photochemically "unreactive" complexes in the $Ru^{II}(NH_3)_5L$ series.[6]

$Ru(NH_3)_5(py)^{2+}$ is an example of a photoactive complex for which the dissociative LF state is thought to lie below the MLCT

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levels;[6] here λ_{max} (MCLT) = 407 nm (see inset in Figure 2). The Raman spectra observed under both low-power 441.6-nm and high-power 354.7-nm (Figure 2) excitation exhibit scattering only from the complexed ground-state py ligand[21] and show only slight variation in relative peak intensities at the two excitation wavelengths. Although excitation in either case leads initially to MLCT, rapid deactivation by internal energy relaxation presumably leaves the complex in a lower lying LF excited level. It is possible that scattering from a short-lived $Ru^{III}(NH_3)_5(py^-\cdot)^{2+}$ species might not be enhanced at 355 nm. Although the pyridine radical anion has an absorption peak near 340 nm in MTHF solution,[22] the proximity of the metal cation may blue-shift the transition sufficiently to move it off resonance. Thus failure to observe py⁻· scattering in these experiments does not prove that the photoactive LF state lies below the MLCT state in **1**, although it is consistent with Ford's picture.[6]

Excited-state Raman scattering from transition-metal complexes had been reported heretofore only for molecules containing the bpy ligand.[1-5] The observation of MLCT scattering from Ru-$(NH_3)_5(acpy)^{2+}$ suggests that the resonance Raman technique may be utilized to charaterize low-lying excited electronic states of complexes containing multiple pyridyl ligands. We report the result of one such investigation in the following paper.[23]

Registry No. $Ru^{II}(NH_3)_5(acpy)(BF_4)_2$, 71964-20-0; $Ru^{II}(NH_3)_5$-$(py)(BF_4)_2$, 41706-94-9.

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Resonance Raman Spectra of Ground and Lowest Excited Electronic States of Some Ruthenium(II) Mixed-Ligand Complexes

Y. C. Chung, N. Leventis, P. J. Wagner,* and G. E. Leroi*

*Department of Chemistry, Michigan State University
East Lansing, Michigan 48824*

Received August 27, 1984

Several examples of resonance Raman (RR) scattering from excited electronic states of d^6 transition-metal complexes which contain the 2,2'-bipyridine (bpy) ligand have been published.[1-6] In the preceding paper we report the first observation of such scattering from a different ligand, 4-acetylpyridine (acpy) in $Ru(NH_3)_5(acpy)^{2+}$.[7] Here we describe RR spectra of complexes that contain both bpy and monodentate pyridyl ligands. The results suggest that the localized excitation model proposed by Woodruff and co-workers for $Ru(bpy)_3^{2+}$ (**1**)[1,2] and supported in

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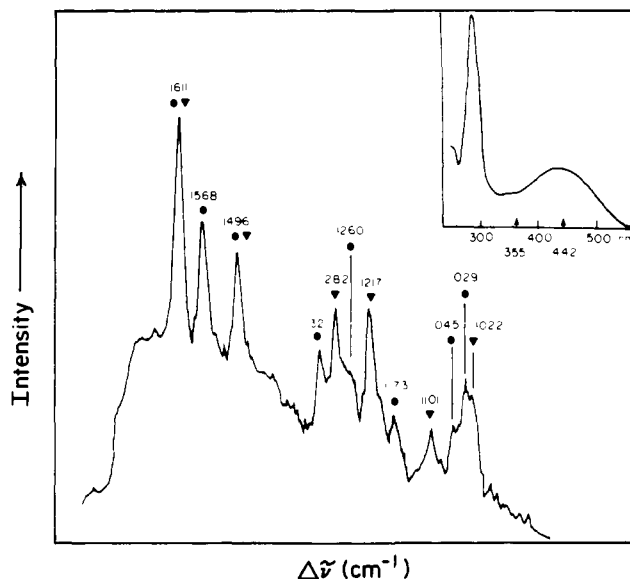
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Figure 1. Resonance Raman spectrum of deoxygenated 10^{-4} M aqueous solution of $Ru^{II}(bpy)_2(acpy)_2(BF_4)_2$ under pulsed excitation at 354.7 nm. Wavenumber shifts are given above the peaks. Key to band assignments: (●) bpy, (▼) acpy. (Inset: Absorption spectrum in the 250–600-nm region.)

subsequent work[3-6] applies as well to these more general coordination complexes. They also indicate some limitations of ns timescale measurements.

RR spectra at selected excitation wavelengths have been obtained for ~10^{-4} M aqueous solutions of *cis*-$Ru^{II}(bpy)_2(L)_2(BF_4)_2$ salts, where L = acpy (**2**) or pyridine (py) (**3**). The complexes were synthesized and identified according to the literature,[8,9] and RR spectra were acquired as described in the accompanying paper.[7]

The UV–vis spectrum of **2** (Figure 1, inset) differs little from that of **1**, the metal-to-ligand charge-transfer (MLCT) absorption in the blue being somewhat broadened here due to overlapping transitions to the bpy and acpy ligands. RR spectra of each group in its lowest MLCT excited state have been observed previously under pulsed 355-nm excitation.[1,2,4-7] Yet in the mixed-ligand complex **2** *no* excited electronic state Raman scattering is obtained under these conditions; the RR spectrum shown in Figure 1 is essentially a superposition of the ground-state scattering from bpy and acpy under UV excitation. An excitation profile obtained at several points in the composite MLCT absorption shows smooth variations in the relative intensities of the ground state bpy and acpy Raman peaks, reflecting the changing mixture of π^* levels of the two ligands across the absorption envelope.[10] The absence of detectable excited-state scattering from **2** may indicate that the lifetimes of the excited states formed by 355-nm excitation are too short for the nanosecond timescale of these Raman measurmenets. Even the lowest excited state may be shorter lived than that of **1**, since we have been able to detect only very weak luminescence from **2**, and that only at 77 K.[11]

The lowest MLCT state of $Ru(bpy)_2(py)_2^{2+}$ (**3**), however, has a lifetime approaching that of the tris bpy complex, **1**.[12] The absorption spectrum of **3** (inset, Figure 2) is distinguished from those of **1** and **2** primarily by the presence of a peak at 338 nm (ϵ 20.4 × 10^3), which we attribute to metal-to-pyridine CT. RR spectra of **3** in the 1000–1650-cm⁻¹ region are shown in Figure 2. Under 442-nm CW excitation (top frame) seven peaks are observed; all have been previously identified as ring stretching modes of the bpy ligand in its ground state.[1,5,13] No py scattering

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