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Characterization of the Lowest Excited States of $[\mathrm{Rh}(\mathrm{bpy}\text{-}h_8)_n(\mathrm{bpy}\text{-}d_8)_{3-n}]^{3+}$ by Highly Resolved Emission and Excitation Spectra

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Highly resolved emission, excitation, and resonantly line-narrowed spectra, as well as emission decay properties of $[\mathrm{Rh}(\mathrm{bpy}\text{-}h_8)_n(\mathrm{bpy}\text{-}d_8)_{3-n}]^{3+}$ ($n = 0, 2, 3$; bpy = 2,2′-bipyridine) doped into $[\mathrm{Zn}(\mathrm{bpy}\text{-}h_8)_3](\mathrm{ClO_4})_2$ are presented for the first time. $[\mathrm{Rh}(\mathrm{bpy}\text{-}h_8)_3]^{3+}$ and $[\mathrm{Rh}(\mathrm{bpy}\text{-}d_8)_3]^{3+}$ exhibit one low-lying triplet T_1 at 22 757 ± 1 and 22 818 ± 1 $\mathrm{cm^{-1}}$, respectively (blue shift 61 $\mathrm{cm^{-1}}$), while $[\mathrm{Rh}(\mathrm{bpy}\text{-}h_8)_2(\mathrm{bpy}\text{-}d_8)]^{3+}$ has two low-lying triplets at 22 757 ± 1 and 22 818 ± 1 $\mathrm{cm^{-1}}$. The well-resolved vibrational satellite structures show, that the equilibrium positions of the triplet and the singlet ground S_0 state are not very different and that the force constants in T_1 are mostly slightly smaller than in S_0. Moreover, the vibrational satellite structure is strongly dominated by vibrational ligand modes, which demonstrates the $\pi\pi^*$ character of the corresponding transition. However, the occurrence of several very weak vibrational modes of metal−ligand character displays a small influence of the metal ion. This is supported by the emission decay behavior. $[\mathrm{Rh}(\mathrm{bpy}\text{-}h_8)_2(\mathrm{bpy}\text{-}d_8)]^{3+}$ exhibits an emission which is clearly assignable to the protonated ligand(s), even when the deuterated ligand is selectively excited. Obviously, an efficient intramolecular energy transfer from the deuterated to the protonated ligand(s) occurs, presumably mediated by the small $\mathrm{Rh^{3+}}$ d-admixture. A so-called “dual emission” is not observed. Moreover, a series of spectroscopic properties of the lowest excited state of $[\mathrm{Rh(bpy)_3}]^{3+}$ (energies of electronic origins, emission decay times, zero-field splittings, structures of vibrational satellites, etc.) is compared to properties of bpy, $[\mathrm{Pt(bpy)_2}]^{2+}$, $[\mathrm{Ru(bpy)_3}]^{2+}$, and $[\mathrm{Os(bpy)_3}]^{2+}$. This comparison displays in a systematic way the increasing importance of the metal d and/or MLCT character for the lowest excited states and thus provides guidelines for an experimentally based classification. In particular, the lowest excited states of $[\mathrm{Rh(bpy)_3}]^{3+}$ may be ascribed as being mainly of $^3\pi\pi^*$ character confined to one ligand in contrast to the situation found for $[\mathrm{Ru(bpy)_3}]^{2+}$ where these states are covalently delocalized over the whole complex.

1. Introduction

Transition metal complexes with organic ligands have found an increasing interest within the last decade, since these complexes exhibit an enormous potential for the discovery of new physical and chemical properties and applications. For example, supramolecular chemistry involving transition metal complexes as subunits represents an important field that is developing rapidly.[1,2] Further, photoredox processes, for solar energy conversion,[3] information storage systems,[4] laser materials,[5] and biosensors[6] have already been explored or are under current investigation. Most of the possible applications are related to properties of the lowest excited electronic states which, therefore, are intensively investigated. In addition, there is substantial scientific interest to come to a better understanding of these metal complexes with organic ligands, especially since they exhibit new electronic and vibronic properties, which are found neither in pure and well-studied organic molecules (for example, see refs 7, 8) nor in simple transition metal complexes with dd*-transitions.[9] For example, complexes with electronic states of metal-to-ligand-charge-transfer (MLCT) character, like $[\mathrm{Ru(bpy)_3}]^{2+}$[10−13] and $[\mathrm{Os(bpy)_3}]^{2+}$,[11,14,15] or complexes with a very small amount of metal-d contributions in the lowest excited states, like $\mathrm{Pd(2\text{-}thpy)_2}$ (2-thpy$^-$: ortho-C-deprotonated 2-(2-thienyl)pyridine)[16−18] and $[\mathrm{Rh(bpy)_3}]^{3+}$,[19−27] belong to such compounds. For these it is still a challenge to derive a com-

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prehensive description of their excited states' properties. It is generally agreed that the lowest excited state of $[Rh(bpy)_3]^{3+}$ can be classified as a triplet (T_1) being mainly ligand centered (LC) of $\pi\pi^*$ character, while the ground state is a singlet (S_0).[19-27] However, the metal ion Rh^{3+} with a $4d^6$ electron configuration distinctly influences these states, but its importance is not yet fully clear. For example, the zero-field splittings of T_1 are not very different from those of the uncoordinated ligands.[21-24,28] This would allow one to conclude on a relatively small d-orbital admixture. Further, from the reported occurrence of a "dual emission", corresponding to an independent emission from two different ligands in heteroleptic Rh-complexes, one would even deduce an *extremely* small metal influence on the low-energy ligand-centered T_1 state(s). This model of an independent emission has been proposed to interpret the broad emission spectra of $[Rh(bpy)_n(phen)_{3-n}]^{3+}$ ($n = 0-3$; phen = 1,10-phenanthroline).[19,25-27] On the other hand, the radiative decay rate of T_1 of the complex is by a factor of about 1000 larger than that for the uncoordinated bpy-ligand. (Compare refs 21−24 with ref 28). This clearly reveals the important influence of the metal. Therefore, an occurrence of a "dual emission" must be regarded as very doubtful, since an intramolecular energy transfer mediated by the metal would be very efficient and thus preclude such an emission property.

The information, hitherto available for $[Rh(bpy)_3]^{3+}$ is not sufficient to allow a deeper insight into the properties of the complex. Therefore, (i) it is the subject of this investigation to try to obtain highly resolved emission and excitation spectra by doping the chromophores into an inert matrix (for example, see refs 13, 15−18, 29, and 30) and by using the method of phosphorescence line-narrowing (for example, see refs 31 and 32). Indeed, the spectra obtained are by a factor of more than 100 better resolved than published previously. (ii) It is further intended to investigate a heteroleptic compound with the smallest possible distortion compared to $[Rh(bpy)_3]^{3+}$. Such a compound is represented by the partially deuterated $[Rh(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{3+}$ complex, which is investigated here for the first time. In the case that one obtains also highly resolved spectra of this compound, one can directly see whether the two different, isotopically marked ligands emit independently or not. Indeed, the answer can be given. In partially deuterated compounds only the energetically lower lying protonated ligand or ligands emit. (iii) It is also a subject of this contribution to use the information displayed in the high-resolution vibrational satellite structures of $[Rh(bpy\text{-}h_8)_n(bpy\text{-}d_8)_{3-n}]^{3+}$ (n = 0, 2, 3) with mainly ligand-centered transitions for a contrasting comparison with the vibrational satellite structures of $[Ru(bpy\text{-}h_8)_n(bpy\text{-}d_8)_{3-n}]^{2+}$ and $[Os(bpy\text{-}h_8)_n(bpy\text{-}d_8)_{3-n}]^{2+}$ ($n = 0-3$) with pronounced MLCT transitions. It can be shown that the satellite structures clearly display the differences of the strongly covalent and delocalized MLCT transitions compared to the spatially isolated LC transitions. Interestingly, this comparison, which requires the knowledge of highly resolved spectra, will also provide guidelines for classifying different types of electronic transitions or states.

2. Experimental Section

The preparation of $[Rh(bpy\text{-}h_8)_3](ClO_4)_3{\cdot}3.5H_2O$ is described in the literature.[33] The perdeuterated compound was synthesized analogously using bpy-d_8. Deuterated 2,2′-bipyridine (bpy-d_8) was prepared following the method of Cook et al.[34] and purified by vacuum sublimation. The final degree of deuteration was better than 98%, as was determined by mass spectroscopy. Infrared spectra showed intense ν(C−D) bands at 2250−2295 cm^{-1} but no ν(C−H) bands. No preferred position of deuteration occurred as was checked by recording the ^{1}H-NMR spectrum of bpy-d_8. $[Rh(bpy\text{-}h_8)_2(bpy\text{-}d_8)](ClO_4)_3{\cdot}3.5H_2O$ was prepared from cis-$[Rh(bpy\text{-}h_8)_2Cl_2]Cl$[35] and a small excess of bpy-d_8 by refluxing it (at 80 °C) in ethanol/water (1:1) for 24 h. Then it was treated with animal charcoal until a colorless solution was obtained. The solvent was distilled off, and the remaining crystalline product was washed with acetone. The chloride salt was then dissolved in aqueous solution. By adding $NaClO_4$ the solid $[Rh(bpy\text{-}h_8)_2(bpy\text{-}d_8)](ClO_4)_3{\cdot}3.5H_2O$ salt was obtained. $[Zn(bpy\text{-}h_8)_3](ClO_4)_2$ was synthesized as is previously reported.[36] Elemental analysis of C, H, and N was performed (D and H are determined simultaneously by a thermoconductrometric standard method; therefore all values for D are expressed in terms of H). Anal. Calcd for $[Rh(bpy\text{-}h_8)_3](ClO_4)_3{\cdot}3.5H_2O$: C, 38.63; H, 3.35; N, 9.01. Found: C, 38.59; H, 3.30; N, 8.97. Anal. Calcd for $[Rh(bpy\text{-}d_8)_3](ClO_4)_3{\cdot}3.5H_2O$: C, 37.65; H, 3.27; N, 8.78. Found: C, 37.63; H, 3.29; N, 8.74. Anal. Calcd for $[Rh(bpy\text{-}h_8)_2(bpy\text{-}d_8)](ClO_4)_3{\cdot}3.5H_2O$: C, 38.30; H, 3.32; N, 8.93. Found: C, 38.58; H, 3.10; N, 8.88. Anal. Calcd for $[Zn(bpy\text{-}h_8)_3](ClO_4)_2$: C, 49.18; H, 3.30; N, 11.47. Found: C, 49.07; H, 3.35; N, 11.48. The utilized substances 2,2′-bipyridine (Aldrich), $RhCl_3{\cdot}xH_2O$ (Degussa), $NaClO_4$ (Riedel-de Haen), $Zn(ClO_4)_2{\cdot}6H_2O$ (Alfa), and D_2O (Aldrich) were obtained commercially and used as purchased.

Crystals of the Rh(III) complexes doped into $[Zn(bpy\text{-}h_8)_3](ClO_4)_2$ were grown from bidistilled water/acetone (1:4) by evaporation of the solvent at room temperature. In solution the molar ratio Rh(III):Zn(II) was 0.01. The crystals were placed on a copper tongue and introduced into a helium bath cryostat (Leybold, BBK 100). For measurements at high magnetic fields a combi-cryostat (Oxford Instruments, MD 10-S 12/14/64/53) was used. Temperatures of T = 1.3 K could be achieved by pumping off the helium. For measurements of non-resonantly narrowed emission spectra the samples were excited with a nitrogen laser (λ_{exc} = 337.1 nm, Lambda Physik M 1000), while for the excitation and line-narrowed emission spectra a dye laser was applied (Lambda Physik FL 2000; line half-width 0.15 cm^{-1}). As dyes we used coumarine 120 in methanol (440−425 nm) and stibene 3 in methanol (425−415 nm), respectively. The dyes were pumped by an Nd/YAG laser (λ_{exc} = 355 nm, Spectron Laser Systems SL 800). The optical detection system is described in ref 37. The emitted light was dispersed by a double monochromator (SPEX 1401) and registered with an extended S-20 photomultiplier (RCA 7164 R) cooled to −30 °C (Joule-Thomson cooling system, B. Könnecke Messtechnik, 13355 Berlin). The multiplier signals were collected and processed by a computer-controlled photon counting system. The emission spectra were corrected for the spectral response of the detection system, while the excitation spectra were not corrected for laser intensity. The monochromator readout was calibrated with a krypton low-pressure lamp (UVP Penray) to ±1 cm^{-1}. Decay curves were registered with a fast multiscaler (minimum dwell time 5 ns/channel) combined with a multichannel data processor (CMTE 7885 TOF/MCS and MCD/PC, FAST Com Tec GmbH, 82041 Oberhaching, Germany). For the Raman measurements a Raman spectrometer (Perkin-Elmer Series 1700X FT) with a c.w. Nd/YAG laser (λ_{exc} = 1064 nm, Spectron Laser Systems) was used at powers of 100−500 mW.

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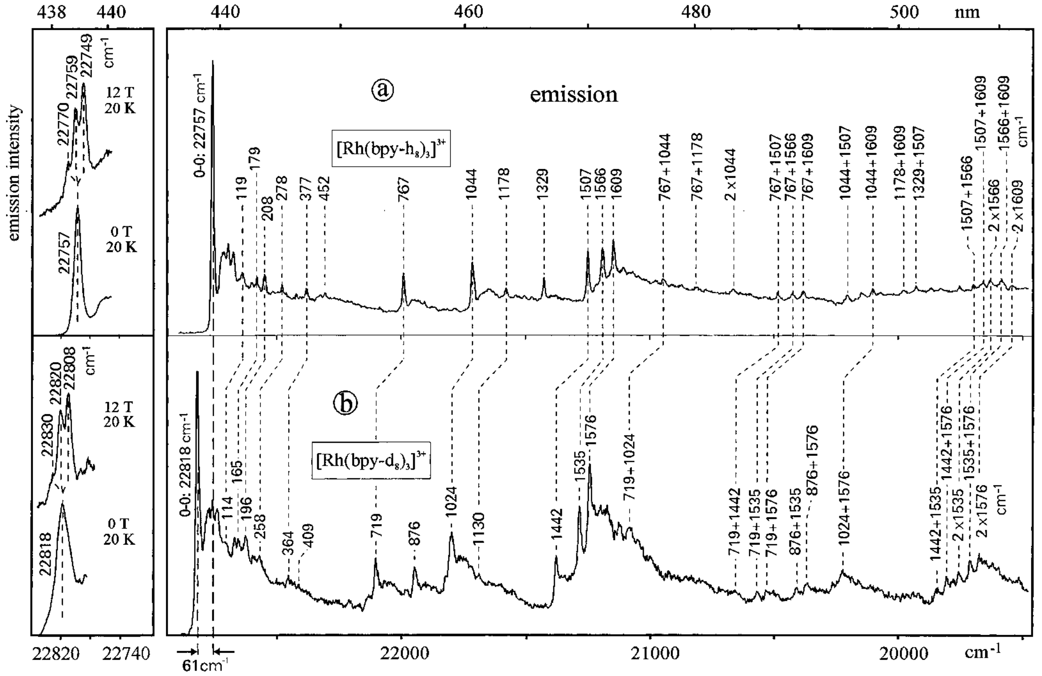

Figure 1. Emission spectra at $T = 1.3$ K of (a) $[Rh(bpy\text{-}h_8)_3]^{3+}$ and (b) $[Rh(bpy\text{-}d_8)_3]^{3+}$ doped into $[Zn(bpy\text{-}h_8)_3](ClO_4)_2$ excited at 337.1 nm. The energies of the vibrational satellites are specified relative to the corresponding electronic origin line (0−0). The emission intensities for the different compounds are not comparable. The regions of the electronic origins are shown with enlarged scales for $B = 0$ T and $B = 12$ T ($T = 20$ K).

3. Results and Discussion

3.1. Doping into Crystalline $[Zn(bpy)_3](ClO_4)_2$. Very often it is not possible to obtain highly resolved optical spectra from a neat material, since, for example, energy transfer and inhomogeneity effects broaden the spectra. Thus, the technique of doping transition metal complexes with organic ligands in suitable crystalline matrices has often been applied.[13,15,16−18,30,32,36,38−41] Indeed, this procedure is also successful for $[Rh(bpy)_3]^{3+}$ guests diluted in a crystalline $[Zn(bpy)_3](ClO_4)_2$ host. This host material is photophysically inert in the spectral region of interest. Due to the different charges of the Rh(III) and Zn(II) complexes the dopants will not symmetrically substitute the host molecules. Therefore, the site symmetries of the guests cannot be specified. Moreover, the molar concentration of 1% Rh(III):Zn(II) in solution will not necessarily occur in the doped crystals; even an aggregation of $[Rh(bpy)_3]^{3+}$ complexes, as found for $[Ru(bpy)_3]^{2+}$,[41] has to be taken into account. Nevertheless, the low-temperature spectra obtained for $[Rh(bpy)_3]^{3+}$ are by a factor of about 100 better resolved than has hitherto been published. And indeed, these spectra display the information needed for a more detailed characterization of the lowest excited states.

3.2. Electronic Origins, Triplet Sublevels, and Emission Decays. $[Rh(bpy\text{-}h_8)_3]^{3+}$ and $[Rh(bpy\text{-}d_8)_3]^{3+}$. Figure 1a shows the emission of $[Rh(bpy\text{-}h_8)_3]^{3+}$ at $T = 1.3$ K. The dominating line at 22 757 ± 1 cm^{-1} represents the peak of highest energy. It lies at the same energy as the dominating line of lowest energy in the excitation spectrum (Figure 2a). Therefore, this transition is classified as the electronic origin (0−0 line). This assignment is further supported by the very good correspondence of the energies of the vibrational satellites (relative to the 0−0 line) with the vibrational Raman energies (see below and Table 1). Equivalent arguments can also be applied to $[Rh(bpy\text{-}d_8)_3]^{3+}$. Its lowest electronic origin lies at 22 818 ± 1 cm^{-1}. (See Figures 1b and 2c.) Thus, the perdeuteration of the complex leads to a blue shift of the electronic origin of 61 ± 1 cm^{-1}. The occurrence of a blue shift shows that the vibrational force constants in the excited states are smaller than those of the ground states (for example see ref 36). For the uncoordinated bpy one finds (in a *n*-heptane Shpol'skii matrix) a deuteration-induced blue shift of 86 cm^{-1}.[42] A comparison of the two values indicates that an excitation of T_1 of the complex induces slightly smaller changes of force constants than in the uncoordinated ligand.

The electronic transitions discussed are assigned as singlet-triplet transitions ($S_0 \leftrightarrow T_1$). The corresponding zero-field splittings (zfs) are not observable with the resolution obtained. But by ODMR spectroscopy it was possible to determine these zfs for different neat $[Rh(bpy\text{-}h_8)_3]X_3$ salts (with $X^- = Cl^-$, $(BF_4)^-$, $(ClO_4)^-$).[21−24] The values for these salts deviate slightly. For example, for $[Rh(bpy\text{-}h_8)_3](ClO_4)_3$ Westra and Glasbeek[22,23] obtained zfs of 1.18 GHz ($2|E| \approx 0.04$ cm^{-1}), 2.32 GHz ($|D| - |E| \approx 0.078$ cm^{-1}), and 3.49 GHz ($|D| + |E| \approx 0.12$ cm^{-1}), respectively. As expected, a high magnetic field, of for example $B = 12$ T, leads to a large splitting of the electronic origins. For the perprotonated and the perdeuterated compound, one finds three resolvable components with a total splitting of 21 and 22 cm^{-1}, respectively. (See the origin structures of Figure 1.) These splittings correspond to $g \approx 1.9 \pm 0.1$, representing a typical value for spin triplets.

Generally, the different triplet sublevels are not in a fast thermal equilibrium at $T = 1.3$ K, since the spin−lattice relaxation is very slow at this temperature.[17,18,43,44] In this situation the sublevels emit according to their individual occupation and decay properties. Indeed, also for $[Rh(bpy\text{-}h_8)_3]^{3+}$ the emission is clearly multi-exponential and may be

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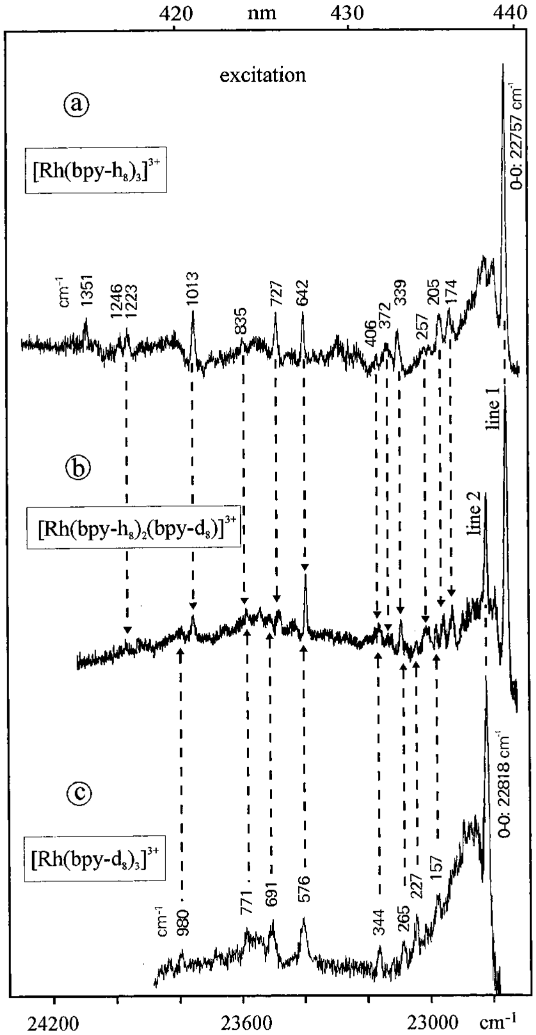

Figure 2. Excitation spectra of (a) $[Rh(bpy\text{-}h_8)_3]^{3+}$, (b) $[Rh(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{3+}$ and (c) $[Rh(bpy\text{-}d_8)_3]^{3+}$ doped into $[Zn(bpy\text{-}h_8)_3](ClO_4)_2$ at 1.3 K. The emissions of compounds a and b are detected at 21 148 cm^{-1} (1609 cm^{-1} vibrational satellite to the 22 757 cm^{-1} origin) and of c at 21 242 cm^{-1} (1576 cm^{-1} vibrational satellite to the 22 818 cm^{-1} origin). The intensities of the different spectra are not comparable.

fitted triexponentially with $\tau_I = 4.5 \pm 0.5$ ms, $\tau_{II} = 1.35 \pm 0.1$ ms, and $\tau_{III} = 0.65 \pm 0.05$ ms for $[Rh(bpy\text{-}h_8)_3]^{3+}$ and with $\tau_I = 13.6 \pm 0.5$ ms, $\tau_{II} = 1.55 \pm 0.1$ ms, and $\tau_{III} = 0.7 \pm 0.05$ ms for $[Rh(bpy\text{-}d_8)_3]^{3+}$. Interestingly, microwave-induced rapid-passage experiments with neat $[Rh(bpy\text{-}h_8)_3](ClO_4)_3$ led to lifetimes being not very different ($\tau_I = 6.7$ ms,[23] $\tau_{II} = 4.6$ ms,[23] and $\tau_{III} = 0.6$ ms,[23] compare also to ref 21). The deviations may be ascribed to the different matrices investigated. The longest component of the perdeuterated complex is by more than a factor of 3 larger than that of the perprotonated complex. This is a known effect. By deuteration, the nonradiative deactivation rates are efficiently reduced, yielding an increase of decay times.[13,15,45]

With temperature increase the spin-lattice relaxation becomes faster and finally results in a thermal equilibrium of the three sublevels often already near $T = 5$ K.[17,18,28,43,44] This leads to a monoexponential decay with an average decay time, which can be expressed by the three low-temperature values, $\tau_{av} = 3(1/\tau_I + 1/\tau_{II} + 1/\tau_{III})^{-1}$.[43] Using the values for $[Rh(bpy\text{-}h_8)_3]^{3+}$ doped into $[Zn(bpy)_3](ClO_4)_2$, one obtains $\tau_{av} = (1.2 \pm 0.1)$ ms. Indeed, at $T = 5$ K the thermal equilibration is fast and the emission decays mono-exponentially. The measured decay time of 1.4 ± 0.1 ms is in a good agreement with the calculated τ_{av}. For $[Rh(bpy\text{-}d_8)_3]^{3+}$ one finds an equivalent situation. At $T = 5$ K, the measured decay time is 1.6 ± 0.1 ms compared to $\tau_{av} = 1.4 \pm 0.1$ ms. A similar behavior has also been observed for other transition metal complexes, like Pd(2-thpy)$_2$[16−18] and Pt(qol)$_2$[46] (qol$^-$: 8-quinolinolate). For comparison, we give also the emission decay components for the uncoordinated (bpy-h_8), measured[28] at $T = 1.2$ K (4, 0.77, 0.48 s) and at $T = 12$ K (0.82 s).

$[Rh(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{3+}$. The excitation spectrum of the partially deuterated compound shows two dominating lines at 22 757 ± 1 cm^{-1} (line 1) and at 22 818 ± 1 cm^{-1} (line 2) (Figure 2b). These transitions have within limits of experimental error the same energies as the electronic origins of the perprotonated and the perdeuterated compounds. Therefore, the two lines, 1 and 2, of the partially deuterated complex are assigned to electronic origins of the protonated and the deuterated ligand(s), respectively. This assignment is further supported by the vibrational satellite structures observed in the excitation spectra (Figure 2; see also section 3.3). The energies of these satellites fit very well to a superposition of satellites of the perprotonated and of the perdeuterated complexes, when referring to the 22 757 cm^{-1} line for the vibrations of the protonated ligands and to the 22 818 cm^{-1} line for those of the deuterated ligand. Apparently, the energy of the electronic origin of an individual (coordinated) ligand does not depend on the other ligands (within limits of experimental error). Thus, this behavior is consistent with the assignment of the lowest transitions as ligand centered transitions with only very small electronic ligand−ligand coupling.

This result points to an interesting aspect. Each of the three ligands should exhibit its $S_0 \leftrightarrow T_1$ transition and further, each triplet should split into three sublevels. In the case where the intrinsic D_3 symmetry of the complex is not strongly distorted by the matrix, one expects to find the three triplets or the nine sublevels in an energy proximity. Thus, the question arises whether all these sublevels of $[Rh(bpy\text{-}h_8)_3]^{3+}$, for example, lie within the range of the half-width of about 9 cm^{-1} of the 22 757 cm^{-1} line. Indeed, this situation seems to occur as is seen by comparing the excitation spectra of the differently deuterated compounds. (Figure 2) The deuteration of *one* ligand leads to the occurrence of an additional electronic origin in the spectrum blue-shifted by 61 cm^{-1}. The intensity ratio of this "new" line (line 2) at 22 818 cm^{-1} relative to the intensity of the unshifted line (line 1) at 22 757 cm^{-1} (corresponding to the two triplets of the two protonated ligands in $[Rh(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{3+}$) is, as expected, approximately one half. (Figure 2b)

Interestingly, the emission spectrum of the partially deuterated complex displays a totally different behavior. The emission is definitely ascribed to the protonated ligand(s). This is demonstrated by comparing the resonantly excited spectra shown in Figure 3. By exciting into the lowest origins, one obtains spectra which are line-narrowed by more than a factor of 2 compared to the spectra excited at 337.1 nm. An excitation of $[Rh(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{3+}$ at the energy of the electronic origin of the protonated ligand(s) at 22 757 cm^{-1}, of the deuterated ligand (at 22 818 cm^{-1}), or at any other higher energy (for example excitation into a singlet) leads to the same vibrational satellite structure as is shown in Figure 3b (apart from an increase of the inhomogeneous line widths). It is clearly seen that the vibrational satellite structure of the emission observed for the partially deuterated complex can only be correlated to the

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Table 1. Vibrational Satellites [cm^{-1}] in the Emission from the Lowest Excited Triplet State of $[Rh(bpy\text{-}h_8)_3]^{3+}$ and $[Rh(bpy\text{-}d_8)_3]^{3+}$ Doped into $[Zn(bpy\text{-}h_8)_3](ClO_4)_3$ ($T = 1.3$ K) Compared to Raman Active Vibrations (R)[a] and Vibrational Energies of $[Pt(bpy\text{-}h_8)_2]^{2+}$ [b] (s, Strong; m, Medium; w, Weak)

$[Rh(bpy\text{-}h_8)_3]^{3+}$ 0−0 ($T_1 \rightarrow S_0$): 22 757 ± 1 cm^{-1}	$[Rh(bpy\text{-}d_8)_3]^{3+}$ 0−0 ($T_1 \rightarrow S_0$): 22 818 ± 1 cm^{-1}	assignments $[Rh(bpy\text{-}h_8)_3]^{3+}$	assignments $[Rh(bpy\text{-}d_8)_3]^{3+}$
33 m	33 m	lattice modes	
46 m	47 m	lattice modes	
62 m	60 m	lattice modes	
82 m	81 m	lattice modes	
119 m	114 m		
	150 m		
179 m	165 m	175 R, 174 (Pt)[b]	167 R
208 m	196 m		
	229 m		
242 w			
278 m	258 m	279 R	
339 w			
	341 w		
377 m	364 w	382 R, 382 (Pt)[b]	
421 w	379 w	M−L modes[c]	
439 w	395 w	M−L modes[c]	
452 w	409 w	M−L modes[c]	
	572 w		
672 w	613 w		
	690 w		
767 s	719 s	767 R, 767 (Pt)[b]	722R
800 w	753 w	767 + 33	719 + 33
829 w	777 w	767 + 62	719 + 60
849 w		767 + 82	
	844 w		
891 w	876 s		
	915 w		
	934 w		
	958 w		
980 w			
	1001 w		
1044 s	1024 s	1048 R, 1046 (Pt)[b]	1030 R
1053 m			
1077 w	1059 w	1044 + 33	1024 + 33
1104 w	1081 w	1044 + 62	1024 + 60
1125 w	1105 w	1044 + 82	1024 + 81
1178 m	1130 w	1178 (Pt)[b]	
1218 w	1205 w		
1251 w	1222 w		
1282 w	1269 w		
1329 s		1327 R, 1331 (Pt)[b]	
1363 w		1329 + 33	
1392 w		1329 + 62	
1410 w		1329 + 82	
1507 s	1442 s	1503 R, 1502 (Pt)[b]	1440 R
1535 w		2 × 767, 1535 (Pt)[b]	
1566 s	1535 s	1570 R, 1566 (Pt)[b]	1537 R
1609 s	1576 s	1600 R, 1611 (Pt)[b]	1575 R
1648 w			
1683 w			
1745 w			
1773 w			
1784 w			
1811 w	1743 w	767 + 1044	719 + 1024
	1773 w		
1848 w	1822 w		
1885 w			
	1900 w		876 + 1024
1945 w		767 + 1178	
1986 w		767 + 1218	
2088 w		2 × 1044	
2222 w		1044 + 1178	
2274 w	2161 w	767 + 1507	719 + 1442
2333 w	2254 w	767 + 1566	719 + 1535
2376 w	2295 w	767 + 1609	719 + 1576
	2411 w		876 + 1535
	2452 w		876 + 1576
2551 w		1044 + 1507	
2610 w	2559 w	1044 + 1566	1024 + 1535
2653 w	2600 w	1044 + 1609	1024 + 1576
2685 w		1178 + 1507	
2834 w		1329 + 1507	
2893 w		1329 + 1566	
2936 w		1329 + 1609	
3014 w	2884 w	2 × 1507	2 × 1442
3073 w	2977 w	1507 + 1566	1442 + 1535
3118 w	3018 w	1507 + 1609	1442 + 1576
3132 w	3070 w	2 × 1566, 3 × 1044	2 × 1535, 3 × 1024
3175 w	3111 w	1566 + 1609	1535 + 1576
3218 w	3152 w	2 × 1609	2 × 1576

[a] The Raman spectra were measured at room temperature with neat $[Rh(bpy\text{-}h_8)_3](ClO_4)_3$ and $[Rh(bpy\text{-}d_8)_3](ClO_4)_3$ compounds, respectively. [b] Vibrational energies of $[Pt(bpy\text{-}h_8)_2]^{2+}$ are taken from ref 41. [c] M−L modes = metal−ligand vibrations. All other satellites (beside the lattice modes) are assigned to ligand modes.

electronic origin at 22 757 cm^{-1} of the protonated ligand(s), while a correlation with the electronic origin of the deuterated ligand can distinctly be excluded. (See also section 3.3.) Obviously, an efficient intramolecular energy transfer occurs from the deuterated ligand to the protonated ligand(s). This precludes the appearance of an emission from the deuterated ligand and thus excludes the occurrence of a "dual emission". The intramolecular radiationless energy transfer is very probably described by the Dexter exchange mechanism[47] due to the very small spatial separations between donor and acceptor. (See also section 3.5.)

The emission decay measured at the electronic origin line of the partially deuterated complex (excited at 337.1 nm) is also triexponential at $T = 1.3$ K ($\tau_I = 6.3 \pm 0.5$ ms, $\tau_{II} = 1.4 \pm 0.1$ ms, τ_{III} 0.65 ± 0.05 ms). Interestingly, the deuteration of one ligand leads to a slightly longer τ_I decay compared to the value found for the perprotonated complex (4.5 ms), although in both complexes the emission is confined to the protonated ligands. This behavior seems to be connected with the very weak occurrence of low-energy metal−ligand (M−L) satellites, which display a vibrational coupling of different ligands. (See section 3.3.)

3.3. Vibrational Satellite Structures. The vibrational satellite structures of a molecule display a series of interesting properties of the involved electronic states. This information, however, is only accessible if highly resolved spectra are available. Fortunately, the title compounds show well-resolved and rich vibrational satellite structures in the excitation and emission spectra. These satellites are assigned to transitions into vibrational levels of the ground state (emission) and of the lowest excited states (excitation), respectively. A comparison of the vibrational ground state energies to Raman data shows a very good correspondence and thus confirms the given assignments of the electronic origins. (Table 1)

The satellites for all three title compounds investigated appearing in emission and excitation spectra up to about 100 cm^{-1} from the electronic origins, are assigned to result mainly from lattice modes (phonons). The energies of these, at least in the low-energy range, are largely determined by the $[Zn(bpy\text{-}h_8)_3](ClO_4)_2$ matrix. Thus, one partly finds the same energies also for $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ doped into this matrix.[13,15,36]

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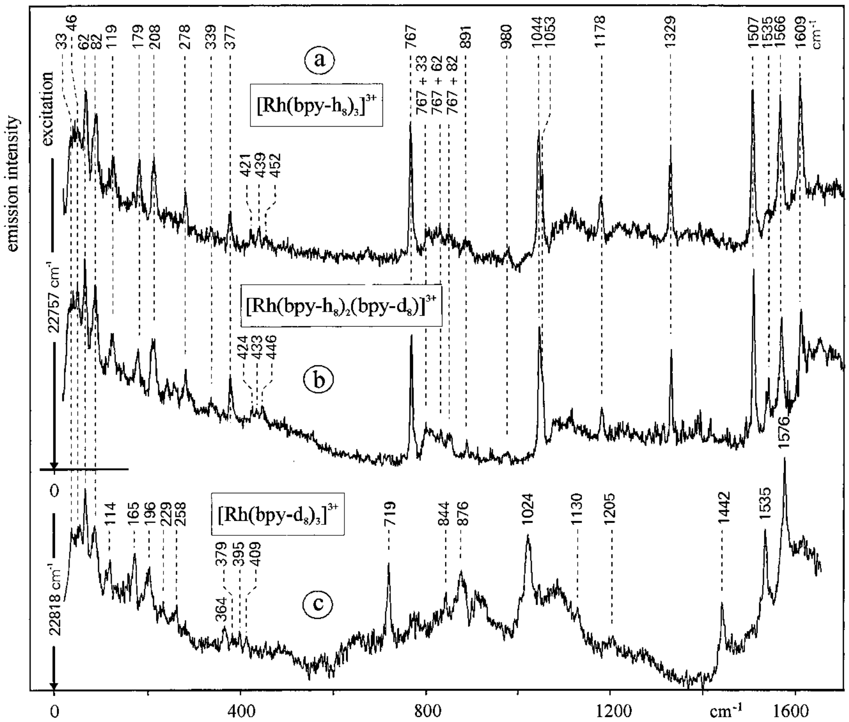

Figure 3. Resonantly line-narrowed emission spectra of (a) $[Rh(bpy\text{-}h_8)_3]^{3+}$, (b) $[Rh(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{3+}$ and (c) $[Rh(bpy\text{-}d_8)_3]^{3+}$ doped into $[Zn(bpy\text{-}h_8)_3](ClO_4)_2$ at 1.3 K. For a better comparison, the excitation energies are set to zero on a wavenumber scale. The excitation energies were 22 757 cm^{-1} for compounds a and b and 22 818 cm^{-1} for compound c. The intensities of the different spectra are not comparable.

Although a normal coordinate analysis is not yet available, important assignments can still be given. The vibrational satellite structure is distinctly determined by ligand modes, beside the phonon satellites and some very weak satellites of metal−ligand (M−L) character. This is concluded from the fact that $[Pt(bpy\text{-}h_8)_2]^{2+}$, where the lowest electronic states are also of $^3LC\text{-}\pi\pi^*$ character, exhibits a very similar vibrational satellite structure like $[Rh(bpy\text{-}h_8)_3]^{3+}$ with respect to the energies and even the intensity distribution[41] (Table 1). A comparison with the vibrational energies of the uncoordinated bpy is not successful, since by coordination to the metal these energies are strongly altered.

The satellite structures of the emission spectra of the perprotonated and the partially deuterated compounds are nearly identical, with the exception of very weak satellites between 421 and 452 cm^{-1}, which are well-resolvable in the line-narrowed spectra. (Figure 3) These modes are slightly shifted upon deuteration of that ligand, which is not involved in the lowest electronic transition. Apparently, the increasing reduced masses are responsible for these shifts. Such a behavior is expected for M−L modes, which are determined by the metal and the three ligands. This assignment is supported by the fact that other modes of lower and higher energy, which are not of M−L character, are not shifted according to a deuteration of the electronically noninvolved ligand. The very weak occurrence of M−L modes displays the very weak metal contribution to the electronic wave function(s) of the involved state(s).[13,41,48]

The vibrational satellite structue of the perdeuterated complex exhibits drastic changes with respect to the other title compounds, since the emission from the deuterated ligands shows all the effects which are usually observed upon deuteration of the emitting centers.[13,15,36,45] In particular, (i) all vibrational energies (except phonons) are red shifted. (Figure 1) (ii) The intensity distribution of the vibrational satellite structure is partly changed due to alterations of the forms (PED's) of the normal coordinates[49] (see the 876 cm^{-1} region of Figure 1) (iii) The emission lifetime increases, and (iv) the electronic transitions are blue shifted (section 3.2.).

It is an interesting result that the vibrational satellite structures do not show any dominating vibrational Franck−Condon (FC) progression as might be deduced from the less well resolved spectra, hitherto published (for example, see refs 19, 20, 24, and 25). However, the emission spectra reveal that for some prominent vibrational modes one finds 0−1 and also 0−2 members of weak progressions. For example, the corresponding fundamentals are found at 1044, 1566, and 1609 cm^{-1} for the perprotonated complex and at 1442, 1535, and 1576 cm^{-1} for the perdeuterated complex. (Figure 1, Table 1) The intensity distributions of these weak progressions may be used to determine the corresponding Huang−Rhys factor *S*. *S* describes the shift of the nuclear equilibrium positions (of the potential hypersurfaces) between ground and excited states for that specific vibrational mode and may be used to determine the corresponding Franck−Condon factor.[31,50]

These progression-forming FC modes are generally (with the exception of Jahn−Teller active modes) totally symmetric (for example see ref 51). For all progressions observed for the title compounds one obtains $S \approx 0.3$, using the expression $S = v\,(I_v/I_{v-1})$, with I_v being the intensity of one member of a specific progression and v the vibrational quantum number.[52] Nearly the same value of 0.3 has also been found for the uncoordinated bpy.[42,48] Compared to the known range of *S* values observed for other compounds—values up to 10 have been reported (for

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Table 2. Comparison of Vibrational Energies (cm^{-1}) of the Ground State (S_0) and the Lowest Excited State (T_1) of $[Rh(bpy\text{-}h_8)_3]^{3+}$ and $[Rh(bpy\text{-}d_8)_3]^{3+}$ in $[Zn(bpy\text{-}h_8)_3](ClO_4)_2$

ground state (S_0) vibrational energies[a]		excited state (T_1) vibrational energies[b]	
$[Rh(bpy\text{-}h_8)_3]^{3+}$	$[Rh(bpy\text{-}d_8)_3]^{3+}$	$[Rh(bpy\text{-}h_8)_3]^{3+}$	$[Rh(bpy\text{-}d_8)_3]^{3+}$
62[c]	62[c]	62[c]	62[c]
179	165	174	157
377	364	339	
767	719	727	691
1044	1024	1013	980

[a] From emission spectra (Figure 3). [b] From excitation spectra (Figure 2). [c] Lattice mode.

example, see refs 31, 50, 52−54)—it follows that a Huang−Rhys factor of 0.3 must be regarded as being very small. This implies similar equilibrium positions of the hypersurfaces of the triplet state and the ground state for the complexes investigated.

All prominent vibrational satellites are accompanied by phonon satellites. For example, combinations of the 767 cm^{-1} mode with the 33, 62, and 82 cm^{-1} lattice modes are clearly discernible for $[Rh(bpy\text{-}h_8)_3]^{3+}$. (Figure 3a, Table 1) However, in most cases these phonon satellites are smeared out to bands. These bands are in part responsible for the unresolved background observed in the emission spectra. In particular, one finds unusual structures, when several vibrational satellites with their respective phonon side bands overlap (for example see the range of the 1507, 1566, and 1609 cm^{-1} peaks in Figure 1a). In low-resolution spectra, such a triple-structure will appear as *one* dominating peak and might be taken as one member of a fictitious progression. (See also the examples given in refs 16 and 36).

All the clearly discernible peaks in the emission spectra (Figure 1) at energies larger than about 1650 cm^{-1} are assigned to combinations of prominent vibrational modes or to members of very weak Franck−Condon progressions. (Table 1) The occurrence of combinations in the vibrational satellite structures indicates shifts along different normal coordinates (for example, see ref 54). Apparently, the intensities of the combinations are in the same order as those of the second member of progressions. Therefore, these shifts are also of minor importance.

A comparison of the excitation (Figure 2) with the emission (Figure 1) spectra allows to obtain an information about changes of vibrational energies or (indirectly) of force constants due to an excitation of T_1. For this comparison one has to identify modes which correspond to each other. However, normal coordinate analyses of ground and excited states are not available. But for the title compounds, which do not exhibit extreme changes upon excitation, one can also use the information displayed in the structures and intensity distributions of the spectra to specify a series of correlated vibrations. Such a procedure is further justified, if the obtained correlation fits also for the equivalent mode of the related perdeuterated complex. Corresponding modes are summarized in Table 2. For example, one finds that the energy of the 767 cm^{-1} ground state mode of $[Rh(bpy\text{-}h_8)_3]^{3+}$ is reduced to 727 cm^{-1} in T_1, while the energy of the equivalent mode of $[Rh(bpy\text{-}d_8)_3]^{3+}$ undergoes a shift from 719 cm^{-1} (in S_0) to 691 cm^{-1} (in T_1). These reductions of vibrational energies are not unexpected for $\pi\pi^*$ transitions and were already anticipated in section 3.2. from the value of the blue shift of the electronic transition upon deuteration by 61 cm^{-1}. (Compare with ref 36.)

The long-lived triplet sublevel (called I in section 3.2.) corresponds to a forbidden transition, and it is expected that Herzberg−Teller (HT) vibrational modes will open radiative deactivation paths. This effect should be displayed by specific vibrational satellites.[17,51,55−57] The spectral information presented in this contribution does not allow us to clearly identify HT modes. However, recent time-resolved spectra measured with a long delay time of about 3 ms seem to display HT activity for $[Rh(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{3+}$ for example, for the 545 and 746 cm^{-1} satellites to the 22 757 cm^{-1} origin (spectra not reproduced).

3.4. Comparison of Different 2,2′-Bipyridine Compounds. The discussion in the previous sections shows that the lowest excited electronic state of $[Rh(bpy)_3]^{3+}$ may largely be assigned as ^{3}LC of $\pi\pi^*$ character with a very weak ligand-ligand coupling. On the other hand, the relatively high absorption of the $S_0 \rightarrow T_1$ transition (conventional excitation spectra are measurable in contrast to organic molecules, Figure 2) and the drastic decrease of the emission lifetime by a factor of about 1000 (when compared to the uncoordinated ligand[28]) indicates that an admixture of metal character to the triplet sublevels is present and induces an increase of the spin−orbit coupling to higher lying states. In analogy to the comprehensive discussion by Azumi et al.[58,59] of $[Rh(phen)_3]^{3+}$ and related complexes it is proposed that the lowest triplet state contains small dd* and MLCT admixtures and thus may be characterized as

$$|T_1\rangle = a|\,^3\pi\pi^*\rangle + b|\,^3\mathrm{d}\pi^*\rangle + c|\,^3\mathrm{dd}^*\rangle + \text{singlet admixtures}$$
$$\text{with } a \gg b,\, c$$

The consideration of such metal contributions is very reasonable since the lowest dd* state ($^3T_1$ in O_h symmetry) is expected to lie near 25 000 cm^{-1},[60,61] thus being only about 2000 cm^{-1} higher than the emitting triplet.

At present, the amount of d-admixtures to the lowest $\pi\pi^*$ triplet cannot be calculated, but it seems to be possible to develop a classification based on experiment, which allows one to signify the importance of this admixture with respect to a series of physical properties. This can be achieved by a comparison with a number of different, already well studied transition metal complexes and with bpy itself. Such a series of trends is summarized in Table 3. There, the compounds are arranged according to an increasing importance of d-character for the lowest excited and emitting states. (1) The first row shows that the transition energies are red shifted with respect to the transition of the uncoordinated bpy. This stabilization results from the formation of the complex and from an increasing dd* and/or MLCT admixture to the lowest ^{3}LC states for $[Rh(bpy)_3]^{3+}$ and $[Pt(bpy)_2]^{2+}$, while for $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ an MLCT character becomes dominant.[10−13,15,41,48] (2) With increasing d-admixtures and spin-orbit coupling the spin selection rules are weakened. This leads to a drastic increase of allowedness of the corresponding transition and, as

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Table 3. Trends of Spectroscopic Properties for Different 2,2′-Bipyridine Compounds[a]

	properties	bpy[42] in n-heptan	$[Rh(bpy)_3]^{3+}$ [b] in $[Zn(bpy)_3](ClO_4)_2$	$[Pt(bpy)_2]^{2+}$ [41] neat $[Pt(bpy)_2](ClO_4)_2$	$[Ru(bpy)_3]^{2+}$ [13,36,41,48] in $[Zn(bpy)_3](ClO_4)_2$	$[Os(bpy)_3]^{2+}$ [15,48] in $[Zn(bpy)_3](ClO_4)_2$
1	lowest electronic transition[c] (cm^{-1})	23 504	22 757	21 237	17 684	14 223
2	emission lifetime[d] (μs)	4×10^6 [28]	4.5×10^3	50	230	22
3	zero-field splitting[e] (cm^{-1})	0.118 [28]	0.116 [22]	*f*	61	211
4	*I*(M−L vibr)/*I*(all vibr)[g] (%)	0	<0.5	2	40	60
5	Huang−Rhys factor *S*[h]	0.3	0.3	0.3	0.1	0.08
6	deuteration-induced blue shift[i] (cm^{-1})	86	61	*f*	40	32
7	characterization of the electronic transition	$^3\pi\pi^*$	^{3}LC ($\pi\pi^*$) + small dd* admixtures	^{3}LC ($\pi\pi^*$) + small MLCT admixtures[j]	^{3}MLCT ($d\pi^*$)	^{3}MLCT ($d\pi^*$)

[a] Data given for protonated compounds. [b] This work. [c] Electronic origins being mainly of triplet character. [d] Longest emission decay component at $T = 1.3$ K. [e] Total zero-field splitting of the lowest triplet state. [f] Not yet determined. [g] Ratio of the integrated intensities of vibrational satellites with an appreciable M−L character relative to the intensity of all vibrational satellites (excluding phonons). For this rough estimate only M−L modes between ≈200 and ≈550 cm^{-1} were taken into account. [h] Largest Huang−Rhys factor observed (see text). [i] Blue shift of the electronic origin upon perdeuteration. [j] For a more detailed classification see section 3.4. and ref 41.

row 2 shows, to the decrease of the lifetimes. (3) The zero-field splitting (zfs) does not seem to react very sensitively on small dd* or MLCT admixtures (row 3), since the total zfs is nearly the same for the bpy[28] and $[Rh(bpy)_3]^{3+}$.[21−24] But for MLCT states, which dominate the properties of the lowest excited states of $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$, this splitting becomes very large. (4) An increasing d-contribution to the lowest excited LC states is equivalent to a larger spread of charge density into the molecular region between the metal and the ligands. Thus, an electronic transition will induce an increasing rearrangement of charge density also in that molecular region. Since such changes determine the intensities of vibrational satellites of metal−ligand (M−L) character, one expects that a growing d-contribution leads to a larger intensity of M−L satellites in the optical spectra.[13,48] This effect should even be more significant for MLCT transitions. Indeed, this behavior is clearly displayed in row 4 in the normalized intensities of M−L satellites.

For all compounds summarized in Table 3, the nuclear equilibrium positions (of the potential hypersurfaces) are very similar for the respective ground state and the lowest excited triplet state. This is manifested by the very small value of the Huang−Rhys factor *S* (row 5) for *all* vibrational modes (section 3.3). Interestingly, this property does not react very sensitively to small MLCT or dd* admixtures, but for compounds with MLCT states, the *S* value, being already very small, is further reduced by a factor of 3−4. This means that $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ have even less different equilibrium positions of ground and excited states than $[Rh(bpy)_3]^{3+}$. Moreover, row 6 shows that the deuteration induced blue shifts of the lowest transitions become also distinctly smaller. (See section 3.2. and ref 36.) Although this value represents only an average measure, it strongly indicates that the vibrational force constants of ground and lowest excited states become increasingly similar for the compounds in the series presented. The tendencies shown in rows 5 and 6 are expected, since they simply display the increasing covalency in the series from $[Rh(bpy)_3]^{3+}$ to $[Os(bpy)_3]^{2+}$. (See also ref 48.) Finally, row 7 of Table 3 gives a rough classification of the discussed transitions. A comparison of the various properties makes it more obvious, where $[Rh(bpy)_3]^{3+}$ has to be placed in the series presented. It represents a compound with an extremely small d-admixture to the lowest triplet.

Interestingly, even this small d-admixture supplies enough electronic coupling between the different ligands in the partially deuterated Rh complex to accomplish an efficient inter-ligand energy transfer from the deuterated ligand to protonated ligands. Thus, one observes only an emission from the energetically lower lying protonated ligands. (See sections 3.2., 3.3., and 3.5.) However, this coupling between the triplets on different ligands seems to be far too small to delocalize the excitation energy in the sense of a "molecular excitation", as can be concluded from ODMR results.[22] Presumably, the coupling is much smaller than the inhomogeneous broadenings (of ≈4 cm^{-1}, Figure 3) experienced by the triplet states confined to the different ligands. In contrast, $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ exhibit a strong electronic coupling, induced by the d-orbital interactions via the metal. This leads to a covalent situation for the lowest excited MLCT states. Thus, these states have to be described as being delocalized over the metal and the different ligands.[13,15,36,48,62] (For more details see the recent review[41] where the current models are compared.) Consequently, the partially deuterated compounds, like $[Ru(bpy\text{-}h_8)_n(bpy\text{-}d_8)_{3-n}]^{2+}$ and $[Os(bpy\text{-}h_8)_n(bpy\text{-}d_8)_{3-n}]^{2+}$ (with $n = 1$, 2), show an emission which clearly involves both types of ligands,[13,15,41,48] contrary to the situation found for the corresponding Rh complexes.

3.5. Intramolecular Energy Transfer vs Dual Emission. In sections 3.2. and 3.3. it has been shown that in $[Rh(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{3+}$ only an emission from the protonated ligand or ligands is observed, even in the case where the higher lying state of the deuterated ligand is selectively excited. Thus, it is concluded that an effective intra-molecular energy transfer occurs from the deuterated ligand (donor D) to the protonated ligand(s) (acceptor A). An intramolecular energy transfer over small distances of 3−4 Å is very probably described by the Dexter exchange mechanism.[47] The alternative mechanisms of multipole interactions, in particular, the Förster mechanism,[47] are expected to be relatively unimportant due to the low oscillator strength of the singlet-triplet absorption of the acceptor.

Apparently, the energy transfer in $[Rh(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{3+}$ is fast enough to quench the emission from the deuterated ligand. Thus, we have the transfer rate $P_{D-A} \gg \pi_{III}{}^{-1}$, where $\pi_{III}{}^{-1}$ is the decay rate of the fast decaying sublevel of the donor (deuterated ligand). From section 3.2., one obtains $\pi_{III}{}^{-1} \approx 1.7 \times 10^3\ s^{-1}$. This value represents a lower limit for the energy transfer rate. Since this limit is extremely small for a resonant energy transfer, the effective rate is presumably several orders of magnitude larger. On the other hand, this estimate shows that already a very small transfer rate will quench the donor emission and thus will prevent an occurrence of a "dual emission". Obviously, these considerations are similar for $[Rh(bpy)_n(phen)_{3-n}]^{3+}$ compounds (with $n = 1$, 2) mentioned above, since the phen ligands exhibit appreciably longer lifetimes[21,58,59] than the bpy ligands. This implies that even a smaller transfer rate would be sufficient to preclude a "dual emission". However, several authors reported the occurrence

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(62) Yersin, H.; Braun, D. *Coord. Chem. Rev.* **1991**, *111*, 39.

of such a “dual emission” for $[Rh(bpy)_n(phen)_{3-n}]^{3+}$ in glassy matrices.[19,25,27] But the effects observed may be interpreted alternatively, as has already been discussed by Henderson and Imbusch[31] for Cr^{3+} ions in a glass-forming matrix and by Güdel et al.[63] for the Rh(III) complex discussed. (Compare also with ref 64.) According to these considerations, the “dual emission” could result from superpositions of spectra resulting from the same chromophores, which, however, occupy different types of sites in the matrix. For one specific type of sites the LC transitions of the phen ligands are energetically stabilized, while for the other sites (other environments) the transitions of the bpy ligands are lower in energy. In this situation, it might be difficult to interpret the spectral information correctly, especially if the spectra are not well resolved.

4. Conclusion

The low-temperature investigation of the lowest triplet states and their sublevels of $[Rh(bpy)_3]^{3+}$ by high-resolution spectroscopy (emission, excitation, line-narrowing) and by analyzing the emission decay behavior supplies a deep insight into the properties of these states. In particular, the excitation, being mainly of $^3\pi\pi^*$ character, is centered on one ligand, due to a decoupling even by weak distortions. However, in the heteroleptic $[Rh(bpy\text{-}h_8)_2(bpy\text{-}d_8)]^{3+}$, a relatively fast excitation energy transfer (in the sense of an incoherent hopping from ligand to ligand), presumably enhanced by very small dd* admixtures, prevents an occurrence of a “dual emission”. Although the three different triplet sublevels of every ligand are spectrally not resolvable the individual sublevels display their properties in the emission decay behavior. The results obtained are in agreement with ODMR investigations of other groups.[21−24]

Moreover, in this contribution an interesting classification is worked out, which allows to signify semiquantitatively the importance of metal d-character for a series of different metal-bpy compounds by comparing a number of spectroscopic properties of the lowest excited states (Table 3). In particular, this leads to a ranking of the amount of d-admixture to the lowest excited triplet state of $\pi\pi^*$-character of $[Rh(bpy)_3]^{3+}$, which is found to be very small. With increasing d-character several properties change drastically. Thus, compounds like $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$, with a very large amount of d-character in the typical MLCT states, represent very covalent situations, where the charge density is largely delocalized over the metal and the different ligands. According to this covalency, one finds for $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ even smaller changes of force constants or changes of nuclear equilibrium positions upon excitation into the lowest excited states than for $[Rh(bpy)_3]^{3+}$. The conclusions deduced from the detailed information displayed in the highly resolved spectra show that the complexes discussed exhibit somewhat different properties, than previously assumed.

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