The Electronic Spectrum of $Ru(bpy)_3{}^{2+}$

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Abstract: The electronic absorption spectra of $Ru(bpy)_3{}^{2+}$ in single crystals of $Zn(bpy)_3SO_4\cdot 7H_2O$ and $Zn(bpy)_3Br_2\cdot 6H_2O$ at 8 K have been measured. Analysis shows the presence of two spin-allowed transitions in the visible region, polarized perpendicular to the C_3 axis of the complex. Spin-forbidden analogues of these two transitions occur at lower energy in both σ and π polarizations. The σ intensity comes from spin-orbit coupling within the d orbitals of the Ru^{2+}, while the π intensity arises from another mechanism, probably through electron exchange between metal ion and π-bonding ligands. Fluorescence polarization measurements in a rigid glass cannot be interpreted on the basis of D_3 symmetry. A distribution of distorted geometries of the complex ion in a rigid glass can explain the results. Similarly, for an interpretation of the results of Crosby and co-workers, matrix-induced distortions of the complex have to be considered.

Introduction

The origin of the luminescence from $Ru(bpy)_3{}^{2+}$ was discussed first by Paris and Brandt.[2] Since then there have been many studies of the luminescence from this complex ion and a number of different assignments have been proposed.[3-12] The most recent model is due to Crosby and co-workers.[10-12] It treats the luminescent complex in terms of a $4d^5$ Ru^{3+} core and three bipyridine ligands, with one transferred electron in the lowest energy antibonding π^* orbital of the coupled ligands (assumed to belong to the a_2 representation of the point group D_3). It was developed to give theoretical justification to an empirical energy level scheme which Crosby and co-workers[7-9] had derived from computer fits of quantum-yield and lifetime data as a function of temperature. These data, obtained from studies in poly(methyl methacrylate) (PMM) matrices as well as in Ru^{2+}-doped single crystals of $Zn(bpy)_3SO_4\cdot 7H_2O$,[9] were well accounted for by an arbitrary level scheme which, in final form, had three levels. The computer fits provided two energy separations, three quantum yields, and three lifetimes. The levels were assigned the symmetry representations A_1, E, and A_2, in order of increasing energy, originally on the basis of degeneracy and lifetime, but subsequently incorporated in the theoretical treatment by Hipps and Crosby.[12]

In the final analysis an assignment of the luminescence spectrum must evolve from an assignment of the electronic absorption spectrum and the establishment of an energy level scheme for the excited electronic states. So far, a detailed consideration of the absorption spectrum has been avoided, for understandable reasons. The assignment of the absorption bands in the visible region to a metal to ligand charge-transfer process has not been contested, but the bands are broad and it is difficult to go beyond a descriptive $t_2 \rightarrow \pi^*$ label. The symmetry group for $Ru(bpy)_3{}^{2+}$ is D_3, which means that there are six possible excited singlet states, three of which are orbitally degenerate (^1E), associated with each electron transfer to a particular π^* orbital of bpy. In addition, there are six corresponding triplet states. Obviously, the assignment of 12 excited states, for each transfer to a π^* orbital, in a broad absorption spectrum is extremely difficult.

Although each charge-transfer configuration gives rise to 12 states, the intensities of symmetry-allowed transitions from the ground state will be widely different and only a few selected transitions will dominate the spectrum. A central issue is therefore an understanding of the mechanism of the absorption (and emission) of light in the charge-transfer region. For this, the measurement of linearly polarized spectra in single crystals is necessary. Day and Sanders[13] have shown that charge-transfer intensity between metal and ligand in a D_3 complex such as $Ru(bpy)_3{}^{2+}$ should be dominated by σ polarization. We therefore measured the absorption spectrum of $Ru(bpy)_3{}^{2+}$ in crystalline media, following the earlier work of Palmer and Piper,[14] but at temperatures down to about 5 K. However, assignments still proved to be either ambiguous or uncertain, particularly because of the unknown role of spin-orbit coupling, so that the study was enlarged to include the corresponding Fe^{2+} and Os^{2+} complexes. These data have provided a better understanding of the electronic spectrum of $Ru(bpy)_3{}^{2+}$, but a definitive assignment of all of the excited states is still not possible from these measurements alone, because of the complexity of the problem. The present paper deals with our results for $Ru(bpy)_3{}^{2+}$, while a subsequent paper deals with $Fe(bpy)_3{}^{2+}$ and $Os(bpy)_3{}^{2+}$. A preliminary account of some of our conclusions has been given recently.[15]

Although the present work cannot establish a complete delineation of the charge-transfer states, it does allow an assessment of the model used by Hipps and Crosby[12] and it focuses attention on aspects of transition mechanism which have so far been neglected. Further understanding can be expected to come from the use of MCD and CD techniques and measurements are underway.

Experimental Section

The complexes were prepared according to methods in the literature.[14,16] Single crystals of $Zn(bpy)_3SO_4\cdot 7H_2O$ and $Zn(bpy)_3Br_2\cdot 6H_2O$ containing $Ru(bpy)_3{}^{2+}$ were grown by evaporation of aqueous solutions at 45 °C. Particular care was taken to eliminate iron contaminations by repeatedly extracting the H_2O_2-containing Zn^{2+} solution with chloroform/acetylacetone. Atomic absorption spectroscopy showed the Fe contents to be less than 10^{-3} mol %. The description of the crystal morphology of the sulfate given by Palmer and Piper [14] was followed and spectra polarized parallel (π) and perpendicular (σ) to the normal to the cleavage plane were measured. For the bromide we noticed that at the concentration of Ru^{2+} we used (0.5 mol %) the crystals were not uniaxial between crossed polarizers for light propagating along the hexagonal axis. True uniaxial behavior was observed for the pure host crystal, however. Figure 1 shows the extinction directions (σ^x and σ^y) which were always the same for the three ions in the bromide crystal. This behavior was not the phenomenon, reported by Palmer and Piper,[14] of a change from a pseudohexagonal to a true hexagonal form, subsequent to the removal of the crystals from the mother liquor. In our case the anisotropy was permanent. We assume that it results from a distortion of the $Ru(bpy)_3{}^{2+}$ which removes the threefold axis. The extent of the distortion, judged from the polarized axial spectra, is temperature dependent and it is largest for the Os^{2+} and least for the Fe^{2+}.

Crystals suitable for absorption spectroscopy were selected under a low-power binocular microscope and mounted over small apertures in aluminum strips. These strips were placed in a flow tube cooled by controlled boil-off of liquid helium in the sample compartment of a Cary 17 spectrophotometer. A pair of matched Glan-Taylor prisms was used to polarize the light.

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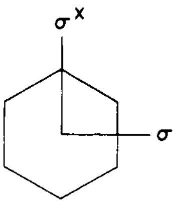

Figure 1. Extinction directions observed with crystals of $Zn(bpy)_3Br_2 \cdot 6H_2O$ containing Fe^{2+}, Ru^{2+}, and Os^{2+}. The *c* axis is normal to the paper.

Measurements of polarization of fluorescence in glassy solutions of water and ethylene glycol (1:2) were carried out with an apparatus described elsewhere.[17] Fluorescence spectra of these solutions were determined using a 1-m Spex monochromator to disperse the fluorescence, which was excited by irradiation with monochromatic light obtained using a Spex 1402 double monochromator and a high-pressure xenon lamp. The polarization ratio P is defined as $P = (I_\| - I_\perp)/(I_\| + I_\perp)$, where $I_\|$ and $I_\perp$ are the intensities of emission recorded parallel and perpendicular, respectively, to the direction of the electric vector of the exciting light.

Theoretical Considerations

Orgel[18] showed that as a consequence of the C_2 symmetry retained by the bpy in the tris complex ion, there is a difference in the interaction between metal t_2 orbitals and the two sets of ligand π orbitals, The latter are either symmetric (χ) or antisymmetric (ψ) to rotation about the C_2 axis retained by the ligand. The coordinate system used by Orgel is shown in Figure 2 and the symmetry orbitals are as follows:

$$a_1(\chi) = (\chi_a + \chi_b + \chi_c)/\sqrt{3}$$

$$e(\chi) \begin{cases} = \chi_b - \chi_c)/\sqrt{2} \\ = (2\chi_a - \chi_b - \chi_c)/\sqrt{6} \end{cases}$$

$$a_1(t_2) = (d_{xy} + d_{yz} + d_{xz})/\sqrt{3}$$

$$e(t_2) \begin{cases} = (d_{xz} - d_{yz})\sqrt{2} \\ = (2d_{xy} - d_{xz} - d_{yz})/\sqrt{6} \end{cases}$$

$$a_2(\psi) = (\psi_a + \psi_b + \psi_c)/\sqrt{3}$$

$$e(\psi) \begin{cases} = (\psi_b - \psi_c)/\sqrt{2} \\ = (2\psi_a - \psi_b - \psi_c)\sqrt{6} \end{cases}$$

The same convention was used by Day and Sanders.[13] McCaffery et al.[19] used a similar system.

For our main present purpose it is necessary to consider the interaction between the complex ion and a radiation field, leading to absorption of light. We assume that the highest filled MOs of the complex are those which are essentially localized metal ion t_2 orbitals. The lowest energy spin-allowed transitions are therefore from these orbitals into the lowest set of antibonding π^* orbitals of the ligands. We follow the approach of Day and Sanders.[13] We see immediately that only transitions from $e(t_2)$ orbitals to $e(\chi^*)$ and $e(\psi^*)$ antibonding orbitals will carry intensity and the direction of polarization will be perpendicular to the C_3 axis. There is no intensity parallel to this axis, so that, although the group theoretical selection rules allow π polarization for the transition $a_1(t_2) \rightarrow a_2(\psi^*)$, the charge-transfer intensity is zero. The π polarization can only come from other sources of intensity; i.e., it must be borrowed from internal transitions in either the metal ion or the ligands. Day and Sanders[13] showed how these can arise in general, following Murrell.[20]

Next we turn to the consideration of spin-forbidden charge-transfer bands of the complex ion. Here spin-orbit coupling must be introduced and the relevant matrix elements include the operators which transform as rotations. The general matrix elements are

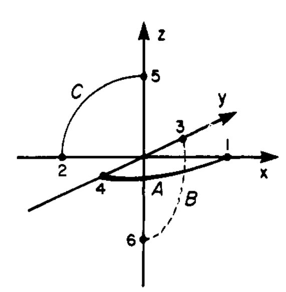

Figure 2. Coordinate system used by Orgel[18] for Ru(bpy)$_3^{2+}$

$$\langle\Psi_G|H_s|\Psi_I\rangle\langle\Psi_I|M|\Psi_F\rangle \text{ and } \langle\Psi_G|M|\Psi_I\rangle\langle\Psi_I|H_s|\Psi_F\rangle$$

where G, I, and F are the ground, intermediate, and final state functions, respectively. M is the electric dipole moment operator and H_s is the spin-orbit operator. Assuming spin-orbit coupling of the metal ion to be the important mechanism, the first term would mix d^6 with other metal ion configurations, such as d^5p. The intensity will be stolen from spin-allowed $d^5p \rightarrow d^5\pi^*$ charge-transfer transitions. These spin-orbit matrix-elements will have large energy denominators.

For the second term, the spin-orbit matrix elements mix singlet and triplet $d^5\pi^*$ configurations and the intensity will be stolen from the spin-allowed $d^6 \rightarrow d^5\pi^*$ charge transfer, in the most important pathway. Here the energy denominators will be much smaller than for the previous case and the stolen intensity correspondingly much higher. Simple analysis shows that two transitions $^1A_1 \leftrightarrow {}^3E$ can obtain intensity from $^1A_1 \leftrightarrow {}^1E$ through this mechanism, but transitions $^1A_1 \leftrightarrow {}^3A_1$ and $^1A_1 \leftrightarrow {}^3A_2$ cannot. The $^1A_1 \leftrightarrow {}^3E$ intensity stolen from the spin-allowed charge transfer will be σ polarized. There are, of course, other (less important) spin-orbit pathways which will have to be considered for optical access to or from $a_2(\psi)^*$ and $a_1(\chi^*)$, but these are too numerous and uncertain to explore at this stage. In any detailed analysis of the triplet states, spin-orbit splitting will have to be taken into account.

Results

Palmer and Piper[14] reported the room temperature absorption spectrum of Ru(bpy)$_3^{2+}$ in $Zn(bpy)_3SO_4 \cdot 7H_2O$ and stated that the intensity of the strong doublet, polarized in the σ direction, showed no temperature dependence between 80 and 300 K. Our measurements differ immediately from theirs in that we found an overall increase of about 5% of the absorption intensity on cooling the crystals. We deal with the sulfate spectrum first.

The crystal structure of $Zn(bpy)_3SO_4 \cdot 7H_2O$ has not been determined. From a comparison of unit cells and morphologies, however, there is little doubt that it is isostructural with $Ni(bpy)_3SO_4 \cdot 7.5H_2O$, the structure of which is known.[21] The Ni(bpy)$_3^{2+}$ complex has approximate D_3 symmetry. Its exact point symmetry is C_1. The pseudothreefold axis of the complex is almost perpendicular to the (001) plane in the crystal.

In taking polarized absorption spectra of the sulfate crystals, particular care must be taken with the orientation of the crystal in relation to the incident light; otherwise incorrect and misleading polarization results can easily be obtained. It is essential that the incident light propagation direction be parallel to the (001) plane, as given by Palmer and Piper.[14] Our arrangement, with the crystal in a flow tube, allowed easy rotation of the crystal about the vertical axis (mounted appropriately) so that the correct alignment was determined by taking a series of spectra to minimize the π-polarized absorption intensity. After this had been done, it was found that the anisotropy of the σ- and π-polarized bands is essentially complete at about 10 K.

Figure 3 shows the 8 K absorption spectrum of Ru(bpy)$_3^{2+}$

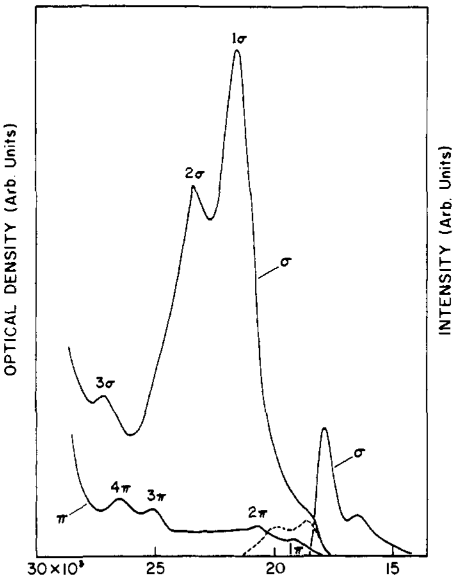

Figure 3. Absorption spectrum at 8 K of $Ru(bpy)_3^{2+}$ in $Zn(bpy)_3SO_4 \cdot 7H_2O$. For σ and π (⊥ and ∥ to the complex C_3 axis, respectively) see text. The σ-polarized fluorescence at 8 K is shown at the right.

Table I. Band Maxima in the Spectrum of Ru^{2+} in $Zn(bpy)_3SO_4 \cdot 7H_2O$ at 8 K

band[a]	max, cm^{-1}	band[a]	max, cm^{-1}
		1π	19 180
1σ	21 550	2π	20 650
2σ	23 360	3π	25 125
3σ	27 100	4π	26 550

[a] See Figure 3.

in the sulfate, polarized according to the definition of Palmer and Piper.[14] The wavenumber positions of the bands indicated by the numbers are given in Table I. Although we do not deal with the fluorescence spectrum in detail here, the 8 K σ-polarized fluorescence spectrum is included in Figure 3. The fluorescence is strongly polarized in the σ direction at all temperatures (5–300 K) used in the present work. The π-polarized fluorescence is identical with the σ fluorescence and is no doubt due to internal scattering from edges, inclusions, and surfaces. Quantitative information about polarization will have to await a more detailed study.

The majority of the bromide crystals, $Ru(bpy)_3Br_2 \cdot 6H_2O$, grow as thin plates normal to the *c* axis, so that axial spectra are easily obtained. However, twinning about the *c* axis was extremely common in our crystals. Twinned crystals cannot be used to measure the anisotropy of the axial absorption and care must be taken in the selection of a suitable specimen. The polarized 8 K axial (σ^x and σ^y) spectrum of a single crystal is shown in Figure 4 and the wavenumber positions of the bands are given in Table II.

A small fraction of the bromide crystals grew with a prismatic habit, large enough to determine the π-polarized spectrum (Figures 4 and 5). These crystals are too thick to measure the σ spectrum, other than the absorption edge, so that the relative σ and π intensities in Figure 4 are not from the same crystal, but estimated from the band edge region.

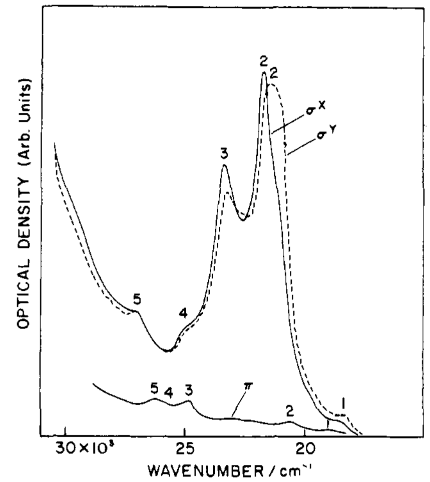

Figure 4. Absorption spectrum of $Ru(byp)_3^{2+}$ at 8 K in $Zn(bpy)_3Br_2 \cdot 6H_2O$. σ^x and σ^y refer to the (axial) polarization directions shown in Figure 1. The π spectrum is for light propagating perpendicular to the *c* axis, polarized parallel to this axis.

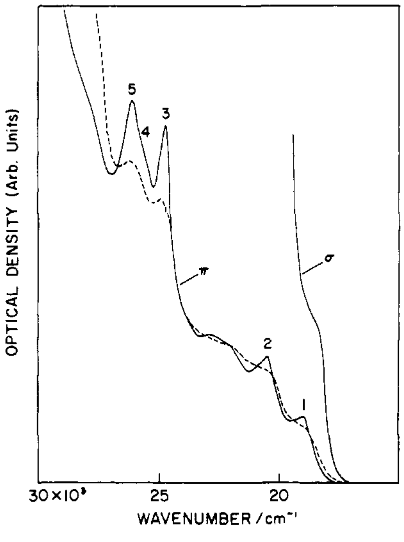

Figure 5. Absorption spectrum of $Ru(bpy)_3^{2+}$ in $Zn(bpy)_3Br_2 \cdot 6H_2O$. The full curves are σ and π spectra taken at 8 K and the broken curve is the π spectrum at 300 K.

Table II. Band Maxima in the Spectrum of Ru^{2+} in $Zn(bpy)_3Br_2 \cdot 6H_2O$ at 8 K

band[a]	max, cm^{-1}	band[a]	max, cm^{-1}
$1\sigma^x$	18 580		
$1\sigma^y$	18 350		
$2\sigma^x$	21 650	1π	18 950
$2\sigma^y$	21 200	2π	20 450
$3\sigma^x$	23 300	3π	24 760
$3\sigma^y$	23 180	4π (sh)	25 600
$4\sigma^{x,y}$ (sh)	24 800	5π	26 130
$5\sigma^{x,y}$	27 000		

[a] See Figure 4.

There are some features which should be noted. First, the π spectrum in the bromide crystal is displaced by a small but definite amount to lower energy compared with the spectrum in the sulfate crystal. Second, the two intense σ-polarized bands are split in the bromide crystal spectrum. Third, all of the bands increase their intensity on cooling, but they do not show the same temperature dependence of wavenumber position. In particular, the π-polarized bands 3–5 move to lower energy on cooling (Figure 5) in contrast to bands 1 and 2, which shift slightly to higher energy on cooling. Exactly analogous temperature behavior of the band positions in the π polarization was found for the corresponding spectra of the complexes of Fe^{2+} and Os^{2+}.[15]

Measurements of the polarization of the fluorescence from $Ru(bpy)_3^{2+}$ in a rigid glass were made by Fujita and Kobay-

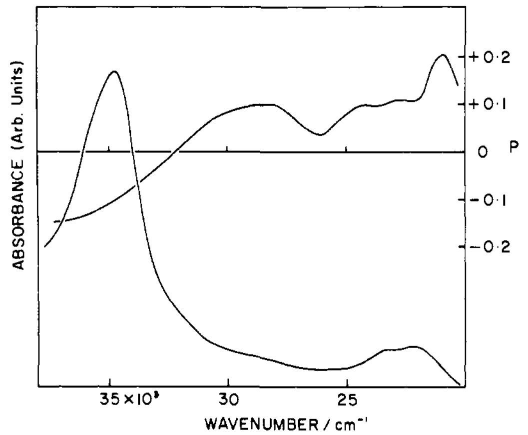

Figure 6. Polarization ratio ($P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$) measured in water and ethylene glycol (1:2) at 203 K. A RCA C31034 photomultiplier observed the total emitted light in a direction 90° to the polarized incident (exciting) light. The room temperature absorption spectrum is shown for reference.

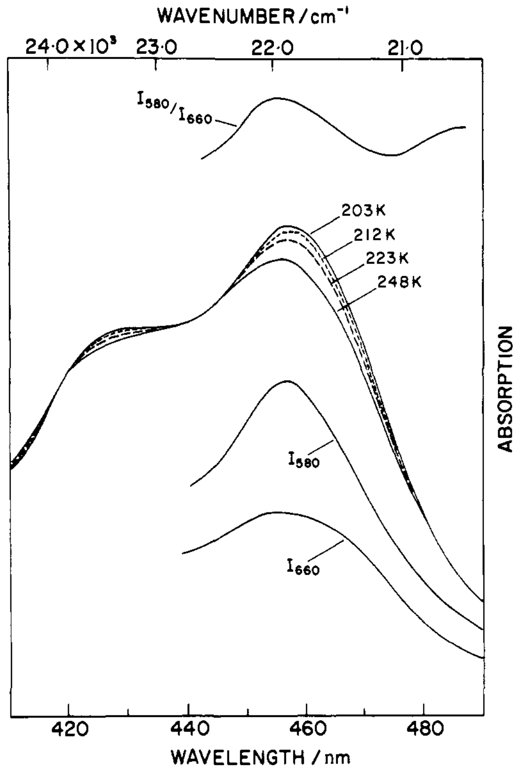

Figure 7. Absorption spectrum of $Ru(bpy)_3{}^{2+}$ in water and ethylene glycol (1:2) at 248, 223, 212, and 203 K. Excitation spectra at 105 K detected at 580 (I_{580}) and 660 nm (I_{660}). The ratio I_{580}/I_{660} is shown at the top of the figure.

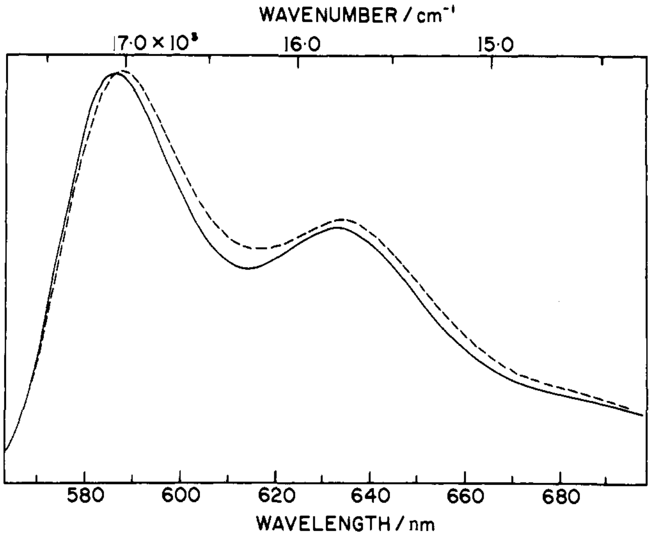

Figure 8. Fluorescence spectra of $Ru(bpy)_3{}^{2+}$ in water and ethylene glycol (1:2) at 105 K. The full curve was obtained by excitation at 456 nm and the broken curve by excitation at 476 nm.

ashi.[22] They found that the polarization ratio P exceeded $+1/7$ for excitation in the region near 21 000 cm^{-1}, but elsewhere P was found to lie between 0 and $+1/7$. The luminescence was therefore interpreted as mainly due to a planar oscillator ($\perp$ to C_3) but some emission was assumed to come from a linear oscillator ($\parallel$ to C_3) to account for the higher value of P near 21 000 cm^{-1}. If this is the case, then we should expect to find correspondingly high values of P wherever there is π polarization in the absorption spectrum. There is a π-polarized band near 21 000 cm^{-1}, but there is also π polarization in the bands in the region 25 000–27 000 cm^{-1} and yet Fujita and Kobayashi[22] observed a minimum value of P in this region. Their interpretation of the high value of P near 21 000 cm^{-1} is therefore open to question and this prompted a reinvestigation of the fluorescence polarization experiments. The results are shown in Figure 6 and they agree well with those of Fujita and Kobayashi[22] in the region of overlap. Our measurements, however, were extended further into the ultraviolet region and they revealed a negative P throughout the π–π^* absorption band at 35 000 cm^{-1}, which is quite inconsistent with the assignment to a planar oscillator in a complex with D_3 symmetry.

Negative values of P imply a loss of the C_3 axis of symmetry and the involvement of linear oscillators. However, the observed values of P do not reach either $+1/2$ or $-1/3$, the maximum and minimum values theoretically possible. A likely explanation is a distribution of molecular geometries dependent on the inhomogeneities inherent in a glassy matrix. Evidence in favor of this explanation was obtained from measurements of the absorption spectrum in water and ethylene glycol at temperatures above 203 K. These showed that, as the solvent viscosity increases, the intensity of the charge-transfer band increases in an asymmetric way, as shown in Figure 7. In addition, although excitation spectra measured at long and short wavelengths of the fluorescence spectrum have the same intensity distribution in fluid solution, they become different as the viscosity increases. This is shown by the two excitation spectra included in Figure 7, one for detection at 580 nm, the other for detection at 660 nm. The ratio of the two excitation spectra is also included in the top of Figure 7. It shows that long-wavelength fluorescence is enhanced by the irradiation near 21 100 cm^{-1} (476 nm), while the short-wavelength fluorescence is favored by irradiation near 22 000 cm^{-1} (456 nm). Finally, measurement of the fluorescence spectra for irradiation at 456 and 476 nm revealed a small shift of the fluorescence intensity distribution, consistent with the excitation spectral measurements, as shown in Figure 8. We conclude, therefore, that, as the glassy solvent matrix gives rise to asymmetries and shifts in the absorption and fluorescence spectra, it is very likely that there is a distribution of molecular geometries of $Ru(bpy)_3{}^{2+}$ in a rigid matrix.

Analysis

The main intensity of the absorption spectrum lies in the two σ-polarized bands (1σ and 2σ, Figure 3) separated by about 1800 cm^{-1}. It might be assumed at first sight that the higher energy band is a vibrational satellite of the more intense lower energy band, However, there are considerations which argue in favor of an assignment to two separate excited electronic states. One of these comes from a comparison with the analogous spectra of $Fe(bpy)_3{}^{2+}$ and $Os(bpy)_3{}^{2+}$ for which similar doublets of σ-polarized bands are observed.[15] The wavenumber separation between the doublets increases from Fe^{2+} to Os^{2+}, whereas the separation should remain approximately the same if the structure has a vibronic origin. We therefore take the step of assigning each of the σ-polarized bands to different ^1E electronic states of the complex ion, i.e., those derived from a transfer of a t_2 electron to ψ^* and χ^* antibonding orbitals of bpy. In support of this assignment we note the different splitting of the two bands (2σ and 3σ in Figure 4) in the bromide host crystal.

A similar behavior is observed in the corresponding Fe^{2+} and Os^{2+} complexes.[15] It is most pronounced in the Os^{2+} spectrum, where the distortion appears to be largest. If the bands 2σ and 3σ (Figure 4) derived from the same excited electronic configuration, similar splittings would be expected upon distortion.

The remaining spectral features cannot be analyzed unambiguously using the data for $Ru(bpy)_3{}^{2+}$ alone and the systematic relationships evident in the spectra of the corresponding Fe^{2+} and Os^{2+} complexes are required to reach a satisfactory conclusion. We concentrate first on the lowest energy σ- and π-polarized bands between 18 000 and 19 000 cm^{-1} (Figures 3 and 4).

The spectrum of the sulfate crystal shows a π-polarized band (1π) at 19 180 cm^{-1} and a more intense σ shoulder at about 18 600 cm^{-1} (see Figure 3 for estimated band shapes). These weak bands occur at almost exactly the same energies as the strong visible bands of $Fe(bpy)_3{}^{2+}$.[14,15] The possibility, however, that they are due to iron contamination can be positively ruled out, since this intensity would correspond to an iron content of about 0.05 mol %, in contradiction to analytical results (cf. Experimental Section). In the corresponding Fe^{2+} and Os^{2+} spectra there are analogous σ- and π-polarized bands. The intensity of the σ absorption increases, relative to the π band, from Fe^{2+} to Os^{2+}, the order of increasing spin-orbit coupling constant. For the σ absorption we estimated the following oscillator strengths from the bromide spectra: Fe^{2+}, $f = 2 \times 10^{-4}$; Ru^{2+}, $f = 1 \times 10^{-3}$; Os^{2+}, $f = 9 \times 10^{-3}$. These values were not obtained from elemental analysis, which is not possible for individual crystals. They were obtained by first equating the room temperature maximum optical density of the intense charge transfer to the solution molar extinction coefficient maximum value, with allowance for the anisotropic distribution of the chromophores in the crystal. The oscillator strengths are therefore good to about 20%. Values of the spin-orbit coupling constants are not well established. From Griffith,[23] we obtain values of 410 cm^{-1} for Fe^{2+} and 990 cm^{-1} for Ru^{2+} and we estimate that a value of 3000 cm^{-1} would not be unrealistic for Os^{2+}. Within these limitations we see that the observed intensities are proportional to the squares of the spin-orbit coupling constants. In both the Ru^{2+} and Os^{2+} complexes the luminescence occurs from this region of the spectrum (see Figure 3). For $Ru(bpy)_3{}^{2+}$ the observed lifetime[24] is of the same order as the lifetime estimated (~2 μs) from the integrated absorption intensity of the σ-polarized absorption (broken line in Figure 3). We examine the possibility that it corresponds to the charge transfer triplet states.

According to earlier theoretical considerations, the most important spin-orbital coupling mechanism will couple the ^3E states to the two ^1E charge-transfer states, but $^3A_1$ and $^3A_2$ states cannot obtain intensity this way. The σ intensity appears to arise from this mechanism, in view of the systematic increase from Fe^{2+} to Os^{2+}. We note (Figure 4) that the polarized axial spectrum of the bromide crystal shows two maxima at different positions (σ^x and σ^y), analogous to the intense spin-allowed charge-transfer bands (orbital symmetry E). This is good evidence that this triplet state is also orbitally degenerate, consistent with the assignment to ^3E. Another ^3E state lies probably about 1500 cm^{-1} higher in energy (see Figure 3 for estimated band contours). The luminescence appears to be associated with the lower of the states, because of the strong σ polarization easily observed, even at room temperature.

So far we have dealt with the assignment of the σ-polarized spectrum and our analysis provides an interpretation which accounts for the linear polarization properties. Apart from the π-polarized absorption near 21 000 cm^{-1}, which we have assigned to an $^1A_2$ state of the spin-allowed charge transfer to the ψ^* orbital, the remainder of the spectrum requires a different interpretation. The marked difference in the temperature shift of the π bands indicates a difference in orbital characteristics. The group in the region 25 000–26 000 cm^{-1} (Figure 5) moves to lower energy on cooling, in contrast to the lower energy bands which move slightly to higher energy. All bands increase their intensity on cooling, which indicates an intensity mechanism dependent on orbital overlap between metal ion and ligands.

As mentioned earlier, the intensities of the π absorption bands do not increase from Fe^{2+} to Os^{2+} in the same proportion as for the σ-polarized absorption associated with the ^3E states. There is an increase by a smaller amount; e.g., the lowest energy π band increases from Fe^{2+} ($\epsilon \approx 300$) to Ru^{2+} ($\epsilon \approx 600$) to Os^{2+} ($\epsilon \approx 1200$). The intensity is therefore not dependent on a metal ion spin-orbit coupling matrix element and another path to get around the spin prohibition must be involved. This must be by way of electron exchange between the metal ion and the bpy, analogous to heavy-atom effects on the singlet-triplet transitions in aromatic molecules. McGlynn et al.[25] have given an extensive discussion of these effects (see aslo Dijkgraaf and Hoijtink[26]). It is beyond the scope of the present work to give a quantitative analysis of the exchange effects in $Ru(bpy)_3{}^{2+}$; indeed all discussions in the literature are qualitative, so we restrict the discussion to qualitative considerations. Two types of exchange effects can be envisaged. In one, the intensity of a singlet-triplet transition, localized in bpy, is enhanced through stealing intensity from allowed internal transitions of the Ru^{2+}. The latter could be d to p transitions. In the other, the intensity of a singlet to triplet charge-transfer transition is enhanced by stealing intensity from an internal transition, singlet to singlet, localized in the bpy. The π spectrum can be qualitatively interpreted on the basis of these two effects.

The band group near 25 000 cm^{-1}, prominent in the π spectrum, is assigned to the lowest triplet state of the bpy in the Ru^{2+} complex. Based on the known triplet emission of $Ir(bpy)_3{}^{3+}$,[27] the lowest triplet state of bpy in $Ru(bpy)_3{}^{2+}$ is expected around 22 000 cm^{-1}, but the actual position will depend on the interaction between metal ion and ligand, just as the positions of the singlet states vary from one ion to another. We note, in passing, that the positions of the lowest triplet states of the bpy ligand in the spectra of the Fe, Ru, and Os tris(bpy) complexes show a linear relation with the $M(bpy)^{3+/2+}$ reduction potentials. The observed shift to lower energy on cooling is typical of internal π-π^* transitions of aromatic molecules. The increase of intensity on cooling is a result of increased overlap at low temperature. As the intensity is stolen from metal-localized transitions (probably d to p) there is no chirality associated with the electronic transition. The small CD observed in that spectral range[15] must be mainly due to the underlying sideband of the intense CT transition (ψ^*).

Discussion

Our assignments are in agreement with earlier conclusions on the basis of MCD measurements on related tris(phenanthroline) complexes.[28]

Recently Mayoh and Day[29] have given theoretical calculations of the hypothetical Ru(bpy)$^{2+}$ mono complex. On that basis they have made assignments of charge-transfer transitions in the tris complex. The two bands near 18 800 (weak) and 21 500 cm^{-1} (strong) were assigned to spin-allowed transitions. The first transition, according to these calculations, has its moment directed along the long bpy axis, the intensity being stolen from the allowed long axis polarized transition of the ligand. In the tris complex, therefore, the 18 800-cm^{-1} band should have its intensity distributed 2:1 ($\pi;\sigma$). Our polarized single crystal absorption experiments do not support this assignment, because $\sigma > \pi$.

We now compare our results with the energy-level scheme devised by Crosby and co-workers,[7-12] in particular Hipps and Crosby.[12] These authors focused their attention on the low-energy, weak absorption band near 19 000 cm^{-1} (cf. Figure 3). It was assigned to a transition from $a_1(t_2)$ to $a_2(\pi^*)$, split by spin-orbit interaction into three states of symmetry A_1, E, and A_2. The important feature of this model is that all three states correlate with the *orbital singlet* of the metal ion and the *orbital singlet* of the ligands, whereas we have shown that the intensity of the bands near 19 000 cm^{-1} is derived by spin-orbit interaction from the spin-allowed transitions to the ^{1}E states and therefore they must be ^3E *states*.

Crosby et al.[7-12] have offered no discussion of an absorption or emission transition mechanism and it is not clear how the optical transitions would occur. The order of states derived from the computer fitting analysis is $A_1 < E < A_2$, with 10.1 cm^{-1} between A_1 and E and 61.2 cm^{-1} between A_1 and A_2. Experimentally, we observed a σ-polarized degenerate state about 600 cm^{-1} below a π-polarized state (1π and 1σ in Figures 3 and 4). The overlap between absorption and fluorescence spectra shows that the same states ($^1A_1$ and ^{3}E) are involved in both processes. It is possible that an undetected $^3A_1$ lies lowest in energy, but not far below ^{3}E. However, we observed no fluorescence polarization change down to about 5 K.

Our results so far provide no information about the possible spin-orbit structure of the lowest observable state (^{3}E). They do, however, show that departure from D_3 symmetry brings a splitting of the band, so that it seems likely that orbital, rather than spin-orbital, factors are still very important for the description of this state. The splitting of $1\sigma^x$ and $1\sigma^y$ in the bromide crystal spectra is of the order of 300 cm^{-1} (Figure 4). There is no orbital degeneracy in the lowest set of states according to the model of Crosby and Hipps,[12] so that a satisfactory interpretation of the σ^x and σ^y spectra in the bromide crystal is difficult to make with their model. On the other hand, a satisfactory explanation of the decay-time and quantum-yield data must be found; otherwise our approach is questionable, although we have not, as yet, carried out a study of the characteristics of the fluorescence in the two crystalline hosts. For the present, our comments are based on literature comparisons. First, we note that the luminescence data for Ru(bpy)$_3^{2+}$ and similar complexes all show a marked increase of lifetime coupled with a decrease of quantum yield below about 50 K.

Several possible mechanisms can contribute to produce this type of behavior: (i) A $^3A_1$ state may lie just below ^{3}E. Electric dipole transitions from $^3A_1$ to the ground state are strongly forbidden. (ii) The symmetry of the complex is lower than D_3, both in crystalline hosts and in glassy matrices. (iii) Spin-orbit splittings of ^{3}E may exist.

We know from our crystal absorption studies that the ^{3}E is orbitally split in the bromide crystal, so that a similar possibility must be kept in mind for other hosts. In support of a matrix effect, we note that the emission spectrum for the poly(methyl methacrylate) (PMM) matrix has an intensity distribution and wavelength position different from spectra in other glassy solvents.[10] In addition, there is a pronounced change of intensity distribution in cooling the matrix from 77 to 4.2 K. This behavior could very well be a consequence of a matrix-induced orbital splitting of the ^{3}E state. The empirical model has enough parameters to allow a computer fit of the data to be obtained, but the assumption of D_3 symmetry could be the weak point in the translation of the parameters into an energy-level scheme for the complex ion. Similar matrix distortions could also occur with other tris complex ions.

Strong experimental evidence to support our suggestion that matrix-induced distortions of the complex must not be neglected in the interpretation of the phenomena reported by Crosby et al.[7-12] comes from our results in Figures 7 and 8. In Figure 7 we note that I_{580}/I_{660} reaches a minimum near 476 nm and a maximum near 456 nm. The former wavelength coincides with that of the maximum value of P (Figure 6), while the latter coincides with the absorption band maximum (Figure 7). Furthermore, the fluorescence spectrum excited by 476 nm is shifted to lower energy compared to that excited by 456 nm.

Recent work[30] has shown that a change of symmetry from D_3 to C_2, obtained by using electron-withdrawing substituents in one of the three bpy ligands, has a greater effect on the lower energy spin-allowed charge-transfer band at 22 000 cm^{-1} than for the higher energy band at 23 800 cm^{-1}. In every case, a shift to lower energy was observed. It is likely that a matrix-induced distortion of the complex ion will lead to a shift of the lower energy band to lower energy. In Figure 7 we see that cooling of the solution to form a rigid glass leads to an increase of the absorption band intensity in an asymmetric way, being greater on the low-energy side. We therefore associate the absorption by distorted complex ions to this spectral region. The fluorescence will then be due to a linear oscillator (C_2 or lower symmetry) and the value of $P > +{}^1\!/_7$ can be understood. It will also lie in a direction which is perpendicular to C_3 in the undistorted complex, because the direction must be metal to ligand, so that absorption polarized parallel to C_3 will have a negative P. The π-π^* transition at 35 000 cm^{-1} arises from a coupling of long axis polarized transitions in each ligand so that P will be negative as is observed. An analogous explanation for the dip in the P values near the π-polarized absorption in the region 25 000-27 000 cm^{-1} also follows.

Next we note (Figure 8) that the fluorescence is shifted to lower energy with increasing distortion. Also, there is an increase in intensity of the first vibrational peak, near 635 nm, with increasing distortion. If we examine Figure 5 of Hager and Crosby[10] we see similar intensity shifts in going from 77 to 4.2 K, which suggest that lowering of the temperature leads to a greater distortion of the complex.

Some comment on the reason for the distortion of the complex ion in a rigid matrix is necessary. The distortions might not be simply due to inhomogeneities in the solvent. They might involve, more directly, the influence of the negatively charged anions providing an asymmetric electric field which alters the energy of the charge-transfer transitions. The low symmetry distortion might also involve different angular twists of the two halves of the bpy ligands as occurring in the structure of the nickel complex.[21]

The present work, although not arriving at a definitive energy-level scheme, does establish that the charge-transfer bands can be classified into spin-allowed and spin-forbidden transitions and the majority of the intensity of the latter derives from a spin-orbit coupling mechanism. The charge-transfer mechanism ensures that for a given charge-transfer configuration only one spin-allowed transition carries much intensity and the polarization lies in the direction metal to ligand. The location of the other charge-transfer states, associated with the same electron configuration, will require other approaches. One such, currently under study, is the controlled removal of the D_3 symmetry by means of substituents on one of the ligands.[30] When such studies, as well as those with the analogous

Os^{2+} complexes, are available, it should be possible to estimate the role of delocalization of excitation energy in determining the level structure of the charge-transfer states.

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The Electronic Spectrum of $Fe(bpy)_3{}^{2+}$ and $Os(bpy)_3{}^{2+}$

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Abstract: The electronic absorption spectra of $Fe(bpy)_3{}^{2+}$ and $Os(bpy)_3{}^{2+}$ have been determined in single crystals of $Zn(bpy)_3SO_4{\cdot}7H_2O$ and $Zn(bpy)_3Br_2{\cdot}6H_2O$ at various temperatures down to 8 K. The main absorption intensity in the visible is assigned to two different charge-transfer transitions polarized perpendicular to the C_3 axis of the complex, consistent with the direction of charge transfer from metal to ligand. The lowest energy spin-forbidden charge-transfer bands of $Fe(bpy)_3{}^{2+}$ appear in σ and π polarization. Other π-polarized absorption, near 23 000 cm^{-1}, is assigned to perturbed singlet to triplet transitions of the bpy ligand. Owing to the much greater influence of spin-orbit coupling, the spin-forbidden transitions of $Os(bpy)_3{}^{2+}$ show significantly higher intensities and predominant σ polarization. A spin-forbidden transition to another triplet state appears in π polarization, its origin lying 75 cm^{-1} higher than the lowest σ-polarized triplet state. The mechanism for the π-polarized intensity is assumed to involve electron exchange between metal ion and ligands.

Introduction

The visible absorption spectrum of $Fe(bpy)_3{}^{2+}$ (bpy is 2,2′-bipyridine) was assigned by Williams[2] to a charge-transfer (t_2–π^*) electronic transition. The assignment was based on the interpretation of spectral band shifts observed with a number of π-bonding ligands. The majority of the absorption intensity associated with this type of transition should be polarized along the direction of metal to ligand, as shown by Day and Sanders.[3] The early work of Palmer and Piper,[4] using polarized single crystal spectra, was consistent with this expectation. The overall assignment to charge transfer is therefore firmly established. However, there are questions of detail which remain unanswered. Important among these are the number of spin-allowed transitions, the assignment of spin-forbidden transitions, and the contributions from different mechanisms to the overall absorption intensity.

The electronic spectrum of $Os(bpy)_3{}^{2+}$ appears to have been studied first by Crosby et al.,[5] at least so far as spectral assignments of both absorption and fluorescence properties are concerned. The strong absorption band system in the visible was attributed to charge transfer while the luminescence and its associated weak absorption were assigned to d–d transitions. Zuloaga and Kasha[6] argued in favor of spin-allowed charge transfer fluorescence. Demas and Crosby[7] then reached the conclusion that the luminescence bands were best ascribed to spin-forbidden charge-transfer transitions. This assignment was also made by Fujita and Kobayashi.[8]

Recently we gave a preliminary account of the polarized crystal spectra of $M(bpy)_3{}^{2+}$ (M = Fe, Ru, Os) in single crystals of $Zn(bpy)_3Br_2{\cdot}6H_2O$.[9] It was shown that answers to the questions raised above can be reached through the measurement of linearly and circularly polarized spectra of these complex ions. A previous paper dealt specifically and in detail with $Ru(bpy)_3{}^{2+}$.[10]

Experimental Section

Experimental details of sample preparation and the measurement of polarized single crystal spectra have been given previously.[4,9,10] We note again that considerable care has to be taken with the orientation of the M^{2+} doped $Zn(bpy)_3SO_4{\cdot}7H_2O$ crystal to obtain pure σ and π spectra.

CD Spectra. Poly(vinyl alcohol) (PVA) foils containing (+)-$Fe(bpy)_3{}^{2+}$ were used for the CD measurements. Since complete racemization was observed during the evaporation of a PVA solution of the resolved complex, a blanc foil was sprayed with a methanol