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Resonance Raman Spectra of the Heptanuclear $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}]^{14+}$ Complex. Excitation Profiles for Three Overlapping Metal-to-Ligand Charge-Transfer Bands

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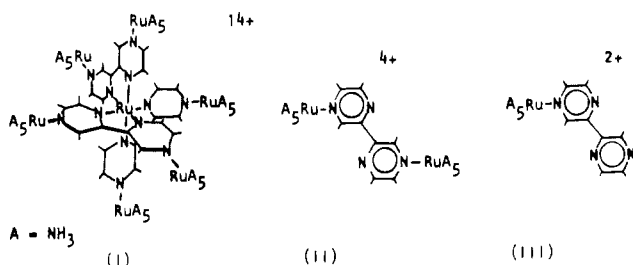
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Resonance Raman (rR) spectra are reported for the $[\{\text{Ru}(\text{NH}_3)_5\}_n\text{bpz}]^{2n+}$ ($n = 1, 2$; bpz = 2,2'-bipyrazine) and $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}]^{14+}$ complexes, with excitation at several wavelengths through the metal-to-ligand charge-transfer (MLCT) bands in the visible region of the electronic spectrum. Excitation profiles for the mononuclear complex show a maximum enhancement of the 2,2'-bipyrazine peaks at 500 nm, coinciding with the $\text{Ru}(\pi) \rightarrow (\text{bpz})\pi^*$ MLCT band. Three types of excitation profiles are observed for the heptanuclear complex, consistent with the existence of three MLCT bands involving the peripheral and central ruthenium(II) ions and two π^* levels of 2,2'-bipyrazine. The observed vibrational frequencies are correlated with those of $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) and the a_{1g} and b_{2u} modes of biphenyl.

Introduction

Resonance Raman spectroscopy (rR) has been a powerful technique in studies of ruthenium 2,2'-bipyridine complexes, because of the occurrence of resonance enhancement arising from the MLCT transitions.¹⁻¹⁴ By means of rR spectroscopy, the nature of the low-energy excited state in $[\text{Ru}(\text{bpy})_3]^{2+}$ has been extensively probed and is consistent, according to most views, with localization of charge on one of the 2,2'-bipyridine ligands.¹⁻³ A comparison of the rR spectra of the $[\text{Ru}(\text{bpz})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes has been published.⁸ The decrease of the rR intensities passing from the 2,2'-bipyridine to the 2,2'-bipyrazine complex is related to an increase of lifetime of the low-energy excited state from 0.685 to 1.04 s, respectively.

Recently, the reactions of the peripheral nitrogen atoms in the $[\text{Ru}(\text{bpz})_3]^{2+}$ complex with pentacyanoferrate(II)¹⁵ and pentaammineruthenium(II)¹⁶ ions were explored, yielding di- to heptanuclear complexes. Because of the presence of several chromophores and the significant overlap of band envelopes in the visible region, a study of the rR spectra of some of these species was initiated. We compare here the rR spectra of $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}]^{14+}$ and $[\{\text{Ru}(\text{NH}_3)_5\}_n\text{bpz}]^{2n+}$ ($n = 1, 2$) (I-III).



In pentaammineruthenium(II) complexes of N-heterocyclic ligands, when the MLCT band is located below 460 nm, photoexcitation leads to ligand replacement by water via population of a lower ligand field state.¹⁷ For charge-transfer bands at longer wavelengths, such as in the protonated pyrazine,¹⁸ ($\lambda_{\text{max}} = 529$ nm), complex, the photosolvation yield decreases sharply since the MLCT state falls below the photoactive ligand field state. The energy of the MLCT band can also be decreased via coordination to Ni(II) ($\lambda_{\text{max}} = 493$ nm) or Cu(II) ($\lambda_{\text{max}} = 508$ nm) ions, and in this manner, the rR spectra of the (pyrazine)pentaammineruthenium(II) complex has been measured.¹⁹ The reversible electron-transfer photochromism in the $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{Cu}^{II}]^{4+}$ complex,¹⁹ and the intervalence properties of the $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{Fe}(\text{CN})_5]$ complex²⁰ have also been successfully probed via rR spectroscopy. Recently the rR studies of the $\text{Ru}(\text{NH}_3)_5\text{L}$ complexes were extended to the 4-acetylpyridine¹¹ ($\lambda_{\text{max}} = 523$ nm) and 4,4'-bipyridine⁹ ($\lambda_{\text{max}} = 480$ nm) derivatives.

Experimental Section

The synthesis and characterization of the several complexes employed in this work have been described previously.¹⁶ The infrared spectra of

the complex dispersed in KBr pellets (or in Nujol/Fluorolube) were recorded on a Perkin-Elmer Model 283 spectrophotometer. The electronic spectra in the visible-UV region were recorded on a Cary 17 or a Hewlett-Packard 8451 diode-array spectrophotometer. Resonance Raman spectra were recorded on a Jarrell-Ash double-monochromator instrument. The visible excitation sources for continuous-wave Raman spectra were two Spectra-Physics argon and krypton ion lasers or a Rhodamine 6G dye laser. Typical laser powers were below 100 mW. The measurements were carried out in aqueous solution containing sodium sulfate (0.1M), using a spinning cell. The relative intensities were measured as peak heights relative to the sulfate Raman band at 980 cm^{-1} .

Results and Discussion

Infrared Spectra. The infrared spectra of $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}]^{14+}$ (PF_6)₁₄ and $[\{\text{Ru}(\text{NH}_3)_5\}_n\text{bpz}]^{2n+}$ ($n = 1, 2$) complexes are shown in Figure 1. The presence of water in the KBr pellets is responsible for the absorption at 3420 cm^{-1} . In the case of the $[\{\text{Ru}(\text{NH}_3)_5\}_2\text{bpz}]^{4+}$ complex, the analysis was consistent with the presence of one acetone molecule in the solid.¹⁶ The absorption peak around 1700 cm^{-1} in Figure 1B is characteristic of the C=O stretching vibration in carbonyl compounds. The vibrational peaks of the hexafluorophosphate ion occur at 560 and 835 cm^{-1} .

The NH_3 vibrational peaks can be seen at 770 cm^{-1} (shoulder) (rocking), 1265-1300 cm^{-1} (symmetric HNH deformation), 1620-1630 cm^{-1} (asymmetric HNH deformation), and 3150-3300 cm^{-1} (symmetric and asymmetric NH_3 stretching). The Ru-N stretching vibration has recently been assigned²¹ in $[\text{Ru}(\text{NH}_3)_6]\text{X}_2$ ($\text{X} = \text{BF}_4, \text{PF}_6, \text{Cl}, \text{Br}, \text{I}$) complexes, to a weak band at 403-423 cm^{-1} . Our pentaammineruthenium complexes also exhibit a band in this region.

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Table I. Comparison of Resonance Raman Frequencies (cm^{-1}) for 2,2'-Bipyridine and 2,2'-Bipyrazine Vibrations and Correlations with Those of Biphenyl

sym (D_{2h})	biphenyl ^a	sym (C_{2v})	$\text{Ru}(\text{bpy})_3^{2+}$ ^b	$\text{Ru}(\text{bpz})_3^{2+}$	$\text{Ru}-\text{Ru}_6^{14+}$ ^c	$\text{Ru}_2\text{bpz}^{4+}$ ^c
A_g	315	A_1		280	310	298
B_{3u}	609	B_1				
B_{2u}	629	A_1	663	684	704	669
A_g	742	A_1	766	808	825	828
B_{3u}	965	B_1				
A_g	1003	A_1	1027		1020	1028
B_{3u}	1008	B_1				
A_g	1030	A_1	1041			
B_{3u}	1040	B_1				
B_{2u}	1074	A_1	1067	1056	1075	1065
B_{2u}	1156	A_1	1109	1170	1145	1145
B_{3u}	1176	B_1			1176	
A_g	1190	A_1	1173	1198	1224	1190
B_{2u}	1272	A_1	1264	1283	1273	1282
A_g	1285	A_1	1317		1315	1314
B_{2u}	1383	A_1	1352	1345	1342	
B_{2u}	1432	A_1	1448	1416	1387	1390
B_{3u}	1482	B_1		1515 ^d		
A_g	1507	A_1	1489	1493	1472	1480
B_{2u}	1571	A_1	1560	1522	1492	1500
B_{3u}	1597	B_1				1580
A_g	1612	A_1	1605	1600	1600	1600

^a From ref 13, 14. ^b Data from ref 3, 9. ^c $[\text{Ru}(\text{bpz})_3[\text{Ru}(\text{NH}_3)_5]_6]^{14+}$ and $\{[\text{Ru}(\text{NH}_3)_5\text{Ru}_2\text{bpz}]^{4+}$ complexes. ^d Weak shoulder.

The 2,2'-bipyrazine vibration bands can be discussed with reference to the normal modes of biphenyl or 2,2'-bipyridine, which have been analyzed in detail by Zerbi and Sandroni,^{22,23} and by Strukl and Walter,²⁴ respectively. The available data for the IR spectra of 2,2'-bipyridine complexes are also quite useful.²⁵⁻²⁹

In general, the aromatic compounds exhibit four IR-active ring-stretching vibrations in the region 1300–1600 cm^{-1} . In the case of 2,2'-bipyridine, these vibration bands occur at 1410, 1448, 1553, and 1579 cm^{-1} . The corresponding bands in the $\{[\text{Ru}(\text{NH}_3)_5\text{bpz}]^{2+}$ complexes can be observed at 1400, 1435, 1530, and 1575 cm^{-1} , while for the $[\text{Ru}(\text{bpz})_3[\text{Ru}(\text{NH}_3)_5]_6]^{14+}$ complex, they occur at 1400, 1450, 1550 sh and 1590 cm^{-1} (Figure 1). According to the potential energy distributions for 2,2'-bipyridine,²⁴ the two high-frequency bands involve a large contribution of the CC and CN stretching, while the other two involve equivalent contributions of the CC, CN stretching and CCH deformation vibrations.

The IR peaks at 1285–1300 cm^{-1} in Figure 1 are also observed in 2,2'-bipyridine corresponding to composite CC, CN, and HCC bending modes. The interring stretching vibration (not allowed in the free ligand) is expected to occur in this region. By comparison with the literature,²⁴ the several peaks at 1100–1190 cm^{-1} can be ascribed to ring-H in-plane bending vibrations. The vibrational peaks at 1010–1070 cm^{-1} correlate with the ring vibrations in 2,2'-bipyridine, including the ring-breathing mode. The out-of-plane ring-H bending vibrations are expected to occur at 740–890 cm^{-1} , being masked by the strong PF_6^- absorption. The ring torsion and ring-bending modes in 2,2'-bipyridine have been observed at 618–710 cm^{-1} , corresponding to the absorption bands at 650–690 cm^{-1} in Figure 1.

Resonance Raman (rR) Spectra. In the case of the $\{[\text{Ru}(\text{NH}_3)_5\text{bpz}]^{2+}$ complexes, the MLCT band is observed at 500 nm ($n = 1$) or 508 nm ($n = 2$), in aqueous solution. As in the preceding examples, the photoaquation process has a poor efficiency, and the resonance Raman spectra can be measured in the usual way. The excited-state symmetry is expected to be the same as that of the ground state. Therefore, the enhancement in the

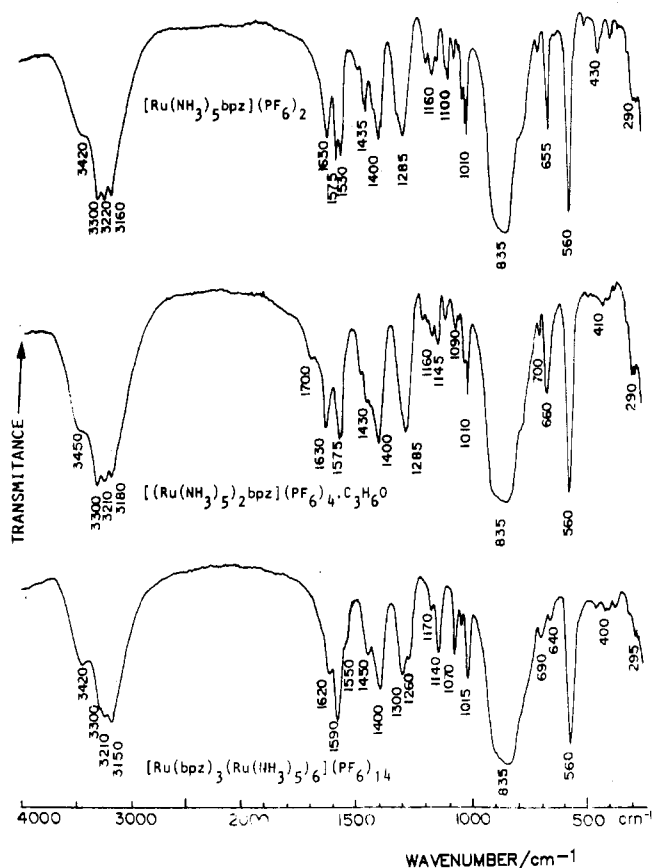


Figure 1. Infrared spectra of ruthenium-bipyrazine complexes in KBr pellets.

rR spectra should be restricted to the totally symmetric modes (a_1) along whose coordinates the excited-state potential is displaced.³⁰ Caswell and Spiro⁹ have shown that the a_{1g} and b_{2u} vibrational modes of biphenyl (D_{2h}) can be correlated with the enhanced Raman peaks of a_1 symmetry in $[\text{Ru}(\text{bpy})_3]^{2+}$, assuming a local C_{2v} symmetry for 2,2'-bipyridine (Table I). They preferred the comparison with biphenyl, rather than free 2,2'-bipyridine because the former is very rich in detail.

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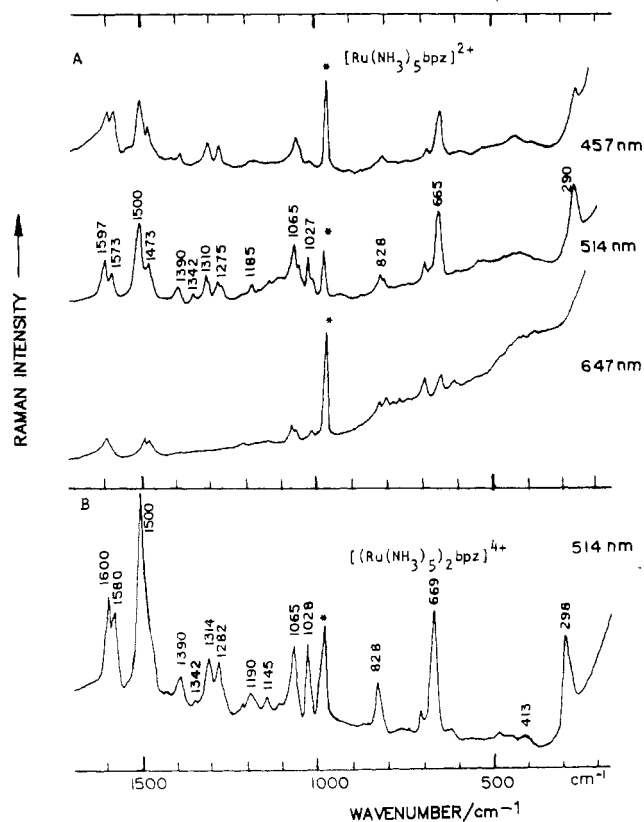


Figure 2. Resonance Raman spectra of pentaammineruthenium(II) complexes of bipyrazine (1×10^{-3} M), in aqueous solution, at excitation wavelengths of 647.1, 514.5, and 457.9 nm. An asterisk denotes the sulfate band.

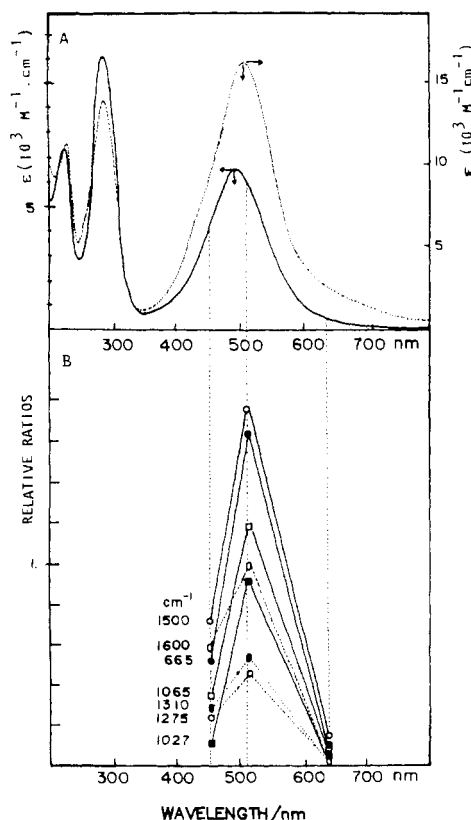


Figure 3. Electronic absorption spectra (A) and typical resonance Raman excitation profiles (B) for the mononuclear pentaammineruthenium(II) bipyrazine complex. The absorption spectrum of the binuclear $[\text{Ru}(\text{NH}_3)_5]_2\text{bpz}^{4+}$ is shown as dotted lines.

Typical rR spectra for the $[\text{Ru}(\text{NH}_3)_5]_n\text{bpz}^{2n+}$ complexes are shown in Figure 2. The vibrational peaks associated with the

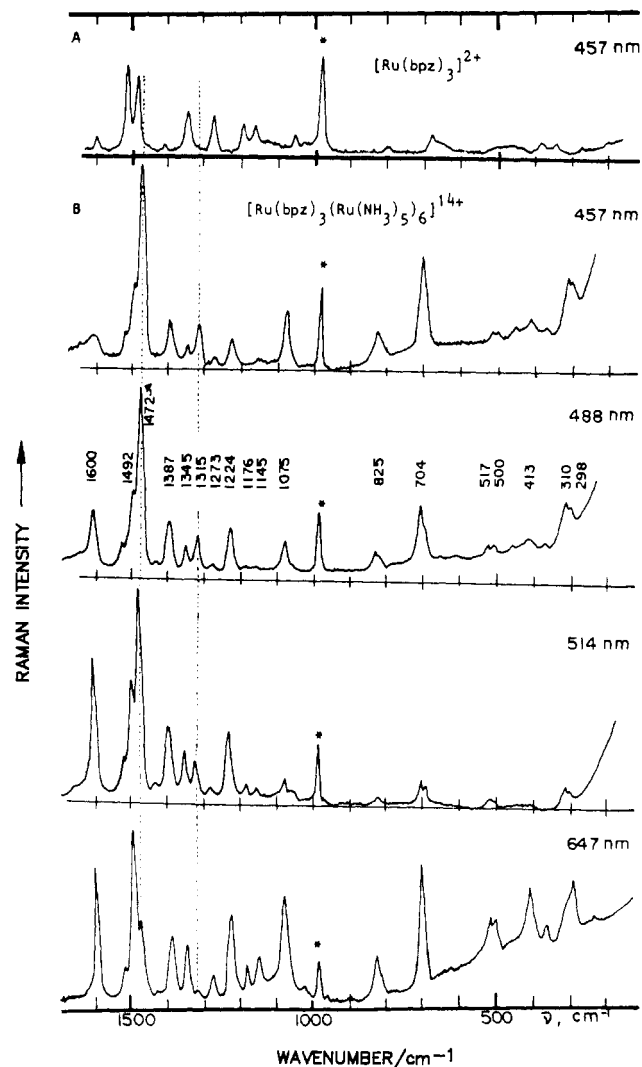


Figure 4. Resonance Raman spectra of (A) $[\text{Ru}(\text{bpz})_3]^{2+}$ and of (B) the heptanuclear pentaammineruthenium(II) complex (2×10^{-5} M), in aqueous solution, at excitation wavelengths of 647.1, 514.5, 488.0 and 457.9 nm (* = sulfate band).

2,2'-bipyrazine ligand are strongly enhanced, exhibiting excitation profiles that follow very closely the $\text{Ru}(d\pi) \rightarrow (\text{bpz})\pi_1^*$ charge-transfer band¹⁶ at 500 nm (Figure 3). In $[\text{Ru}(\text{NH}_3)_5]_2\text{bpz}^{4+}$, the most strongly enhanced bands are those involving the ring vibrations at 298, 669, 1028, 1065, 1500, and 1600 cm^{-1} . A good correlation is obtained between the a_{1g} and b_{2u} vibrational modes of biphenyl and the rR bands of 2,2'-bipyrazine. In the case of the $[\text{Ru}(\text{NH}_3)_5]_2\text{bpz}(\text{PF}_6)_2$ complex, the splitting in the rR bands at 828, 1027, 1065, 1275, 1310, and 1500 cm^{-1} is consistent with the inequivalent pyrazine rings present in this species.

The rR spectra of the heptanuclear $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_6]^{14+}$ complex are shown in Figure 4, in comparison with the spectrum of the $[\text{Ru}(\text{bpz})_3]^{2+}$ cation, previously reported by Balk et al.⁸

The electronic spectrum of the heptanuclear complex (Figure 5) consists of two strong absorption bands at 692 and 490 nm ascribed to charge transfer transitions from the peripheral $[\text{Ru}(\text{NH}_3)_5]^{2+} d(\pi)$ orbitals (designated $\text{Ru}_p(\pi)$), to the low-energy π_1^* and π_2^* orbitals of 2,2'-bipyrazine, namely the $\text{Ru}_p(\pi) \rightarrow (\text{bpz})\pi_1^*$ and $\text{Ru}_p(\pi) \rightarrow (\text{bpz})\pi_2^*$ respectively. The charge-transfer band characteristic of the central ion $[\text{Ru}(\text{bpz})_3]^{2+}$, (designated $\text{Ru}_c(\pi)$, i.e. $\text{Ru}_c(\pi) \rightarrow (\text{bpz})\pi_1^*$, is located around 440 nm,^{31,32} as shown in Figure 5, but it is masked by the strong band at 490 nm. Such a band, however, is evident in the spectrum

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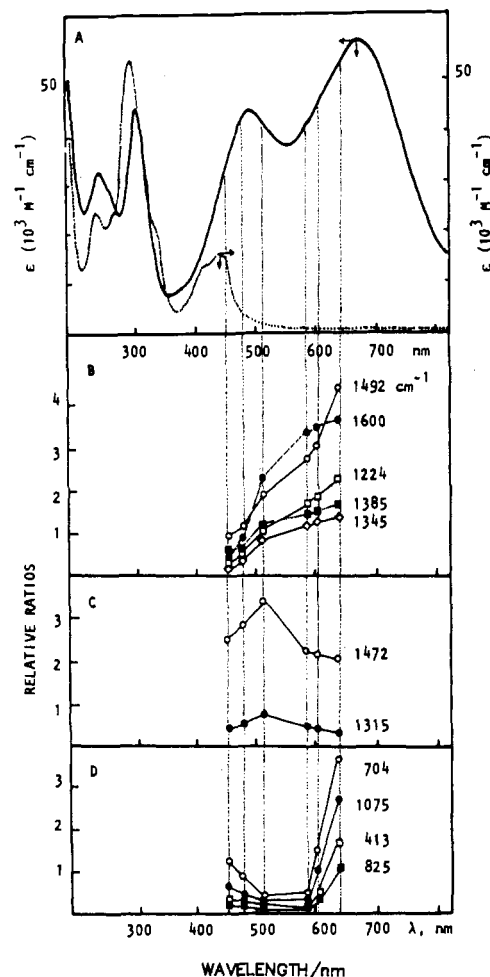


Figure 5. Electronic absorption spectra (A) and typical resonance Raman excitation profiles (B-D) for the $[\text{Ru}(\text{bpz})_3\{\text{Ru}(\text{NH}_3)_5\}_6]^{14+}$ complex. The absorption spectrum of $[\text{Ru}(\text{bpz})_3]^{2+}$ is shown as a dotted line.

of the $[\text{Ru}(\text{bpz})_3\text{Ru}(\text{NH}_3)_5]^{4+}$ complex.¹⁶

In contrast with the $[\{\text{Ru}(\text{NH}_3)_5\}_n\text{bpz}]^{2n+}$ complexes, the rR excitation profiles of the heptanuclear species are quite complicated, exhibiting three distinct patterns (Figure 5). The vibrational peaks at 500, 1145, 1176, 1224, 1273, 1345, 1387, 1492, and 1600 cm^{-1} (type I) follow an excitation profile that increases in the direction of the maximum of the $\text{Ru}_p(\pi) \rightarrow (\text{bpz})\pi_1^*$ charge-transfer band. The vibrational peaks at 1315 and 1472 cm^{-1} (type II) exhibit excitation profiles that follow very closely the $\text{Ru}_p(\pi) \rightarrow (\text{bpz})\pi_2^*$ charge-transfer band at 490 nm. The peaks at 298, 310, 413, 704, 825, and 1075 cm^{-1} (type III) show a minimum around 500 nm in the excitation profiles, increasing with excitation wavelength toward both 647 and 457 nm in the directions of the $\text{Ru}_p(\pi) \rightarrow (\text{bpz})\pi_1^*$ and $\text{Ru}_c(\pi) \rightarrow (\text{bpz})\pi_1^*$ transitions, respectively.

The ratio of the extinction coefficients of the $\text{Ru}_c(\pi) \rightarrow (\text{bpz})\pi_1^*$ and the $\text{Ru}_p(\pi) \rightarrow (\text{bpz})\pi_1^*$ MLCT bands at 440 and 672 nm, respectively, is 1:4. This ratio is close to that of the intensity ratios measured at 457 and 647 nm, for the vibrational peaks that follow the excitation profiles of types I and III. Therefore the excitation at 457 and 647 nm should be related to the same π_1^* level of 2,2'-bipyrazine, in agreement with the previous assignment of the electronic spectrum.¹⁶

Contrasting behavior is associated with the MLCT band at 490 nm. The vibrational frequencies that follow pattern I, are also strongly enhanced at this excitation wavelength, but the enhancement ratios are nearly proportional to the extinction coefficients of the three MLCT bands. A selective enhancement is

only observed for the vibrational frequencies at 1315 and 1472 cm^{-1} , which follow pattern II. These bands are not observed in the rR spectra of the $[\text{Ru}(\text{bpz})_3]^{2+}$ cation. On the other hand, the vibrational peaks that follow pattern III are little enhanced at 490 nm. Therefore, one can conclude that the MLCT band at 490 nm involves a second π^* level of 2,2'-bipyrazine, here denoted as π_2^* . Similar differences have been noted in the 2,2'-bipyridine vibrations coupled to states involving the $(\text{bpy})\pi_1^*$ and $(\text{bpy})\pi_2^*$ orbitals.^{33,34}

The excitation at the MLCT band at 490 nm leads to a preferential enhancement of the vibrational modes above 1000 cm^{-1} , which are strongly coupled with the aromatic ring. Presumably, the H-C bending modes and the ring torsion modes do not contribute to a displacement of the coordinates associated with the π_2^* excited level of 2,2'-bipyrazine.

The rR bands of 2,2'-bipyrazine in the heptanuclear complex are strongly polarized and correlate with the a_{1g} and b_{2u} vibrational frequencies of biphenyl (Table I) as expected for a local C_{2v} symmetry for the 2,2'-bipyrazine ligand. Perhaps the only exceptions are the weak vibrational peaks at 1176 and 1515 cm^{-1} , which seem to correlate with the b_{3u} modes of biphenyl. These bands behave as b_1 , in C_{2v} symmetry, and are only weakly polarized. The occurrence of non totally symmetric vibrations in the rR spectra can be explained in terms of a change of symmetry in the excited state or by the vibronic coupling involving two excited states.³⁰ In the present case, the second hypothesis is more plausible, due to the existence of three overlapping transitions.

The vibrational peak at 413 cm^{-1} is not correlated with the biphenyl vibrations in Table I or with the vibrational frequencies of $[\text{Ru}(\text{bpz})_3]^{2+}$ cation but can be detected in the rR spectra of the $[\{\text{Ru}(\text{NH}_3)_5\}_2\text{bpz}]^{4+}$ complex. These facts, in addition to the strong enhancement associated with coupling to the bpz LUMO orbital (Figure 4), support the assignment primarily to a $\text{Ru}_p\text{-N}(\text{bpz})$ stretching mode, rather than to a Ru-NH_3 stretching mode, though this is likely mixed in. The remaining band at 365 cm^{-1} in the heptanuclear complex and those at 348 and 380 cm^{-1} in the $[\text{Ru}(\text{bpz})_3]^{2+}$ complex are very weak and also do not correlate with the biphenyl vibrations in Table I. The assignment as $\text{Ru}_c\text{-N}(\text{bpz})$ stretching vibrations is not unreasonable, since these bands are close to the frequencies usually reported for metal-bipyridine stretching vibrations.²⁵ However, in light of the strong back-bonding properties of ruthenium(II), one would expect a $\text{Ru}_c\text{-N}(\text{bpz})$ stretching frequency above 400 cm^{-1} , perhaps coinciding with the $\text{Ru}_p\text{-N}(\text{bpz})$ stretching band at 413 cm^{-1} .

Summary. Four MLCT bands associated with the $\text{Ru}_c\text{-bpz-Ru}_p$ framework encompass transitions from the central and peripheral ruthenium atoms to the LUMO and subsequent π^* orbital on 2,2'-bipyrazine. The ability to identify different rR enhancement patterns for the three lower energy transitions is of special interest and provides insight into the vibrational coupling as it changes across the multiple transition envelope. The rR data as interpreted here are fully consistent with the previous electronic assignments,¹⁶ demonstrating, in particular, the common LUMO orbital involved in two of these transitions. We have previously demonstrated that the excited states generated by transitions to the LUMO from the central ruthenium atom and from the several peripheral ruthenium atoms are electronically uncoupled. This study reveals that despite that observation, the electronic distribution of the bpz^- component of the excited state is the same, irrespective of where the electron originates.

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