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Assignment of the Electronic Spectra of Tris(μ-halo)bis(triammineruthenium)(2+) Ions Using Resonance Raman Spectroscopy

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Several assignments have been made previously for the strong visible absorption in the electronic spectra of the tris(μ-halo)bis(triammineruthenium)(2+) ions for the halogens X = Cl, Br. The assignments derived from MCD measurements disagree with those derived from resonance Raman (RR) spectroscopic studies. In the present work, RR spectra in the region of the metal–ligand vibrations have been recorded for exciting wavelengths that cover most of the visible region. In addition, the depolarization ratios of the resonance-enhanced Raman bands have been recorded with greater accuracy and over a wide range of exciting wavelengths. These measurements indicate that intensity enhancement of the Ru–X bands in the RR spectra is due to a z-polarized transition that has been assigned as $\sigma \rightarrow \sigma^*$ (in accord with the previous RR study). The relative enhancements of the Ru–X and Ru–N band intensities vary over the range of exciting wavelengths, and it is proposed that the transition $\sigma^* \rightarrow \pi^*$ contributes to the intensity of the Ru–N band at higher excitation energies. Accordingly, this transition can be assigned in the spectra of the two complexes. From the assignments of the transitions $\sigma \rightarrow \sigma^*$ and $\sigma^* \rightarrow \pi^*$, a reasonable set of assignments for the remaining bands in the electronic spectra has been proposed.

Introduction

The most striking feature of the tris(μ-halo) mixed-valence diruthenium(II,III) complexes (commonly referred to as "ruthenium blues") is the presence of a strong electronic band that dominates the visible region of the spectrum. The complexes also exhibit a narrow absorption in the near-infrared region.[1] The relatively low energy of these bands indicates that the transitions are likely to be between the molecular orbitals that result from interaction of the d orbitals of the two ruthenium atoms. In addition, the observation that the visible absorption lies only 1100 cm^{-1} lower in energy in tris(μ-bromo)bis(triammineruthenium)(2+) bromide compared to the corresponding chloro complex suggests that it is most unlikely that the absorption arises from a halogen–metal charge transfer.

Recently there has been some conflict in the assignment of the electronic transitions in the tris(μ-halo)bis(triammineruthenium)(2+) halide complexes. An assignment of the two lowest energy transitions for the chloro and bromo complexes was made by Hush et al.,[1] using a molecular orbital scheme for a cofacial bioctahedral structure of D_{3h} symmetry (Figure 1). The near-infrared and visible absorption bands were attributed to the $\delta^*(e'') \rightarrow \sigma^*(a_2'')$ (x,y-polarized) and $\sigma(a_1') \rightarrow \sigma^*(a_2'')$ (z-polarized) transitions, respectively.

In order to verify these assignments, Armstrong et al.[2] carried out a resonance Raman (RR) study of the chloro, bromo, and iodo complexes using the exciting lines 568, 647, and 676 nm, respectively (these being the available exciting lines closest to the relevant band maxima). It was found that resonance enhancement occurred for bands attributed to the totally symmetric X–Ru–X bending (ν_4) and Ru–X stretching (ν_2) modes (X = Cl, Br, I). The depolarization ratios of these bands (for X = Cl or Br) ranged from 0.2 to 0.4, close to 1/3, consistent with the assignment of $\sigma(a_1') \rightarrow \sigma^*(a_2'')$ to the strong visible absorption.

Shortly after the publication of these results, the MCD spectra of the chloro and bromo complexes were reported.[3] The MCD measurements indicate that the main visible absorption must result from a number of transitions, and it was suggested that the major component is the x,y-polarized transition $\delta(e') \rightarrow \pi(e')$.

Attempts to prepare single crystals of these complexes suitable for an X-ray crystal structure determination were, until recently, unsuccessful. However, crystal structures of $[\text{Ru}_2(\text{NH}_3)_6\text{Cl}_3][\text{BPh}_4]$[4] and $[\text{Ru}_2(\text{NH}_3)_6\text{Br}_3][\text{ZnBr}_4]$[5] have now been reported, and both confirm the tris(μ-halo) geometry previously proposed. The crystal data are also consistent with the delocalized description of the mixed-valence electronic structure. Analysis of these complexes using the molecular orbital model for a symmetrical cofacial bioctahedral structure is therefore appropriate.

It is clear that the results of the MCD and RR experiments are incompatible. Indeed, it is expected[6] that the depolarization ratios of the Raman bands would be significantly different from 1/3 if the transition was substantially x,y-polarized. Thus, the validity of both sets of experimental results and their interpretations must be questioned. It is well-known that many ruthenium ammine complexes are extremely oxygen sensitive.[7] The mixed-valence complexes are no exception. For this reason, considerable care is required to avoid decomposition during synthesis and characterization. The complexes are also photolabile,[2] and so it was thought that photodegradation may have been the cause of some error in the reported RR experiments. The polarized RR spectra were recorded sequentially, the orientation of the polarizer being changed manually between acquisitions. If the sample had decomposed significantly from one acquisition to the next, then the depolarization ratios obtained would be systematically inaccurate. In this work, the RR experiments were repeated for the chloro and bromo complexes in order to obtain more accurate depolarization ratios. In addition, an extensive RR study over a wide range of exciting wavelengths was undertaken. As a result, it was possible to suggest assignments for all of the absorption bands in the electronic spectra of the chloro and bromo complexes.

Experimental Section

Materials. All procedures were carried out under an atmosphere of argon with deoxygenated solvents.

Tris(μ-chloro)bis(triammineruthenium)(2+) chloride was prepared from hexaammineruthenium(II) chloride and concentrated HCl by using a modified version of the method of Bottomley and Tong.[8] The modification involves allowing the blue solution containing the mixed-valence species to stand for only 90 min instead of 15 h. Although this reduces the yield significantly, hydrolysis of the complex is minimized. The product obtained has a high purity and does not require recrystallization.

Tris(μ-bromo)bis(triammineruthenium)(2+) bromide was prepared in a similar manner from hexammineruthenium(II) bromide and concentrated HBr that had been freshly distilled over red phosphorus.

Methods. The electronic spectra of the complexes in aqueous solution were recorded at room temperature on a Cary Model 17D spectrometer, interfaced to a Commodore PET microcomputer and a Hewlett-Packard 7470A graphics plotter.

RR spectra were recorded at room temperature with use of exciting radiation provided by Spectra Physics 2025-11 Kr^+ and 2025-05 Ar^+

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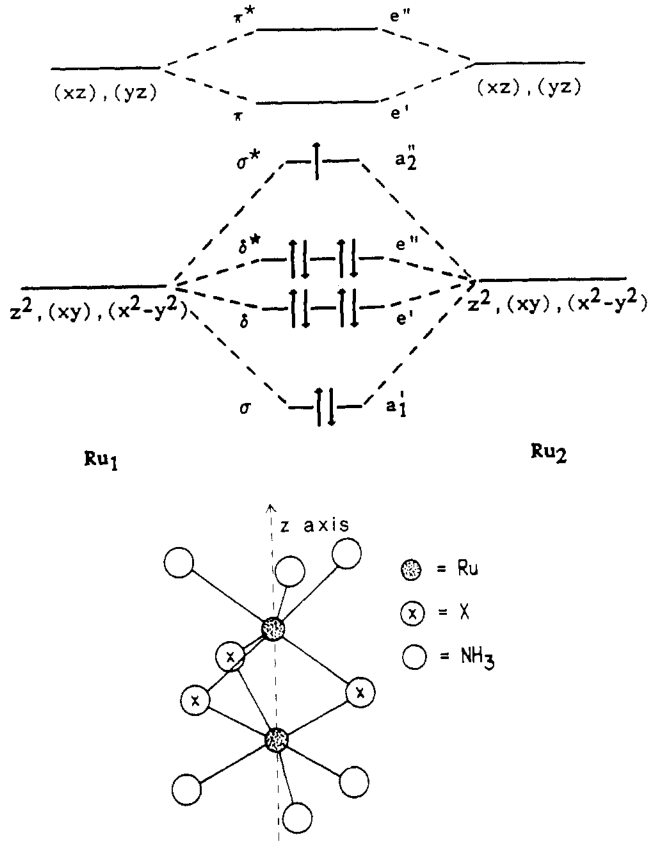

Figure 1. Proposed qualitative Ru 4d-level ordering in the $[Ru_2(NH_3)_6X_3]^{2+}$ complexes. (The diagram at the bottom is an illustration of the $[Ru_2(NH_3)_6X_3]^{2+}$ cation with the molecular axis.)

lasers. The incident laser light was focused on the aqueous sample solution (typically 3.5 mM) contained in a spinning cylindrical quartz cell. For all but two of the exciting lines, the power of the laser beam at the sample was 30–40 mW and was increased to 80–90 mW for the low-energy exciting lines 647 and 676 nm. The light scattered from the sample at 90° was focused by using a Leitz f1.0 collection lens onto the slits of a Jobin-Yvon U1000 double monochromator equipped with a cooled RCA C31034 photomultiplier tube and photon-counting electronics. The data were stored digitally in a Hicom AT computer using ISA Enhanced Prism Software (versions 2.1 and 3.0). The spectra were plotted by using a Hewlett-Packard 7475 graphics plotter.

The bromo complex proved to be more photolabile than the chloro complex, and the photolability of each increased as the energy of the exciting line increased beyond the peak maximum. For the chloro complex, photodecomposition was slow for exciting lines near the peak maximum (568, 647 nm). Here, data points were collected at 0.5-cm^{-1} increments for a total of 2 s/point. Where the enhancements were low, the signal-to-noise ratio had to be increased without increasing the length of the scan. Thus, for the exciting lines 676 and 530 nm, the data points were collected at 1-cm^{-1} increments and the integration time was increased to 5 s/point. The latter conditions were typical for the collection of spectra of the bromo complex using exciting lines 676, 647, and 568 nm.

When long scans (~1 h) were run with high energy excitations ($\leq$530 nm), the section of the solution that was exposed to the beam decolorized and the signal was reduced significantly. However, when the solution was mixed and scanning repeated, the signal increased to almost its original value. Thus, for excitation $\leq$530 nm, a number (typically five) of very short scans (1-cm^{-1} increments of 0.5 s/point) were collected, with the sample being agitated after each scan. The spectra were then summed to give a spectrum with a satisfactory signal-to-noise ratio.

In the polarization experiments, a polarizer and a polarization scrambler were both placed between the collection lens and the slits of the monochromator. For the chloro complex, separate spectra were recorded for the totally symmetric Ru–Cl stretch and bend. The regions recorded were (a) 50–280 cm^{-1} and (b) 250–350 cm^{-1}. For the exciting lines 676, 647, and 568 nm, data points were collected at 0.5-cm^{-1} increments of 5 s/point. For 514- and 530-nm excitation, data points were collected at 1-cm^{-1} increments of 5 s/point, and for 476-nm excitation, 1-cm^{-1} increments of 2.5 s/point were used. For the bromo complex only one region of the spectrum, 50–320 cm^{-1}, was scanned. With 676- and 568-nm excitation, 1-cm^{-1} increments of 10 s/point were used, and for 647- and 530-nm excitation, the integration time was reduced to 5 s/point.

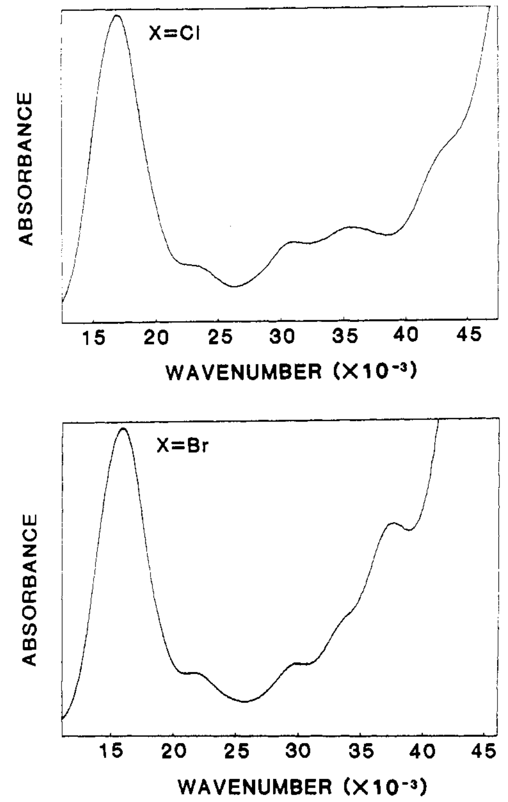

Figure 2. Electronic absorption spectra of $[Ru_2(NH_3)_6X_3]^{2+}$ complexes (X = Cl, Br) in H_2O at room temperature.

Four spectra were recorded sequentially for each region and each exciting wavelength. The parallel component of the scattered light was measured first; then the orientation of the polarizer was switched to collect the second component. This sequence was then repeated so that any decomposition could be quantified.

For purposes of assigning the Ru–N modes, the RR spectrum (568-nm excitation) of $[Ru_2(NH_3)_6Cl_3]^{2+}$ was compared with that of the N-deuterated complex. To prepare the N-deuterated complex, $[Ru_2(NH_3)_6Cl_3]Cl_2$ was dissolved in chilled D_2O, and the solution was left to stand for ~2 h. Under these conditions, deuteration is unlikely to be complete. However, it is more important that hydrolysis of the complex is avoided, as complete deuteration is not essential in order to obtain a suitable difference spectrum. An aqueous solution of $[Ru_2(NH_3)_6Cl_3]^{2+}$ was also prepared, and both solutions were transferred to separate halves of a split cell. As each half of the split cell comes into the laser beam, electronics in the cell spinner assembly gate the signal from the photomultiplier tube to alternate acquisition channels. Consequently, the simultaneous acquisition[9] of the two spectra was possible and differences in the spectra, accurate to the size of the increment, could be measured. Data points were collected at 0.5-cm^{-1} increments for an integration time of 5 s/point.

Results

Electronic Spectra. Aqueous solution electronic absorption spectra are presented in Figure 2. Comparison of these with spectra previously reported confirms that the samples are of high purity.

Resonance Raman Spectra. The RR spectra recorded at 568 and 647 nm, respectively, for the chloro and bromo complexes are shown in Figure 3. The peak positions and their assignments are listed in Table I. As expected, the dominant bands in the spectra of both complexes are the totally symmetric metal–halide bend and stretch. Upon deuteration of the chloro complex, the peak formerly at 487 cm^{-1} shifts ~30 cm^{-1} lower in energy and the shoulder on the high-energy side of the Ru–Cl bend moves from 230 to 215 cm^{-1} and gains intensity. It was also apparent that the Ru–Cl stretch moves a very small amount upon deu-

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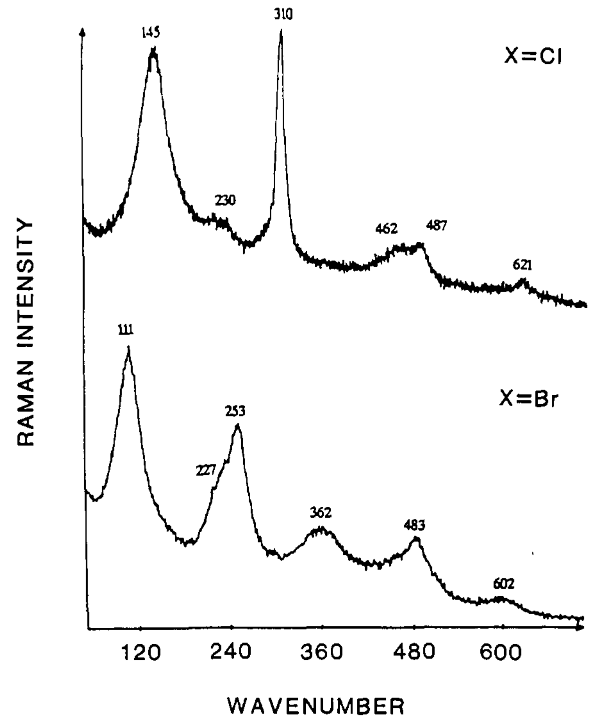

Figure 3. Resonance Raman spectra of $[Ru_2(NH_3)_6X_3]^{2+}$ complexes for X = Cl (568-nm excitation) and X = Br (647-nm excitation).

Table I. Resonance Raman Vibrational Wavenumbers and Assignments for $[Ru_2(NH_3)_6Cl_3]^{2+}$ (568-nm Excitation) and $[Ru_2(NH_3)_6Br_3]^{2+}$ (647-nm Excitation)

cm^{-1}		
$[Ru_2(NH_3)_6Cl_3]^{2+}$	$[Ru_2(NH_3)_6Br_3]^{2+}$	assgnt
145	111	ν_4 X-Ru-X bend (A_1)
230	227	ν_3 N-Ru-N bend (A_1)
310	253	ν_2 Ru-X str (A_1)
462	362	$\nu_2 + \nu_4$
487	483	ν_1 Ru-N str (A_1)
	602	$2\nu_2 + \nu_4$
621		$2\nu_2$

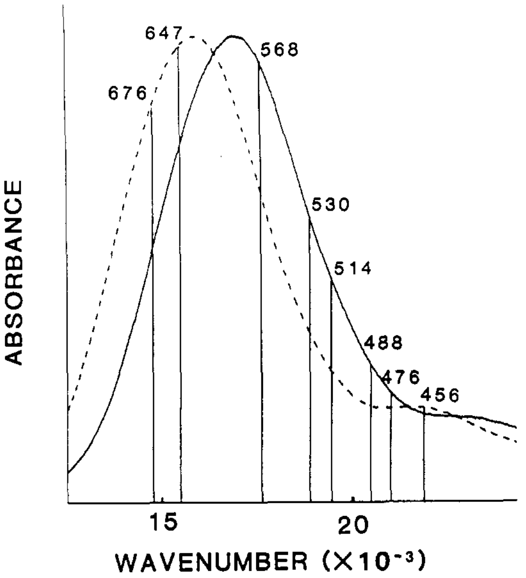

Figure 4. Wavelength (nm) of exciting lines in relation to the absorption maxima of $[Ru_2(NH_3)_6X_3]^{2+}$ for X = Cl (—) and X = Br (---).

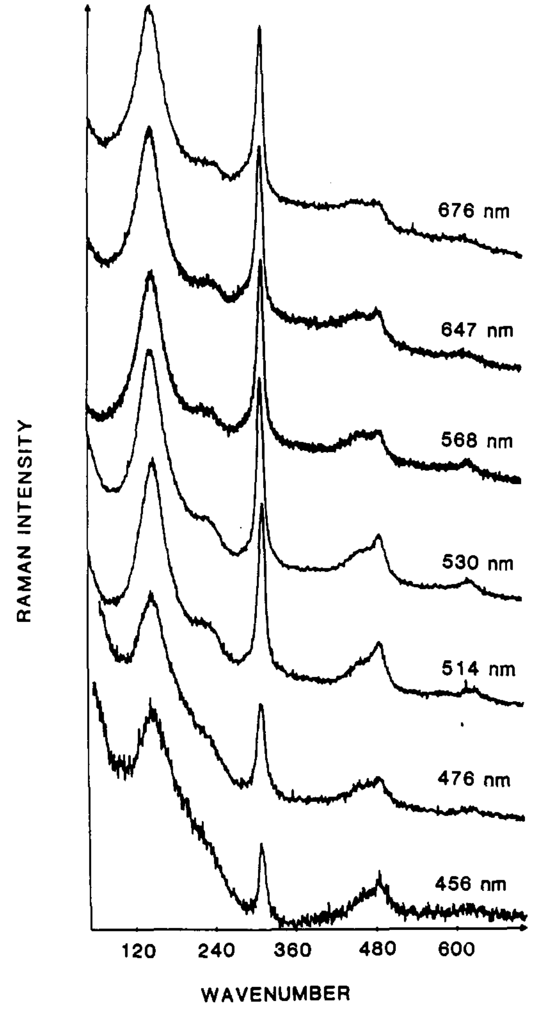

Figure 5. Resonance Raman spectra of $[Ru_2(NH_3)_6Cl_3]^{2+}$ for various excitation wavelengths.

teration (~1 cm^{-1}). These observations strongly suggest that the peaks at 487 and 230 cm^{-1} are derived from Ru–N vibrations.[10] Consequently, the peak at 487 cm^{-1} has been assigned to the A_1 Ru–N stretch (ν_1) and the shoulder at 230 cm^{-1} is assigned to the A_1 Ru–N bend (ν_3). The intensity gain observed for the latter band upon deuteration is attributed to increased coupling of ν_3 and ν_4 in the deuterated compound.

By analogy with the chloro complex, the band at 483 cm^{-1} in the RR spectrum of the bromo complex has been assigned to the A_1 Ru–N stretch (ν_1). The shoulder (227 cm^{-1}) on the band at 253 cm^{-1} has been attributed to the A_1 Ru–N bend (ν_3). Corresponding bands have also been observed[11] in the RR spectrum of the iodo complex at 469 and 254 cm^{-1}, respectively. The observation that the wavenumbers of the Ru–N bands shift (~5 cm^{-1}) as the halide is substituted from chlorine to bromine suggests that there is some mechanical coupling between the Ru–N and Ru–X vibrations.

RR spectra of the chloro and bromo complexes were also recorded by using a range of exciting lines that covers most of the visible-band envelope in both complexes. The relationship between the wavelength of the exciting radiation and the visible band envelopes of the two complexes is shown in Figure 4. The RR spectra of the chloro and bromo complexes are presented in Figures 5 and 6, respectively.

The RR spectra were not internally referenced, as a suitable, noninteracting internal standard could not be found for aqueous solutions of these compounds. Therefore, the relative peak intensities between the spectra can only be compared qualitatively. Resonance enhancement of the Ru–X band intensities decreased as the wavelength of the exciting radiation was moved further from the absorption maximum. This is not obvious from Figures 5 and 6, as the spectra have been scaled to allow easy visual comparison of the relative intensities of the different bands within the spectra. In the absence of an internal standard, absolute excitation profiles

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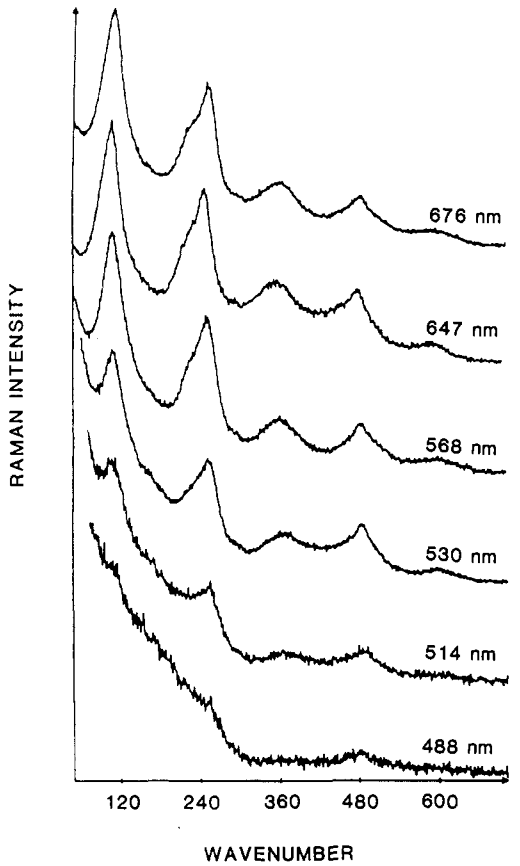

Figure 6. Resonance Raman spectra of $[Ru_2(NH_3)_6Br_3]^{2+}$ for various excitation wavelengths.

Table II. Depolarization Ratios of the Ru–X Stretch and X–Ru–X Bend for Various Excitation Wavelengths[a]

	depolarizn ratio at exc wavelength					
vib band	676 nm	647 nm	568 nm	530 nm	514 nm	476 nm
		$[Ru_2(NH_3)_6Cl_3]^{2+}$				
ν(Ru–Cl)	0.36	0.34	0.36	0.30	0.35	0.33
δ(Cl–Ru–Cl)	0.33	0.36	0.35	0.37	0.31	0.36
		$[Ru_2(NH_3)_6Br_3]^{2+}$				
ν(Ru–Br)	0.33	0.36	0.33	0.30		
δ(Br–Ru–Br)	0.34	0.30	0.32	0.31		

[a] Errors in the depolarization ratios are ±10% for exciting lines 676–568 nm and ±20% for exciting lines 530–476 nm.

could not be calculated. However, the relative band intensities within each spectrum can be compared. The most noticeable change in the spectra of both complexes as the wavelength of the exciting radiation is decreased is the increase in intensity of the Ru–N bands at 487 cm^{-1} (chloro complex) and 483 cm^{-1} (bromo complex) relative to the intensities of the Ru–X bands. This is most pronounced with high-energy excitation.

Depolarization ratios ($\rho(\pi/2)$) for the two Ru–X modes, ν_2 and ν_4, were measured for a range of exciting lines. These are listed in Table II.

Sample Decomposition. Previously it was reported[11] that after 90 min in the 568-nm laser beam, the chloro complex decomposed almost completely. To eliminate any error associated with sample decomposition in the laser beam, simultaneous collection of the polarized spectra would be a suitable technique. Such an experiment was planned; however, for our samples, photolytic decomposition was found to be much slower than reported. For exciting lines close in energy to the absorption maximum, decomposition was not observable until after 3–4 h for the chloro complex and ~2 h for the bromo complex. The rate of decomposition was therefore low enough to allow the polarized spectra to be recorded sequentially without any measurable decomposition from one scan to the next. When high-energy exciting lines were used (≤514 nm for the chloro complex and ≤530 nm for the bromo complex), the rate of photolytic decomposition did increase significantly. Consequently, for these lines, shorter scan times were necessary to prevent sample decomposition occurring during the experiment.

The iodo complex was previously reported[11] to be more photolabile than the corresponding chloro and bromo complexes. Thus, investigations on the iodo complex similar to those reported here were not undertaken.

Discussion

For RR scattering with enhancement due to an electronic transition between known states, it is possible to predict which vibrational bands will be enhanced. Consider the electronic transition $\sigma(a_1') \rightarrow \sigma^*(a_2'')$ (Figure 1). Here an electron is excited from a bonding orbital into an orbital that is antibonding with respect to the Ru–Ru interaction. Such a transition will involve an excited state with a longer Ru–Ru bond length than in the ground state. Because of the geometry of the complex, stretching the Ru–Ru bond necessarily causes large changes in the Ru–X bond lengths and bond angles.

Resonance enhancement occurs for Raman bands associated with the normal coordinates along which the molecular geometry changes upon excitation.[6] The normal coordinate of ν(Ru–Ru) is a linear combination of the normal coordinates of A_1 δ(X–Ru–X) and A_1 ν(Ru–X).[12] Therefore, bands associated with the bending and stretching of the halide bridge are expected to be enhanced in the RR spectrum. *A*-term scattering is the dominant mechanism of resonance enhancement when a single electric dipole-allowed transition is involved. Since *A*-term scattering only occurs for totally symmetric modes, it is usual that only bands derived from these modes are resonance enhanced.[13] Consequently, if the energy of the exciting radiation is close to that of the $\sigma \rightarrow \sigma^*$ transition, then bands of the totally symmetric vibrational modes of the halide bridge should dominate the RR spectrum. Overtone and combination bands of these modes are also likely to appear.[6,13]

The depolarization ratio of a resonance-enhanced band depends on the symmetry of the resonant electronic transition.[6] For a complex of D_{3h} symmetry, the transition symmetry must be either A_2'' (*z*-polarized) or E' (*x*,*y*-polarized) for the electronic transition to be allowed. A vibrational band that is resonance enhanced by a *z*-polarized transition has a depolarization ratio of 1/3. If the resonant electronic transition is *x*,*y*-polarized, then the vibrational band will have a depolarization ratio of 1/8.

In the spectra of both the chloro and the bromo complexes, the most intense bands are those of the totally symmetric Ru–X stretch (ν_2) and bend (ν_4). Overtone and combination bands are observed at 462 cm^{-1} ($\nu_2 + \nu_4$) and 621 cm^{-1} ($2\nu_2$) for the chloro complex and at 362 cm^{-1} ($\nu_2 + \nu_4$) and 602 cm^{-1} ($2\nu_2 + \nu_4$) for the bromo complex. For excitation wavelengths that cover most of the strong visible absorption, the depolarization ratios of the bands assigned as ν_2 and ν_4 are all 1/3 within experimental error (Tables I and II) for both complexes. These results, along with the greater enhancement of the Ru–X bands relative to the Ru–N bands, are entirely consistent with the visible absorption being solely derived from the *z*-polarized transition $\sigma \rightarrow \sigma^*$.

In the case where a Raman band gains intensity from two close-lying transitions, the enhancement due to each transition will have a different wavelength dependence and thus $\rho(\pi/2)$ will be dependent on the excitation wavelength.[6] For wavelengths where there is a similar degree of enhancement from each of the two transitions, very unusual behavior is observed, even to the extent of observing anomalously polarized bands. However, if the degrees of enhancement are very dissimilar, then $\rho(\pi/2)$ will approach that obtained for bands enhanced by a single transition.

The Ru–X depolarization ratios appear to be constant for the entire range of excitation wavelengths for which they were measurable (1/3 within experimental error). This precludes the

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possibility of resonance enhancement of the Ru–X bands having any significant component from anything other than a z-polarized transition. In addition, the depolarization ratio of the Ru–N band at 483 cm^{-1} in the bromo complex (647-nm excitation) was reported[11] to be 0.4. Thus, for exciting wavelengths close to the absorption maximum, all the bands observed in the RR spectrum are enhanced by a z-polarized transition. There is no evidence of any significant enhancement, even for the band of the Ru–N stretch, from an x,y-polarized transition. The RR results therefore indicate that the strong visible absorption derives solely from the z-polarized transition $\sigma \rightarrow \sigma^*$.

The quite rapid photodecomposition of the sample and the weakness of the band intensity of the Ru–N stretch have prevented accurate measurement of depolarization ratios of this band at excitation wavelengths shorter than 568 nm. It was impossible to obtain an adequate signal-to-noise ratio for the perpendicularly polarized spectrum with the short scan times required to prevent sample decomposition. With the low sample concentrations (~3.5 mM) used, the only possible explanation for the appearance of the Ru–N bands in the spectrum is that they are resonance enhanced. The previous discussion overlooks coupling of the Ru–N and Ru–X modes. By symmetry and from the closeness in wavenumber of the two modes ν_1 and ν_2, it is clear that the Ru–N stretching coordinate must contain a certain amount of Ru–X character. In addition, the small shift of the Ru–Cl stretch upon deuteration and the observation that the Ru–N bands shift (~5 cm^{-1}) as the halide is substituted from chloride to bromide confirm that there is coupling between the Ru–N and Ru–X vibrations. Therefore, we expect that the band intensities of the Ru–N modes will be enhanced by the $\sigma \rightarrow \sigma^*$ transition, albeit weakly, by coupling to the Ru–X modes.

As the energy of the exciting radiation is increased, the relative enhancements of the bands of the Ru–X (ν_2) and Ru–N (ν_1) modes change significantly (Figures 5 and 6). This is apparent for the 530-nm and higher energy lines in the spectra of both the chloro and the bromo complexes. The difference in relative enhancements of bands of ν_1 and ν_2 indicates that the two bands have different excitation profiles. For both complexes, the Ru–N stretch starts to gain intensity with excitation around 530 nm. From Figure 4, it can be seen that this is on the high-energy side of the main visible absorption band, where a small shoulder begins to make some contribution to the absorption. We suggest, therefore, that the increase in intensity of the Ru–N band at low wavelengths results from preresonance enhancement as the excitation energy approaches that of the small shoulder. Indeed, if the two bands have different excitation profiles, then there must be a second electronic transition involved.

For the Ru–N band to be preferentially enhanced, the resonant electronic transition must involve a change in the Ru–N bond length. An electron excited into an e_g-type orbital (antibonding with respect to the Ru–N interaction) would weaken and thus lengthen the Ru–N bond in the excited state. This is a condition for obtaining resonance enhancement of bands of totally symmetric Ru–N modes. The main visible absorption has been assigned to the transition $\sigma \rightarrow \sigma^*$, and in previous work,[1] the near-IR absorption (7150 and 6870 cm^{-1} for the chloro and bromo complexes, respectively) was assigned to the transition $\delta^* \rightarrow \sigma^*$. If the two lowest energy observed absorptions are assigned as $\delta^* \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$, then from the molecular orbital diagram (Figure 1), the next lowest energy allowed transition should be $\sigma^* \rightarrow \pi^*$. Consequently, the shoulder (at 23 000 and 22 100 cm^{-1} for the chloro and bromo complexes, respectively) is assigned to the allowed transition of lowest energy between the t_{2g}- and e_g-type orbitals, $\sigma^* \rightarrow \pi^*$ (x,y-polarized). Because of the low intensity of the Ru–N stretch and the rapid sample decomposition at high-energy exciting wavelengths, it has not been possible to verify this assignment by using depolarization ratio measurements of the Ru–N stretch.

If the energies of the three transitions, $\delta^* \rightarrow \sigma^*$, $\sigma \rightarrow \sigma^*$, and $\sigma^* \rightarrow \pi^*$ are known, it is possible to quantify the energies in Figure 1. Neglecting effects such as configuration interaction, approximate energies of all the remaining allowed electronic transitions can be calculated and assignments can be proposed for the observed bands. The transition $\sigma \rightarrow \pi$ is the allowed electronic transition of highest energy derived solely from the metal d orbitals. The energy of this transition for the chloro complex can be estimated from the known transition energies to be at least 40 000 cm^{-1}. Configuration interaction of the excited state with other excited states of the same symmetry would be expected to raise the energy of this transition. It is therefore reasonable to assign the feature observed in the electronic spectrum at 43 500 cm^{-1} to the transition $\sigma \rightarrow \pi$. There should be four allowed transitions of intermediate energy, although only two bands are observed in this region of the spectrum. However, this observation is not surprising, as the splitting of the orbitals due to the δ interaction is only of the order of 2000 cm^{-1} (from comparison of $E(\sigma \rightarrow \sigma^*)$ with $2E(\delta^* \rightarrow \sigma^*)$). Consequently, the bands at 31 300 and 35 700 cm^{-1} have been assigned to the transitions $\delta,\delta^* \rightarrow \pi$ and $\delta,\delta^* \rightarrow \pi^*$, respectively. Owing to possible configuration interaction between the excited states, the assignments of the transitions $\delta,\delta^* \rightarrow \pi$ and $\delta,\delta^* \rightarrow \pi^*$ are only tentative.

Table III. Electronic Band Assignments for $[Ru_2(NH_3)_6X_3]^{2+}$ Complexes

ν/cm^{-1} ($\epsilon/M^{-1}\ cm^{-1}$)			
X = Cl	X = Br	X = I[a]	transn
7150 (1600)	6 870 (1888)		$e''(\delta^*) \rightarrow a_2''(\sigma^*)$
17 000 (4000)	15 900 (4000)	14 100	$a_1'(\sigma) \rightarrow a_2''(\sigma^*)$
23 000 (740)	22 100 (810)	20 000	$a_2''(\sigma^*) \rightarrow e''(\pi^*)$
31 300 (1030)	30 000 (830)		$e'(\delta) \rightarrow e'(\pi)$
			$e''(\delta^*) \rightarrow e'(\pi)$
35 700 (1210)	34 000 (1450)		$e'(\delta) \rightarrow e''(\pi^*)$
			$e''(\delta^*) \rightarrow e''(\pi^*)$
43 500 (2500)	37 500 (2700)		$a_1'(\sigma) \rightarrow e'(\pi)$

[a] Data from ref 11.

The appearance of the electronic spectrum of the bromo complex is qualitatively very similar to the spectrum of the chloro complex, and thus we may expect that the same types of assignments are valid. Qualitatively, the molecular orbital scheme is also similar. However, the splitting between the e_g- and the t_{2g}-type orbitals is expected to be less for the bromo complex. The different positions of the $\delta^* \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions (Table III) in the chloro and bromo complexes are accounted for by the greater Ru–Ru distance[4,5] in the complex bridged by the larger Br atoms. (The Ru–Ru distances are 2.753 and 2.852 Å, for the chloro and bromo complexes, respectively.) The remaining transitions ($\sigma \rightarrow \pi$, $\sigma^* \rightarrow \pi^*$, $\delta,\delta^* \rightarrow \pi$, $\delta,\delta^* \rightarrow \pi^*$) all involve excitation from a t_{2g}-type to an e_g-type orbital. Thus, they are related to the d–d transitions in mononuclear complexes, and their energies are expected to be ligand field dependent. On changing from a RuN_3Cl_3 to a RuN_3Br_3 chromophore, the ligand field, Δ, should be reduced.[14] The mean position of the transitions $\delta,\delta^* \rightarrow \pi$ and $\delta,\delta^* \rightarrow \pi^*$ is expected to be essentially independent of the Ru–Ru interaction and thus gives an indication of the difference in Δ between the two complexes. The spectrum of the bromo complex can be related to that of the chloro complex if $\Delta(Br)$ is taken to be approximately $0.95\Delta(Cl)$. The theoretical relationship between the ligand fields of the two chromophores, RuN_3Cl_3 and RuN_3Br_3, is estimated to be $\Delta(Br) = 0.96\Delta(Cl)$ on the basis of spectrochemical f factors.[14] The complete electronic spectrum of the iodo complex is shown in ref 11. Fewer bands are observed because a ligand–metal charge-transfer band has shifted to lower energy, swamping any lower intensity absorptions that may be in the same region. The transitions that can be assigned by analogy to the chloro and bromo complexes are listed in Table III.

It is also possible to compare the electronic spectra of other known "ruthenium blues" with the spectra of $[Ru_2(NH_3)_6X_3]^{2+}$. A class of ruthenium blues that has been studied recently[15] is the nonahalides $[Ru_2X_9]^{4-}$, X = Cl, Br. These complexes have the

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(14) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: New York, 1984; p 751.

(15) Heath, G. A.; Kennedy, B. J.; Khoo, J. T. To be published.

same symmetry and geometry as the $[Ru_2(NH_3)_6X_3]^{2+}$ complexes, and so the same qualitative molecular orbital scheme can be used to describe their transition energies. Assigning the peaks by analogy with $[Ru_2(NH_3)_6X_3]^{2+}$ gives good agreement with those proposed by Heath et al.[15] Again, the strength of the Ru-Ru interaction can be estimated from the two lowest energy peaks, and it is also expected that Δ for the nonahalides will be lower than Δ for the $[Ru_2(NH_3)_6X_3]^{2+}$ complexes. The transition energies depend on the Ru-Ru interaction as well as the ligand field strength. It is therefore possible to estimate the differences in the ligand field splittings between $[Ru_2(NH_3)_6X_3]^{2+}$ and $[Ru_2X_9]^{4-}$ and thus test the validity of the assignments. To fit the band positions for $[Ru_2Cl_9]^{4-}$ and $[Ru_2Br_9]^{4-}$ with $[Ru_2(NH_3)_6Cl_3]^{2+}$, Δ has to be reduced by a factor of $^3/_4$ and $^2/_3$, respectively. On changing the RuN_3Cl_3 chromophore to RuX_6, the change in Δ can be estimated from the spectrochemical f factors[14] to be 0.78 for X = Cl and 0.70 for X = Br. These values compare well with the estimated values of 0.75 and 0.67. Therefore, the proposed set of assignments for these ruthenium blues provides a good basis for the understanding of their electronic spectra.

Another related system recently studied[16] is the complex $[Ru_2L_2(\mu\text{-}Cl_3)]^{2+}$ (L = 1,4,7-triazacyclononane). The electronic absorption band positions have been reported, and they are virtually identical with those for the $[Ru_2(NH_3)_6Cl_3]^{2+}$ complex.

Conclusion

The results obtained in this study confirm the conclusions of the earlier RR study of these complexes. In addition, the depolarization ratios measured over a wide range of exciting lines are entirely consistent with the visible absorption (centered at 17 000 and 15 900 cm^{-1} for the chloro and bromo complexes, respectively) being assigned as the z-polarized electronic transition, $\sigma \rightarrow \sigma^*$. There is also strong evidence for the weaker transition at 23 000 and 22 100 cm^{-1} for the chloro and bromo complexes, respectively, being assigned as the x,y-polarized transition $\sigma^* \rightarrow \pi^*$.

The energies of the two transitions $\sigma \rightarrow \sigma^*$ and $\sigma^* \rightarrow \pi^*$, as well as the energy of the near-IR transition ($\delta^* \rightarrow \sigma^*$), have been used to assign the remaining absorption bands in the electronic spectra. Thus, all of the allowed transitions between the states derived from metal d orbitals have been assigned to bands observed in the electronic spectra of $[Ru_2(NH_3)_6Cl_3]^{2+}$ and $[Ru_2(NH_3)_6Br_3]^{2+}$. The same ordering of transition energies can be used to give a reasonable set of assignments for the spectra of other related ruthenium blues. This confirms the appropriateness of the assignments using the molecular orbital scheme of Figure 1.

There remains the question of the relation of these assignments to the MCD spectra published. Agreement between the RR and MCD results can only be obtained if it is assumed that the x,y-polarized transition does not cause significant resonance enhancement of any Raman band. This would be unusual behavior for a strongly allowed electronic transition. Furthermore, the main visible absorption band is highly symmetric, suggesting that it derives only from a single electric dipole allowed transition. The MCD results indicate that the absorption derives from at least two transitions, with the dominant transition, $\delta \rightarrow \pi$ (x,y-polarized), lying on the low-energy side of the absorption maximum. Thus, the RR experiments and the profile of the main visible absorption band are not consistent with the MCD results. Further investigation of the MCD spectra is required to rationalize these discrepancies.

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Solvent and Temperature Dependences of the Osmocene(II)/Iodoosmocene(IV) Atom/Electron Exchange

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The rates of the atom/electron exchange process between $OsCp_2$ and $OsCp_2I^+$ as the $CF_3SO_3^-$ salt (Cp represents the cyclopentadienide anion) have been measured by ^1H NMR line broadening as a function of temperature in nine solvents. The apparent second-order rate constants at 20 °C and the activation parameters are given. The rate constant, enthalpy of activation, and entropy of activation range from 1.0×10^3 M^{-1} s^{-1}, 2.1 kcal/mol, and −38 cal/(mol K) in tetrahydrofuran-d_8 to 78.3×10^3 M^{-1} s^{-1}, 11.3 kcal/mol, and 3 cal/(mol K) in acetone-d_6. Concentration studies, varying both Os(II) and Os(IV) concentration, show that there is a significant deviation from simple second-order behavior in chloroform-d_1 and methylene-d_2 chloride. Similar behavior for the analogous reaction of $RuCp_2/RuCp_2I^+$ was attributed to ion pairing, but such an analysis cannot fully explain the results obtained here. Instead, the data conform to a rate law with parallel paths, one that is overall second order and another that is independent of $OsCp_2I^+$ and first order in $OsCp_2$. Such an analysis is also consistent with the previous results for the $RuCp_2/RuCp_2I^+$ reaction. Conductivity studies establish that ion association occurs in the low dielectric constant solvents chloroform-d_1, methylene-d_2 chloride, bromobenzene-d_5, and tetrahydrofuran-d_8. Ion-pair formation constants for $[OsCp_2I]CF_3SO_3$ in methylene chloride at 20 and 35 °C are 4.2×10^5 M^{-1} and 3.8×10^5 M^{-1}, respectively. The analogous pentamethylcyclopentadienide system does not show exchange on the time scale of the NMR experiment.

Introduction

Recently, we reported kinetic studies on the atom/electron transfer reaction between $RuCp_2$ and $RuCp_2X^+$ (X = Br, I) in various solvents.[2] This reaction type generally contrasts with simple one-electron outer-sphere electron-exchange reactions, since atom transfer (e.g. transfer of halides) is involved and mechanistically several pathways are possible. Questions such as whether zero-, one-, or a concerted two-electron transfer occurs and whether bridged intermediates such as $[RuCp_2\text{-}X\text{-}RuCp_2]^+$ are involved and, if so, what their lifetime and electron distribution are have to be asked.

Variation of halide, metal, anion, and the use of pentamethylcyclopentadienide, as well as solvent-, temperature-, pressure-, and concentration-dependence studies, may help to elucidate the reaction mechanisms. Comparisons with recent

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