Inorg. Chem. **1995**, *34*, 1967−1968 **1967**

Energy Transfer between Different Sites in Neat Single-Crystal $[Ru(bpy)_3](PF_6)_2$

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Received May 12, 1994

The photochemistry and photophysics of $[Ru(bpy)_3]^{2+}$ and related compounds was studied thoroughly during the last decades.[1−4] However, a comprehensive interpretation of the behavior of the lowest excited states remained controversial. Recently, the low-temperature X-ray structure of $[Ru(bpy)_3](PF_6)_2$ was determined and revealed the presence of three different sites for $[Ru(bpy)_3]^{2+}$ below $T \approx 200$ K.[5] This crystallographic study confirms spectroscopic investigations on $[Os(bpy)_3]^{2+}$ doped into $[Ru(bpy)_3](PF_6)_2$. In this matrix the guest molecules also display the occurrence of three sites.[6] However, for neat $[Ru(bpy)_3](PF_6)_2$ only one spectroscopic site (designated A in the following) has been at this time recorded.[7−9] In this contribution we want to report on the spectroscopic identification of a second, higher energy site B of $[Ru(bpy)_3]^{2+}$ in single-crystal $[Ru(bpy)_3](PF_6)_2$ and on the radiationless energy transfer to the lower energy site A.

The low-temperature emission spectra of $[Ru(bpy)_3](PF_6)_2$ in the region of the electronic origins are shown in Figure 1 for $T = 1.3$ K and $T = 4.2$ K (compare refs 7 and 8 for the complete spectra, for experimental details see ref 10). At the high-energy side of the emission spectra two peaks designated $A-I_{0-0}$ and $A-II_{0-0}$ appear at 17 809 and 17 816 cm^{-1}, respectively. These lines have been assigned to the electronic origins of the two lowest excited states $|I\rangle$ and $|II\rangle$ of the lower energy site A.[7,8] Interestingly, to higher energy two additional peaks, called $B-I_{0-0}$ and $B-II_{0-0}$, can be found (Figure 1 and Table 1). The intensities of these lines are weaker by a factor of 10−20 than the intensities of the lines $A-I_{0-0}$ and $A-II_{0-0}$. It is an important result that the emission lines B *cannot* be frozen out even at the lowest temperature applied ($T = 1.3$ K). Moreover, the lines $B-I_{0-0}$ and $B-II_{0-0}$ show the same magnetic-field behavior as the lines $A-I_{0-0}$ and $A-II_{0-0}$ (not reproduced, compare refs 10 and 11). Thus, the lines $B-I_{0-0}$ and $B-II_{0-0}$ are assigned to originate from slightly different $[Ru(bpy)_3]^{2+}$ molecules (site B) than the lines $A-I_{0-0}$ and $A-II_{0-0}$ (site A). The lowest excited state $|I\rangle$ of site B lies 19 cm^{-1} above state $|I\rangle$ of site A and the second excited state $|II\rangle$ of site B lies 18 cm^{-1} above state $|II\rangle$ of site A (Table 1).

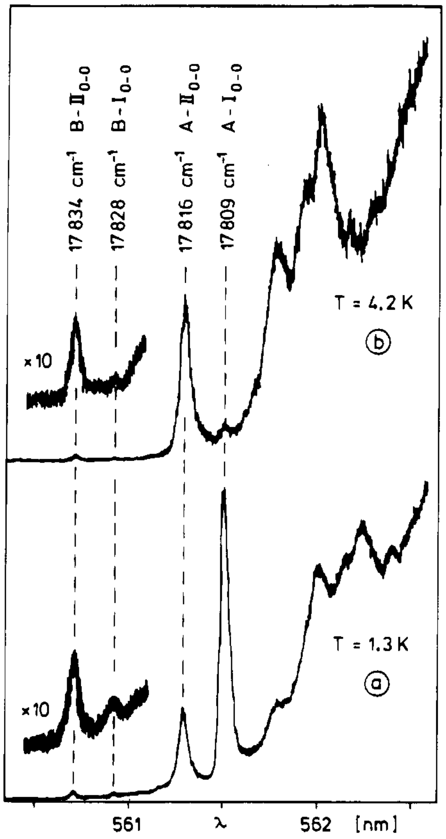

Figure 1. Emission spectra of single-crystal $[Ru(bpy)_3](PF_6)_2$ in the region of the lowest electronic origins I_{0-0} and II_{0-0} of two crystallographic sites A and B: (a) $T = 1.3$ K; (b) $T = 4.2$ K.

Table 1. Energy Positions of the Electronic Origins of the Two Lowest Excited States $|I\rangle$ and $|II\rangle$ of $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ in Neat Single-Crystal $[Ru(bpy)_3](PF_6)_2$ (cm^{-1})

	$[Ru(bpy)_3]^{2+}$		$[Os(bpy)_3]^{2+}$ [a]	
site	$\|I\rangle$	$\|II\rangle$	$\|I\rangle$	$\|II\rangle$
A	17 809	17 816	14 423	14 495
B	17 828	17 834	14 460	14 521
C	*b*	*b*	14 496	14 566

[a] From ref 6. [b] Not identified spectroscopically.

In addition to the energy positions of the lines $B-I_{0-0}$ and $B-II_{0-0}$ we measured the emission decay of line $B-I_{0-0}$ at $T = 1.2$ K. The decay is monoexponential for more than four lifetimes with $\tau_B = (60 \pm 10)$ ns (Figure 2). This value is a factor of about 4000 smaller than the lifetime of site A at the same temperature ($\tau_A \approx 250$ μs). Therefore, the lifetime of site B cannot be explained to be determined by a transition from the lowest excited state $|I\rangle$ to the electronic ground state $|0\rangle$. It is more reasonable to ascribe this short lifetime to be governed by a radiationless energy transfer from site B to site A.

However, although no direct correlation between the individual spectroscopic sites and the crystallographic sites can be made in this contribution, the crystal structure[5] suggests that sites A and B are nearest neighbors. In the plane perpendicular to the needle axis of the crystals each site is surrounded by three complexes of both of the other sites.[5] Thus, it is concluded that the energy transfer process leading to a lifetime of $\tau_B = 60$ ns occurs between nearest neighbors. The relatively small rate corresponding to this energy transfer is due to a very small

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(1) Krause, R. A. *Struct. Bonding* **1987**, *67*, 1.
(2) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
(3) Yersin, H.; Braun, D.; Hensler, G.; Gallhuber, E. In *Vibronic Processes in Inorganic Chemistry*; Flint, C. D., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; p 195.
(4) Krausz, E.; Ferguson, J. *Prog. Inorg. Chem.* **1989**, *37*, 293.
(5) Biner, M.; Bürgi, H.-B.; Ludi, A.; Röhr, C. *J. Am. Chem. Soc.* **1992**, *114*, 5197.
(6) Braun, D.; Gallhuber, E.; Hensler, G.; Yersin, H. *Mol. Phys.* **1989**, *67*, 417.
(7) Yersin, H.; Gallhuber, E.; Hensler, G. *J. Phys.* **1985**, *46*, C7−453.
(8) Hensler, G.; Gallhuber, E.; Yersin, H. *Inorg. Chim. Acta* **1986**, *113*, 91.
(9) Krausz, E. *Chem. Phys. Lett.* **1987**, *135*, 249.
(10) Gallhuber, E.; Hensler, G.; Yersin, H. *J. Am. Chem. Soc.* **1987**, *109*, 4818.
(11) Braun, D.; Gallhuber, E.; Yersin, H. *Chem. Phys. Lett.* **1990**, *171*, 122.

0020-1669/95/1334-1967$09.00/0

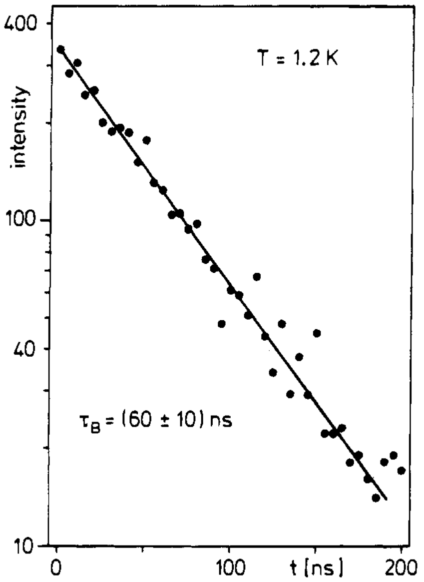

Figure 2. Emission decay measured at the position of the electronic origin line B−I_{0-0} ($\bar{\nu}_{det}$ = 17 828 cm^{-1}) corresponding to the lowest excited state |I⟩ of site B (T = 1.2 K).

spectral overlap[12] between the emission of site B and the absorption of site A.

Interestingly, at T = 1.3 K the emission of the lowest excited state |I⟩ of site B is quenched more effectively by the energy transfer than the emission of the corresponding second excited state |II⟩ (Figure 1a). This is due to a hindered thermalization (slow spin-lattice relaxation) between these two levels at low temperatures[13] and the longer lifetime[14] of state |I⟩ compared to state |II⟩. A similar behavior was found for the energy transfer at low temperature from site A when $[Os(bpy)_3]^{2+}$ is doped into $[Ru(bpy)_3](PF_6)_2$.[15]

Because of the identification of three crystallographic sites one also expects the presence of a third spectroscopic site (site C) which should lie at higher energy than site B. Moreover, when $[Os(bpy)_3]^{2+}$ is doped into $[Ru(bpy)_3](PF_6)_2$ three spectroscopic sites of the guest molecules can be identified. The energy separation between site A and site B of $[Os(bpy)_3]^{2+}$ is nearly equal to the energy separation between site B and site C of $[Os(bpy)_3]^{2+}$ (ref 6 and Table 1). Due to the similarity of $[Os(bpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ this suggests that in neat $[Ru(bpy)_3](PF_6)_2$ the origins of site C should lie approximately 20 cm^{-1} higher in energy than the origins of site B. But the absorption in this spectral region resulting from site A is relatively high. Consequently, the spectral overlap integral and therefore the energy transfer probability[12] from site C to site A increases drastically compared to the transfer from site B to site A. Additionally, an energy transfer from site C to site B is possible. A very fast energy transfer in the *neat* crystal totally quenches the emission of such a site. Consequently, it is not surprising that the third site could not be detected by emission spectroscopy. On the other hand, the absorption resulting from site A at the expected energy position of site C is too strong and thus we could not detect the relatively weak[3,8] origins of site C neither in absorption nor in excitation spectra.

From these considerations it is obvious that the presence of different sites in crystalline environments can lead to serious intricacies for the interpretation of electronic spectra which might even result in misinterpretations. For instance, the occurrence of two different sets of electronic origins in single-crystal $[Ru(bpy\text{-}h_8)_{3-n}(bpy\text{-}d_8)_n](PF_6)_2$ (n = 1,2) led to the erroneous interpretation that the lowest excited states are localized on a single (Ru−bpy) subunit.[16] An assignment of the two sets of electronic origins to *different sites* was not considered in ref 16, although three different crystallographic sites are present in $[Ru(bpy)_3](PF_6)_2$.[5] The observed peaks have nothing to do with a localization process. Moreover, a very recent and detailed analysis of the resolved vibrational satellite structures in the emission of partially deuterated $[Ru(bpy)_3]^{2+}$ doped into $[Zn(bpy)_3](ClO_4)_2$ clearly showed that the localized description can be excluded.[17] This is also valid for the related $[Os(bpy)_3]^{2+}$ doped into the same matrix.[18]

Acknowledgment. The "Deutsche Forschungsgemeinschaft" and the "Verband der Chemischen Industrie" are acknowledged for financial support. We further thank the Degussa AG (Hanau) for a donation of $RuCl_3{\cdot}3H_2O$.

IC940534Z

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(12) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.
(13) Yersin, H.; Braun, D. *Coord. Chem. Rev.* **1991**, *111*, 39.
(14) Hager, G. D.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7031.
(15) Yersin, H.; Braun, D.; Gallhuber, E.; Hensler, G. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 1228.
(16) Riesen, H.; Krausz, E.; Puza, M. *Chem. Phys. Lett.* **1988**, *151*, 65.
(17) Braun, D.; Huber, P.; Wudy, J.; Schmidt, J.; Yersin, H. *J. Phys. Chem.* **1994**, *98*, 8044.
(18) Huber, P.; Yersin, H. *J. Phys. Chem.* **1993**, *97*, 12705.