

Emission Properties of $[\text{Ru}(\text{bpy})_3]X_2 \cdot n\text{H}_2\text{O}$ Powders

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Abstract

Emission spectra and lifetimes for $[\text{Ru}(\text{bpy})_3]X_2 \cdot n\text{H}_2\text{O}$ (with $X = \text{PF}_6, \text{ClO}_4, \text{Cl}, \text{Br}, \text{I}, \text{SCN}, \text{NO}_3, \text{BF}_4, \text{B}(\text{phenyl})_4$) are presented for the first time. The results, recorded between 300 K and 2 K, show drastic effects being connected to the counter-ion X . This paper demonstrates the importance of the second coordination sphere for the properties of the emitting $[\text{Ru}(\text{bpy})_3]^{2+}$ center.

Introduction

During the past decade $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes (bpy = 2,2'-bipyridine) have been investigated intensively. One reason for this widespread interest comes from the possibility to use this compound, at least as a model substance, in a cyclic system for solar energy conversion [1, 2]. The optical spectroscopy has been used to gain insight into the properties of $[\text{Ru}(\text{bpy})_3]^{2+}$ and related compounds [3–9]. For example, from measurements with dissolved complexes it has been concluded that the second coordination sphere (solvent sphere) strongly influences the spectroscopic behavior resulting in energetic shifts of the emission and absorption spectra or changes of emission lifetimes [5, 6, 10, 11]. Therefore, one expects that in crystalline compounds different counter-ions, which also represent a second but more defined coordination sphere, may also affect the spectroscopic properties. Since these influences have not yet been studied it is the aim of this paper to present a series of emission data for different crystalline $[\text{Ru}(\text{bpy})_3]X_2 \cdot n\text{H}_2\text{O}$ compounds.

Experimental

Salts of $[\text{Ru}(\text{bpy})_3]X_2$, with $X = \text{Cl}, \text{Br}, \text{I}, (\text{ClO}_4), (\text{SCN}), (\text{NO}_3), (\text{BF}_4), (\text{B}\phi_4; \phi = \text{phenyl}),$ and (PF_6)

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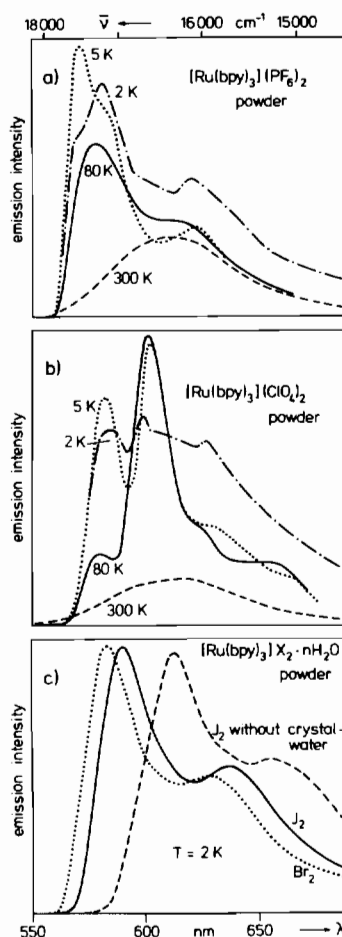


Fig. 1. Emission spectra of $[\text{Ru}(\text{bpy})_3]X_2 \cdot n\text{H}_2\text{O}$ powders. The intensities are not comparable, but see Table I.

were synthesized according to literature methods [12, 13]. The iodide salt without crystal water was prepared by dissolving $[\text{Ru}(\text{bpy})_3]\text{I}_2 \cdot 5\text{H}_2\text{O}$ in ethanol and precipitating with toluene. After drying, the emission was measured immediately to prevent the hygroscopic powder from absorbing water. Excitation of luminescence was achieved by an argon ion laser, by a Nd-YAG laser (third harmonic), or by a Hg-lamp. Details of the emission spectrophotometer are described in an earlier publication [14].

TABLE I. Emission Data of Crystalline $[\text{Ru}(\text{bpy})_3] \text{X}_2$ Powders.

$[\text{Ru}(\text{bpy})_3] \text{X}_2$ compounds	$\bar{\nu}_{\text{max}} [\text{cm}^{-1}]$				$\tau [\mu\text{s}]$ at $\bar{\nu}_{\text{max}}^{\text{a}}$	$I(\text{X})/I(\text{PF}_6)^{\text{b}}$	
	300 K	80 K	5 K	2 K		300 K	80 K
$[\](\text{PF}_6)_2$	16340	17180	17510	17180	2.8 (300 K) 5.8 (50 K) 60 (5 K) ^d 140 (1.7 K) ^d	1.0	1.1
$[\](\text{ClO}_4)_2$	16210	17330	17180	17120	0.9 (300 K)	0.3	0.9
$[\](\text{SCN})_2 \cdot n\text{H}_2\text{O}^{\text{c}}$	16560	17270	17300	17040	1.2 (300 K)	0.3	0.8
$[\]\text{Cl}_2 \cdot 6\text{H}_2\text{O}^{\text{e}}$	16340	17450	17210	16950	1.0 (300 K) 5.6 (50 K) ^d 25 (10 K) ^d	0.1	1.1
$[\]\text{Br}_2 \cdot 6\text{H}_2\text{O}^{\text{e}}$	16750	17330	17480	17180	1.1 (300 K)	0.4	1.0
$[\]\text{I}_2 \cdot 5\text{H}_2\text{O}^{\text{e}}$	16450	17090	17390	16950	1 (300 K) 5 (90 K) 90 (5 K) ^d	0.2	0.9
$[\]\text{I}_2 \cdot n\text{OH}_2\text{O}$	16390	16690		16310	0.1 (300 K) 3 (80 K)	0.02	0.6
$[\](\text{B}\phi_4)_2 \cdot n\text{H}_2\text{O}^{\text{c,e}}$	15980	16290	16260	16150	0.8 (300 K) 5.8 (80 K)	– ^e	– ^e
$[\](\text{BF}_4)_2 \cdot n\text{H}_2\text{O}^{\text{c}}$	16530	16980	16960	16710	1.1 (300 K) 4.3 (80 K)	0.5	0.8
$[\](\text{NO}_3)_2 \cdot n\text{H}_2\text{O}^{\text{c}}$	16590	17160	17310	16820	0.4 (300 K) 4.3 (80 K)	0.1	0.6
$[\]\text{Cl}_2$ dissolved in water	16340	17300	17510	17090	0.4 (300 K) 5 (80 K) 20 (5 K)	–	–

^aThe decay components partly depend on the wavelength of emission. ^bIntensity ratio, normalized to the emission intensity of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ at 300 K. ^cCrystal water content unknown. ^dOnly the longest component has been measured. ^ePhoto-activity.

Results and Discussion

$[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$, whose crystal structure is known [15], has been investigated in detail by polarized emission and absorption spectroscopy on single crystals and it was possible to assign the lowest excited states to group theoretical representations [7–9, 16]. The studies also showed that for the lowest excited states of single crystals of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ no compelling reason requires the assumption of a reduced excited-state symmetry compared to that of the ground state, in contrast to conclusions drawn for dissolved complexes [17]. The following excited and emitting states have been identified (classification in D_3): $1E'$, $2E'$ (7 cm^{-1} above $1E'$), $1A'_2$ (30 to 40 cm^{-1} above $1E'$), $3E'$ (100 to 200 cm^{-1} above $1E'$), $2A'_2$ ($\approx 800 \text{ cm}^{-1}$ above $1E'$). It was found by time-resolved and polarized emission spectroscopy that $1A'_2$ is not in thermal equilibrium with $1E'$ and $2E'$, indicating the existence of an energy barrier between the corresponding states [16].

In Fig. 1 and Table I we compare emission data for several $[\text{Ru}(\text{bpy})_3] \text{X}_2 \cdot n\text{H}_2\text{O}$ powders to those of the

PF_6 -salt. The results clearly demonstrate the importance of the counter-ion in influencing the spectroscopic properties. It is not the aim of this paper to discuss properties of every salt in detail, but we want to point out some obvious X-dependent effects.

The emission quantum yield is highest for the PF_6 -salt and shows a relatively small temperature dependence. Therefore, we normalized the different values of quantum yields to that of the PF_6 -salt at $T = 300 \text{ K}$. From Table I it is seen that these values range from 1.0 ($X = \text{PF}_6$) to 0.02 ($X = \text{I}$ without crystal water) at 300 K. An equivalent tendency is found for the emission lifetime which covers a range from 2.8 μs ($X = \text{PF}_6$) to 0.1 μs ($X = \text{I}$ without crystal water) at 300 K. With temperature reduction to 80 K the emission quantum yields come to comparable values for all salts. The corresponding lifetime data seem to follow the same trend. These properties can be understood on the basis of electronic states coupled to the environment of the emitting center, only accessible over an X-dependent activation barrier. A similar behavior has been found for dissolved complexes [5,

10]. The corresponding quenching state(s) have been assigned in [10] to a charge-transfer-to-solvent state and in [5] to a Ru-4d state. Our results suggest, in a loose analogy to [10], that a charge-transfer state connecting the bpy center to the second coordination sphere (counter-ion) is responsible for the quenching properties (compare also [18]).

Different counter-ions shift the energetic positions of the peak maxima over a range of about 10^3 cm^{-1} (Table I). Possibly these shifts are also caused by an interaction of the above mentioned counter-ion dependent charge-transfer state with the low-lying excited states of the $[\text{Ru}(\text{bpy})_3]^{2+}$ center.

Two of the investigated salts ($X = \text{PF}_6, \text{ClO}_4$) exhibit a more structured emission than do, the other ones (Fig. 1). This behaviour is connected to a characteristic energetical width of the blue side emission flank. For $X = \text{PF}_6$ and ClO_4 this width is (at $T = 5 \text{ K}$) about 250 cm^{-1} (10% to 100% height of the emission maximum) while for the other salts it is $\approx 550 \text{ cm}^{-1}$ with the exception of $X = \text{I}$ (without crystal water), for which it is as broad as $\approx 750 \text{ cm}^{-1}$. Moreover, the first two salts exhibit a well-resolved fine structure with a 2 cm^{-1} halfwidth at the blue side of the emission (the sharp emission lines lie at 17809, 17816 cm^{-1} for $X = \text{PF}_6$ and at 17605, 17614, 17663 cm^{-1} for $X = \text{ClO}_4$). In a further investigation [16] these lines were identified as zero-phonon lines. It is not unlikely that the discussed variation of flank widths is connected to different site distributions of the emitting $[\text{Ru}(\text{bpy})_3]^{2+}$ centers. These non-homogeneous broadening effects may be caused by the crystal water, having a wide variation of bonding strengths. Crystal defects and different numbers of molecules per crystal unit cell may also be responsible for a modulation of the environmental conditions which are seen by the emitting centers in the various salts. Thus, for salts with relatively large non-homogeneous effects the zero-phonon lines are hidden. Further, different strengths of the electron-phonon coupling may be responsible for the occurrence or non-occurrence of the fine structures [16].

Conclusion

The drastic influence of the second coordination sphere in crystalline $[\text{Ru}(\text{bpy})_3]X_2 \cdot n\text{H}_2\text{O}$ compounds on the spectroscopic properties cannot be ignored. However, further investigations are required to explain the studied effects in more

detail. Moreover, it might be possible that the observed symmetry reduction in the excited state(s) found by other authors is also coupled to the properties of the second coordination sphere.

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