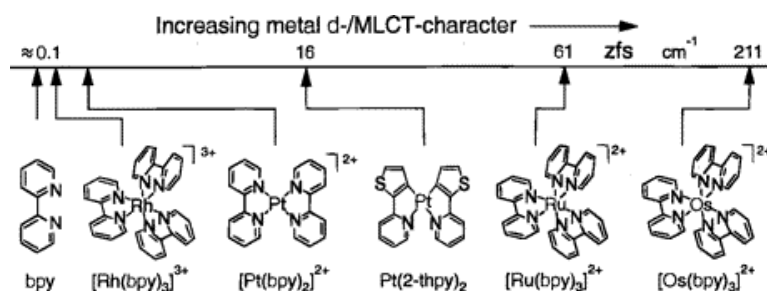


Spatial Extensions of Excited States of Metal Complexes. Tunability by Chemical Variation

Hartmut Yersin, and Werner Humbs

Inorg. Chem., **1999**, 38 (25), 5820-5831 • DOI: 10.1021/ic990582p • Publication Date (Web): 13 December 1999

Downloaded from <http://pubs.acs.org> on March 3, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

Spatial Extensions of Excited States of Metal Complexes. Tunability by Chemical Variation

Hartmut Yersin* and Werner Humbs

Institut für Physikalische und Theoretische Chemie, Universität Regensburg,
D-93040 Regensburg, Germany

Received May 20, 1999

The ligand–ligand coupling in excited states of homoleptic metal–organic and related compounds of the platinum metal group depends strongly on the metal d or MLCT character in these states. In particular, in triplet states, which mostly represent the lowest excited states, the metal participation is displayed in the amount of zero-field splitting (zfs). Detailed investigations in recent years have demonstrated that complexes with very small metal participation and thus small zfs, like $[\text{Rh}(\text{bpy})_3]^{3+}$ and $[\text{Pt}(\text{bpy})_2]^{2+}$, exhibit spatially localized or ligand-centered triplets. Compounds with large metal character as in $^3\text{MLCT}$ states have large zfs, and the states are delocalized over the metal and the different ligands, as found for $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$. By chemical variation, it is possible to obtain a compound characterized by an intermediate position between the two extreme situations. Such a compound is $\text{Pt}(\text{2-thpy})_2$ with $\text{2-thpy}^- = 2\text{-(2-thienylpyridinate)}$. It is one of the main subjects of this investigation to study whether in $\text{Pt}(\text{2-thpy})_2$ the lowest excited triplet is spatially extended over both ligands. This is done by comparing highly resolved emission (and excitation) spectra of perprotonated $\text{Pt}(\text{2-thpy-}h_6)_2$, partially deuterated $\text{Pt}(\text{2-thpy-}h_6)(\text{2-thpy-}d_6)$, and perdeuterated $\text{Pt}(\text{2-thpy-}d_6)_2$. These spectra display clear *fingerprints* with respect to spatial extensions of the excited states. The required high resolution is obtained when the compounds are dissolved in an *n*-octane matrix (Shpol'skii matrix) and are measured at low temperature ($T = 1.3$ and 4.2 K). The deuterated compounds are studied for the first time. Interestingly, it is found that all three triplet sublevels of $\text{Pt}(\text{2-thpy})_2$ are spatially extended over both ligands. This result is of high importance, since it tells us that already a moderate metal d or MLCT character in the lowest triplet state of homoleptic compounds of the platinum metal group leads, at least in a rigid matrix, to spatially delocalized excited states.

1. Introduction

During the last one or two decades it has become apparent that complexes of the platinum metal group with organic ligands exhibit an enormous potential for new applications. For example, systems involving photoredox processes usable for solar energy conversion,^{1–9} photovoltaic devices,^{10,11} molecular photodiodes,¹² or chemical synthesis,¹³ information storage systems,¹⁴ chemical sensors and biosensors,^{15–18} low-dimensional

semiconductors with extreme tunabilities of optical transitions under high pressure,^{19–22} and supramolecular systems with wide-range definable photophysical properties^{23,24} have already been explored or are under current investigation. All of these properties and potential applications are related to the characteristics of the lowest excited electronic states and the ground states. Therefore, it is highly desirable to obtain as much information as possible about these states and to learn how to tune the properties of interest, for example, by chemical methods. If highly resolved optical spectra can be recorded, which is often achievable when the powerful methods of laser and time-resolution spectroscopy are applied, it becomes possible to extract very detailed and reliable information. Having such information available, the consequences of chemical variations may be studied, classified, and exploited with regard to specific properties.

It has been shown that the lowest triplet states of metal–bipyridine compounds, for example, are largely ligand centered (LC) of $\pi\pi^*$ character with small metal *d* admixtures or of metal-to-ligand-charge-transfer (MLCT) character, depending

- (1) Connolly, J. S., Ed. *Photochemical Conversion and Storage of Solar Energy*; Academic Press: New York, 1981.
- (2) Harriman, A.; West, M. A., Eds. *Photogeneration of Hydrogen*; Academic Press: London, 1982.
- (3) Calzaferri, G., Ed. Proceedings of the 10th International Conference on Photochemical Transformation and Storage of Solar Energy. *Sol. Energy Mater. Sol. Cells* **1995**, 38, 1–573.
- (4) O'Regan, B.; Grätzel, M. *Nature* **1991**, 353, 737.
- (5) Grätzel, M. *Platinum Met. Rev.* **1994**, 38, 151.
- (6) Juris, A.; Balzani, V.; Barigelli, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, 84, 85.
- (7) Vogler, A.; Kunkely, H. *J. Am. Chem. Soc.* **1981**, 103, 1559.
- (8) Cummings, S. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1996**, 118, 1949.
- (9) Paw, W.; Cummings, S. D.; Mansour, M. A.; Connick, W. B.; Geiger, D. K.; Eisenberg, R. *Coord. Chem. Rev.* **1998**, 171, 125.
- (10) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, 115, 6382.
- (11) Heimer, T. A.; Bignozzi, C. A.; Meyer, G. J. *J. Phys. Chem.* **1993**, 97, 11987.
- (12) Marfurt, J.; Zhao, W.; Walder, L. *J. Chem. Soc., Chem. Commun.* **1994**, 51.
- (13) Leitner, W. *Angew. Chem.* **1995**, 107, 2391.
- (14) Goulle, V.; Harriman, A.; Lehn, J. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1034.
- (15) Kosch, U.; Klimant, I.; Werner, T.; Wolfbeis, O. S. *Anal. Chem.* **1998**, 70, 3892.
- (16) Maede, T. J.; Kayyem, J. F. *Angew. Chem.* **1995**, 107, 358.

- (17) Terpetschnick, E.; Szmajnski, H.; Malak, H.; Lakowicz, J. R. *Biophys. J.* **1995**, 68, 342.
- (18) Holmlin, R. E.; Barton, J. K. *Inorg. Chem.* **1995**, 34, 7.
- (19) Stock, M.; Yersin, H. *Solid State Commun.* **1978**, 27, 1305.
- (20) Yersin, H.; Riedl, U. *Inorg. Chem.* **1995**, 34, 1642.
- (21) Yersin, H.; von Ammon, W.; Stock, M.; Gliemann, G. *J. Lumin.* **1979**, 18–19, 774.
- (22) Yersin, H.; Trümbach, D.; Strasser, J.; Patterson, H. H.; Assefa, Z. *Inorg. Chem.* **1998**, 37, 3209.
- (23) Balzani, V.; Scandola, F. *Supramolecular Chemistry*; Horwood: Chichester, U.K., 1991.
- (24) Lehn, J. M. *Supramolecular Chemistry*; Verlag Chemie: Weinheim, Germany, 1995.

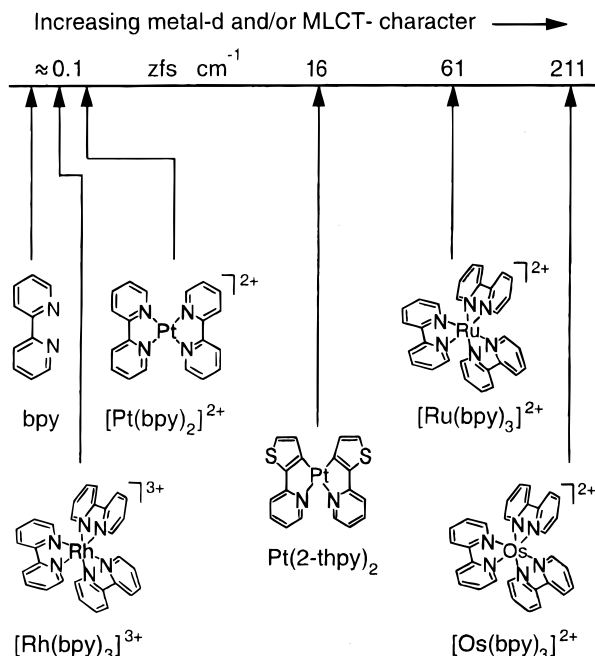


Figure 1. Complexes are arranged according to increasing metal d and/or MLCT character in the lowest excited triplet state. The amount of zero-field splitting (zfs) reflects the importance of the metal character, though not in a linear or simple relation.

on the position in the sequence given in Figure 1. The importance of the metal involvement in these triplets is displayed in many photophysical properties. Of particular significance is the amount of splitting of the triplet into sublevels under zero magnetic field (zero-field splitting, zfs), which in general increases with increasing d character. Also other properties exhibit correspondingly systematic changes, like emission decay times, relaxation properties between the triplet sublevels, radiative rates of the transitions to the ground states, distinctness of Franck–Condon progressions, blue shifts of the transition energy upon deuteration, etc.^{25–30} Interestingly, also the spatial extension of the lowest excited states is controlled by the amount of metal or MLCT character in these states, since this property determines crucially the electronic ligand–ligand coupling in these compounds. Thus, in complexes with small metal character in the corresponding states, such as [Rh(bpy)₃]³⁺²⁶ and [Pt(bpy)₂]²⁺³¹ with zfs values of the order of 0.1 cm^{−1},³² the lowest excited states are ligand centered (LC) and localized on one ligand^{26,27,29,31} (left-hand side of Figure 1), while for those compounds with distinct MLCT character, the metal induces a strong ligand–ligand coupling. This leads to excited states being delocalized over the metal and the different ligands as in [Ru(bpy)₃]²⁺ and [Os(bpy)₃]²⁺.^{27,29,33–35} These compounds exhibit zfs values of 61 and 211 cm^{−1}, respectively^{29,34} (right-hand side of Figure 1).

With respect to this issue, it seems appropriate to make some remarks. The properties of the excited states of [Ru(bpy)₃]²⁺,

for example, are described in the scope of three different models. Two of these favor a localization of the excitation on one ligand. In the first model (i) it is assumed that a relatively strong distortion (order of 10³ cm^{−1}) is required for a localization (for example, see refs 36 and 37), while according to a second model (ii) an extremely weak distortion (order of 0.1 cm^{−1}) is sufficient to localize the excitation on one (Ru–bpy) subunit (see ref 38). Obviously, both models cannot be valid, equally. On the other hand, the third model (iii) describes the excited state properties in a delocalized description. In recent reviews,^{27,29} these three models are thoroughly compared, and it is shown that both localization models cannot describe the spectroscopic properties of [Ru(bpy)₃]²⁺ doped into a rigid [Zn(bpy)₃](ClO₄)₂ matrix. In particular, model ii is based on artifacts (details in ref 29), while the excited state distortion predicted by model i should lead to a number of spectroscopic fingerprints which are definitely not present.²⁹ (See also section 3.) However, model i, as proposed for [Ru(bpy)₃]²⁺ in a polar and fluid solution, does not have to be in contradiction to model iii, developed for the rigid situation. For example, it has already been shown, though for a different compound, that an increase of the stiffness of the matrix, induced by application of high pressure, can indeed tune off a localization tendency by reducing the energy gain, which is connected with the localization process.^{19,39} Possibly, the stiffness of the crystalline matrix is already high enough to prevent a localization in the excited states of [Ru(bpy)₃]²⁺ (for details, see ref 29). In summary, model iii describes the properties of the excited states of [Ru(bpy)₃]²⁺ and [Os(bpy)₃]²⁺ in a crystalline matrix most adequately.

The bpy–metal complexes shown in Figure 1 seem to display two extreme situations. Consequently, it is of interest to investigate a compound, that lies between these situations with respect to the metal character. Fortunately, the new ortho-metalated Pt(II) compounds, first prepared by von Zelewsky's group,^{40–44} fit well into the series discussed, as has been shown by a number of investigations.^{41–47} Of particular interest in this respect is Pt(2-thpy)₂. Its triplet state is mainly of LC character, but an MLCT admixture leads to a total zfs of 16 cm^{−1}. (See refs 45–47.) Obviously, in this situation of a distinctly smaller MLCT character and consequently a smaller metal-induced electronic ligand–ligand coupling than in [Ru(bpy)₃]²⁺ and [Os(bpy)₃]²⁺, it is not clear to which of the two situations Pt(2-thpy)₂ belongs. Thus, it is the main goal of this investigation to find out, whether for this intermediate compound the metal-induced electronic ligand–ligand coupling is sufficiently large

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

(26) Humbs, W.; Yersin, H. *Inorg. Chem.* **1996**, *35*, 2220.

(27) Yersin, H.; Humbs, W.; Strasser, J. *Coord. Chem. Rev.* **1997**, *159*, 325.

(28) Yersin, H.; Strasser, J. *J. Lumin.* **1997**, *72–74*, 462.

(29) Yersin, H.; Humbs, W.; Strasser, J. In *Electronic and Vibronic Spectra of Transition Metal Complexes, Vol. II*; Yersin, H., Ed.; Topics in Current Chemistry 191; Springer-Verlag: Berlin, 1997; p 153.

(30) Strasser, J.; Donges, D.; Humbs, W.; Kulikova, M. V.; Balashev, K. P.; Yersin, H. *J. Lumin.* **1998**, *76–77*, 611.

(31) Humbs, W.; Yersin, H. *Inorg. Chim. Acta* **1997**, *265*, 139.

(32) Westra, J.; Glasbeek, M. *Chem. Phys. Lett.* **1990**, *166*, 535.

(33) Humbs, W.; Strasser, J.; Yersin, H. *J. Lumin.* **1997**, *72–74*, 677.

(34) Huber, P.; Yersin, H. *J. Phys. Chem.* **1993**, *97*, 12705.

(35) Braun, D.; Huber, P.; Wudy, J.; Schmidt, J.; Yersin, H. *J. Phys. Chem.* **1994**, *98*, 8044.

(36) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 3877.

(37) Krausz, E.; Ferguson, J. *Prog. Inorg. Chem.* **1989**, *37*, 293.

(38) Riesen, H.; Krausz, E. *J. Chem. Phys.* **1993**, *99*, 7614.

(39) Rössler, U.; Yersin, H. *Phys. Rev. B* **1982**, *26*, 3187.

(40) Chassot, L.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 2814.

(41) Maestri, M.; Balzani, V.; Deuschel-Cornioley, C.; von Zelewsky, A. *Adv. Photochem.* **1992**, *17*, 1.

(42) Maestri, M.; Sandrini, D.; Balzani, V.; Chassot, L.; Joliet, P.; von Zelewsky, A. *Chem. Phys. Lett.* **1985**, *122*, 375.

(43) Balzani, V.; Maestri, M.; Melandri, A.; Sandrini, D.; Chassot, L.; Cornioley-Deuschel, C.; Joliet, P.; Maeder, U.; von Zelewsky, A. In *Photochemistry and Photophysics of Coordination Compounds*; Yersin, H., Vogler, A., Eds.; Springer-Verlag: Berlin, 1987; p 71.

(44) Deuschel-Cornioley, C.; Lüönd, R.; von Zelewsky, A. *Helv. Chim. Acta* **1989**, *72*, 377.

(45) Wiedenhofer, H.; Schützenmeier, S.; von Zelewsky, A.; Yersin, H. *J. Phys. Chem.* **1995**, *99*, 13385.

(46) Schmidt, J.; Strasser, J.; Yersin, H. *Inorg. Chem.* **1997**, *36*, 3957.

(47) Yersin, H.; Huber, P.; Wiedenhofer, H. *Coord. Chem. Rev.* **1994**, *132*, 35.

to delocalize the lowest excited triplet or whether the coupling is still so small that weak distortions, for example induced by the environment or a partial deuteration, are sufficient to localize the excitation on one ligand. We study for the first time properties of partially and completely deuterated $\text{Pt}(\text{2-thpy})_2$ compounds and compare the results with those obtained previously for the perprotonated compound. It will be shown that our main question can be answered by using the technique of isotopic labeling combined with high-resolution spectroscopy and emission decay measurements. The result is not what was anticipated. Already a moderate MLCT character of the lowest excited triplet is sufficient to delocalize the excitation.

The paper is organized as follows: After the Experimental Section, we give a brief introduction to spectroscopic effects which occur upon perdeuteration and partial deuteration and it is shown that these effects can be applied to develop fingerprints which clearly display a localized and a delocalized situation, respectively (section 3). The results and interpretations are presented in section 4, and section 5 concludes the paper.

2. Experimental Section

The preparation of $\text{Pt}(\text{2-thpy-}h_6)_2$ is described in ref 40. The perdeuterated compound was synthesized analogously using deuterated 2-thienylpyridine. Deuterated 2-thienylpyridine (2-Dthpy- d_6) was prepared as follows: 3.1 g of protonated 2-Hthpy- h_6 (Lancaster), 50 mL of 1 M NaOD (from 1.15 g of Na in 50 mL of D_2O (Aldrich)), and 0.8 g of Pd/C (10%) (Aldrich) were heated for 8 days at 200 °C in a Teflon autoclave. After cooling and filtration, the precipitate was washed with D_2O and dried over MgSO_4 . Finally, 2-Dthpy- d_6 was purified by vacuum sublimation. Infrared spectra showed intense C–D peaks between 2250 and 2295 cm^{-1} but no C–H peaks. The final degree of deuteration was better than 95% for positions 3 to 5', while position 6' was deuterated to 82%, as was confirmed by the ^1H NMR spectrum of 2-Dthpy- d_6 using 2,2'-azo(bisisobutyronitrile) (Acros) as a reference. Partially deuterated $\text{Pt}(\text{2-thpy-}h_6)(\text{2-thpy-}d_6)$ was synthesized by adding dropwise 2-Li-thpy- d_6 (from 50 mg of 2-Dthpy- d_6 in 5 mL of diethyl ether and 0.19 mL of $t\text{-BuLi}$ (Aldrich)) to a suspension of 150 mg of $\text{Pt}(\text{2-thpy-}h_6)\text{ClEt}_2\text{S}^{44}$ at -78 °C under an N_2 atmosphere. After 30 min, the mixture was hydrolyzed with D_2O at 0 °C. After extracting several times with CH_2Cl_2 and evaporation of the organic solvent, the reddish precipitate was recrystallized from $\text{CH}_2\text{Cl}_2/n\text{-hexane}$. The utilized solvents were obtained commercially (Aldrich) and used as purchased.

Elemental analyses of C, H, and N are as follows (D and H were determined simultaneously by a thermoconductometric standard method; therefore all values for D are expressed in terms of H). Calcd for $\text{Pt}(\text{2-thpy-}h_6)_2$: C, 41.73; H, 2.34; N, 5.41. Found: C, 41.70; H, 2.36; N, 5.39. Anal. Calcd for $\text{Pt}(\text{2-thpy-}d_6)_2$: C, 40.82; H, 2.28; N, 5.29. Found: C, 40.89; H, 2.31; N, 5.31. Anal. Calcd for $\text{Pt}(\text{2-thpy-}h_6)(\text{2-thpy-}d_6)$: C, 41.29; H, 2.31; N, 5.35. Found: C, 41.52; H, 2.35; N, 5.30.

To measure highly resolved spectra, the $\text{Pt}(\text{2-thpy-}h_6)_{2-n}(\text{2-thpy-}d_6)_n$ compounds ($n = 0, 1, 2$) were dissolved in 1,4-dioxane (Aldrich) and then the solutions were diluted with $n\text{-octane}$ (Aldrich) to a ratio of 1:50 v/v. The final concentrations of the complexes were estimated to be 10^{-5} M. The solutions were filled into quartz cuvettes and rapidly introduced into the cryostat, cooled to liquid helium temperature, to obtain Shpol'skii matrixes. For measurements at high magnetic fields, a combi-cryostat (Oxford Instruments, MD 10-S) was used. Temperatures of 1.3 K could be achieved by pumping off the helium. For measurements of nonresonantly excited emission spectra, the samples were excited with an argon ion laser (Coherent Innova 90). For resonantly excited emission spectra, as well as for excitation spectra, a dye laser was used (Lambda Physik FL 2000; nominal line half-width 0.15 cm^{-1}). The dyes were pumped by an Nd:YAG laser ($\lambda_{\text{exc}} = 355$ nm, Spectron Laser Systems SL 800). The optical detection system is described in refs 48 and 49. The emitted light was dispersed by a double monochromator (SPEX 1401) and registered with an extended S-20 photomultiplier cooled to -50 °C (cooling system from B.

Könnecke Messtechnik, 13435 Berlin). The photomultiplier signals were collected and processed by a computer-controlled photon-counting system. Lifetime measurements were performed with a fast multichannel scaler (MCS 7886, FAST Com Tec). The emission spectra are corrected for the spectral response of the detection system, while the excitation spectrum is not corrected for the laser intensity. The monochromator readout was calibrated with a krypton low-pressure lamp (UVP Penray) to ± 1 cm^{-1} .

3. Deuteration Effects and Fingerprints for Spatial Extensions of States

The purpose of this section is to introduce the characteristic spectroscopic changes which are connected with deuteration of the ligand(s) of metal complexes. Further, it is intended to show that a comparison of photophysical properties of perprotonated and perdeuterated compounds to those of partially deuterated compounds will provide reliable fingerprints for the spatial extensions of excited and emitting electronic states. Thus, information about localization/delocalization behavior becomes available.

3.1. Perdeuteration. Perdeuteration of transition metal complexes like $[\text{Rh}(\text{bpy})_3]^{3+}$, $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Os}(\text{bpy})_3]^{2+}$, etc. leaves the complex symmetries usually unchanged. Nevertheless, a number of characteristic changes can mostly be observed:

(a) Vibrational Frequencies. Commonly, all vibrational frequencies are shifted to lower energies (red shifts) if compared with those of the perprotonated species. The amount of red shift is connected with the contribution of C–H/C–D vibrational components of the corresponding vibrational mode. Red shifts of more than 50 cm^{-1} for ligand vibrations in the 1000–1500 cm^{-1} range are not unusual. (For example, see refs 26, 27, 29, 31, 33–35, and 50–56 and the results of this investigation, below.)

(b) Emission Intensity and Decay Time. Usually, the emission intensity and decay time increase due to deuteration of a molecule. This is a consequence of the higher number of vibrational quanta which are in the deuterated case necessary to fit the energy difference between the electronic ground state and the excited state. Thus, the Franck–Condon factors between the lowest vibrational level of the excited electronic state and the isoenergetic, highly vibrationally excited levels of the electronic ground state become smaller (e.g., see ref 57). The consequence is a reduction of the nonradiative deactivation. For example, an emission intensity increase by a factor of 3 (e.g., see refs 53 and 58) up to a factor of 100 (ref 59) has been observed. (Compare also the increase of decay time for $\text{Pt}(\text{2-thpy})_2$; see Figure 4.)

(c) Vibrational Satellite Structure. Interestingly, the vibrational satellite structure, for example of the emission spectrum, is altered due to two different effects. Because of the red shift of the vibrational modes, as mentioned above, one observes the

- (48) Yersin, H.; Gliemann, G. *Messtechnik* **1972**, 80, 99.
- (49) Stock, M.; Yersin, H. *Chem. Phys. Lett.* **1976**, 40, 423.
- (50) Poizat, O.; Sourisseau, C. *J. Phys. Chem.* **1984**, 88, 3007.
- (51) Maruszewski, K.; Bajdor, K.; Strommen, D. P.; Kincaid, J. R. *J. Phys. Chem.* **1995**, 99, 6286.
- (52) Strommen, D. P.; Mallick, P. K.; Danzer, G. D.; Lumpkin, R. S.; Kincaid, J. R. *J. Phys. Chem.* **1990**, 94, 1357.
- (53) Yersin, H.; Huber, P.; Braun, D. *J. Phys. Chem.* **1990**, 94, 3560.
- (54) Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand Reinhold: New York, 1945, Vol. II, p 282; 1966, Vol. III, p 181.
- (55) Watmann-Grajcar, L. *J. Chim. Phys. Phys.-Chim. Biol.* **1969**, 66, 1023.
- (56) King, G. W.; So, S. P. *J. Mol. Spectrosc.* **1971**, 37, 543.
- (57) Lipert, R. J.; Colson, S. D. *J. Phys. Chem.* **1989**, 93, 135.
- (58) Yersin, H.; Braun, D. *Chem. Phys. Lett.* **1991**, 179, 85.
- (59) Yanagida, S.; Hasegawa, Y.; Murakoshi, K.; Wada, Y.; Nakashima, N.; Yamanaka, T. *Coord. Chem. Rev.* **1998**, 171, 461.

Table 1. Spectroscopic Trends and Deuteration-Induced Blue Shifts for the Complexes Shown in Figure 1

| complex | lowest triplet sublevel I, ^d cm ⁻¹ | total zfs, cm ⁻¹ | blue shift, cm ⁻¹ | blue shift per proton, ^g cm ⁻¹ | assigns and refs |
|--|--|-----------------------------|------------------------------|--|--|
| bpy ^a | 23 504 | ≈0.1 ^e | 86 | 10.8 | ³ ππ*; ref 29 |
| [Rh(bpy) ₃] ³⁺ ^b | 22 757 | ≈0.1 ^f | 61 | 7.6 | ³ LC(³ ππ*) + small dd* admixtures, localized to one ligand; ref 26 |
| Pt(2-thpy) ₂ ^c | 17 156 | 16 | 36 | 3 | ³ LC(³ ππ*) + MLCT admixtures, delocalized; this work |
| [Ru(bpy) ₃] ²⁺ ^b | 17 684 | 61 | 40 | 1.7 | ³ MLCT(³ dπ*), delocalized; refs 29, 33, 47 |
| [Os(bpy) ₃] ²⁺ ^b | 14 223 | 210 | 32 | 1.3 | ³ MLCT(³ dπ*), delocalized; refs 29, 34 |

^a In *n*-heptane. ^b In [Zn(bpy)₃](ClO₄)₂. ^c In *n*-octane. ^d Protonated complexes. ^e From ref 74. ^f From ref 73. ^g Referring to the number of protons involved in the spatial region where the electronic transition occurs.

satellites at lower energies relative to the electronic origin. On the other hand, the vibronic coupling property of a vibrational mode depends on the specific normal coordinate of that individual mode. Since the coordinates partly change with deuteration, the intensity of the corresponding vibronic satellite may be modified distinctly. This effect is also observed when the vibronic intensities found for Pt(2-thpy-*h*₆)₂ are compared to those of Pt(2-thpy-*d*₆)₂, as is shown in Figures 5 and 6. (See also refs 52, 53, 57, and 60.)

(d) Shifts of Electronic Origins (0–0 Transitions). A further isotope effect seems to be less well-known although it has already been well studied for organic molecules (e.g., see refs 54–57 and 58, 60–63) and metal complexes (e.g., see refs 26, 27, 29, 33–35, and 58). Due to this effect, the electronic origins are mostly shifted to higher energy upon deuteration. For example, the compounds shown in Figure 1 exhibit values of blue shifts as are summarized in Table 1. This behavior results from the fact that the so-called purely electronic transition between two electronic states occurs—as a physical principle—always between the zero-point vibrational energies of the two states. A reduction of vibrational energies, which is always connected with a deuteration, leads also to a decrease of the zero-point vibrational energies in the ground state and the excited state. Due to different force constants in these states, the reductions are different. Consequently, a shift to higher energy (blue shift) of the electronic origin line occurs upon deuteration if the vibrational force constants of the electronic ground state are (on the average) larger than those of the excited state.⁵⁸ Often, the amount of blue shift is largely independent of the matrix material (see below and ref 55). In this situation, the value of the blue shift may be used to characterize the change of force constants according to the excitation process.^{58,63}

3.2. Partial Deuteration. The question of whether different ligands of a homoleptic complex are electronically involved in the low-lying excited states can be answered by investigating spectral changes which result from a partial deuteration, for example, of one ligand. Interestingly one observes distinctly different spectroscopic features if the localized situation is compared to the delocalized one. This method has been tested thoroughly for several compounds.^{26,27,29,31,33–35} Nevertheless, it is useful to summarize briefly the crucial points.

3.2.1. Fingerprints of a Localized Excitation. In the situation of a weak electronic coupling between the different ligands, these manifest themselves by different electronic origins. In homoleptic complexes with symmetry-related ligands or in only weakly distorted complexes, the origins lie in most cases

nearly at the same energy.^{26,31} Deuteration of one ligand leads to a blue shift of the corresponding electronic origin by a value which corresponds approximately to the total amount observed for one single coordinated ligand. The blue shift may be as large as 60 cm⁻¹, as has been found for [Rh(bpy)₃]³⁺.²⁶ The 0–0 transition will occur as an additional electronic origin. Consequently, one observes superimposed absorption or *excitation* spectra which correspond to the protonated and the deuterated ligands, respectively, both giving their individual vibrational satellite structures.

However, the structures of the *emission* spectra will show different features due to a fast intramolecular energy transfer from the deuterated ligand to the protonated one. The occurrence of such a process may be visualized if one assumes (for a moment) to have two separated ligands (molecules), a deuterated and a protonated one. In this situation, the deuterated molecule with its higher transition energy can act as donor, while the protonated molecule with the lower transition energy can be the acceptor. The resonance condition for an energy transfer is fulfilled, as may be expressed by a nonzero spectral overlap integral. Then, the coupling between donor and acceptor is taken into account. This will open the path for the energy transfer. If both donor and acceptor belong to the same molecule, it is easily visualized that even a weak coupling can still induce an efficient intramolecular radiationless energy transfer. (Compare ref 29, p 170, and ref 26.) Thus, even if the energetically higher lying electronic origin of the deuterated ligand is excited selectively, the emission will occur only from the energetically lower lying protonated ligand(s) due to the fast excitation energy transfer. Consequently, the vibrational satellite structure of the emission spectrum will exhibit the characteristic vibrational frequencies of the *protonated* ligand(s), while the satellites corresponding to the *deuterated* ligand are not expected to occur.

For completeness, it is mentioned that the behavior described above additionally implies that the vibrational coupling between different vibrations occurring through space or induced by the heavy central metal is weak. Indeed, the occurrence of a weak vibrational coupling is well established, at least for the high-energy ligand modes. Therefore, these modes can be regarded as localized vibrations.^{64–68} However, some changes in the range of metal–ligand (M–L) vibrational modes between 100 and ≈550 cm⁻¹ are expected to occur due to the vibrational coupling induced by the metal for these M–L vibrations. In fact, these properties have been observed and are discussed in detail in refs 26, 27, 29, 31, and 33.

(64) McCarthy, P. K.; Blanchard, G. J. *J. Phys. Chem.* **1996**, *100*, 14592.

(65) Weidlein, J.; Müller, U.; Dehnicke, K. *Schwingungsspektroskopie*; Georg Thieme Verlag: Stuttgart, Germany, 1982; p 52.

(66) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1978; p 197.

(67) Mohan, N.; Cyvin, S. J.; Müller, A. *Coord. Chem. Rev.* **1976**, *21*, 221.

(68) Gastilovich, E. A. *Sov. Phys. Usp. (Engl. Transl.)* **1991**, *34*, 592.

(60) Johnson, P. M.; Ziegler, L. *J. Chem. Phys.* **1972**, *56*, 2169.

(61) Ochs, F. W.; Prasad, P. N.; Kopelman, R. *Chem. Phys.* **1974**, *6*, 253.

(62) Khalil, O. S.; Hankin, S. W.; Goodman, L. *Chem. Phys. Lett.* **1977**, *52*, 187.

(63) Callomon, J. H.; Dunn, T. M.; Mills, I. M. *Philos. Trans. R. Soc. London* **1966**, A259, 499.

In conclusion, the most important criterion for the assignment of a ligand-localized situation is displayed in the vibrational satellite structure of the emission spectrum of the partially deuterated compound. If this structure is determined by high-energy vibrational modes of the protonated ligand, which is the most probable case for this weakly coupled situation, the lowest excited state will be localized on the protonated ligand(s). One may express this criterion more generally. The vibrational satellite structure (corresponding to a specific electronic origin) reflects that spatial region of a molecule in which electronic charge is redistributed during an electronic transition. (Compare also ref 68.)

3.2.2. Fingerprints of a Delocalized Excitation. In a situation of electronically delocalized excited states with a necessarily significant electronic ligand–ligand coupling, the resulting states are characterized by properties of the whole molecule. Consequently, a deuteration of one ligand will affect the whole molecule. Therefore, one expects to observe three characteristic features for the delocalized situation.

(1) A deuteration should not lead to additional electronic origins (0–0 transitions). In particular, the same set of three triplet sublevels should occur. Just this behavior is found for delocalized states of organic molecules.^{55,56,61–63}

(2) The lowest electronic transition(s) will be shifted to higher energy. However, since only part of the molecule is deuterated, the amount of blue shift will only be part of that of the perdeuterated compound (provided that matrix-induced site effects are small).

(3) The most characteristic feature, however, will be observed in the structure of the vibrational satellites. The change of the electronic charge distribution due to an electronic transition is experienced by the whole molecule, in particular, both deuterated and protonated ligands. Thus, the emission spectrum will exhibit ligand satellites of both *protonated and deuterated* ligands. Very important is that these satellites belong to the *same electronic 0–0 transition*. For completeness, it is mentioned again that the purely vibrational coupling for internal ligand vibrations of high frequency is also in this situation small compared to the experimental accuracy.^{26,29,31,64–67}

Indeed, it has been shown that the three criteria are valid for partially deuterated [Ru(bpy)₃]²⁺,^{27,29,33,35} and [Os(bpy)₃]²⁺,^{29,34} and it will be shown in section 4.2. that they are also fulfilled for the partially deuterated Pt(2-thpy)₂. But these criteria are not satisfied for partially deuterated [Rh(bpy)₃]³⁺,^{26,27,29,33} and [Pt(bpy)₂]²⁺,^{29,31} in which the excited states are ligand centered localized.

4. Results and Discussion

The focus of the present study is the discussion of properties of Pt(2-thpy)₂. Several investigations^{45–47,69,70} with the perprotonated compound led to a detailed characterization of the lowest triplet state and its sublevels. This was possible, since we obtained, for the first time, highly resolved spectra due to the application of matrix isolation technique. It could be demonstrated that doping of about 10^{–5} mol/L Pt(2-thpy)₂ into *n*-octane, giving a so-called Shpol'skii matrix⁷¹ at low temperature, resulted in spectra that are more than a hundred times better resolved than observed previously. In particular, these

investigations showed that the three sublevels of the lowest triplet state **I**, **II**, and **III** lie at 17 156, 17 163, and 17 172 cm^{–1} above the singlet ground state **0**. Thus, the total zero-field splitting amounts to 16 cm^{–1}. The corresponding excited singlet has not yet been confidently assigned. However, it is not unreasonable to ascribe the relatively strong transition at ≈23 200 cm^{–1}⁷² to this singlet. Interestingly, it could be concluded from several spectroscopic features that at least the lowest triplet is mainly ligand centered of ππ* character but significantly distorted by admixtures of different ³MLCT and ¹MLCT states of Pt 5d–2-thpy–π* character. In particular, these MLCT components are displayed in the value of the total zero-field splitting of 16 cm^{–1}.^{29,45,47}

4.1. Characterization of Pt(2-thpy-d₆)₂ and Comparison to Pt(2-thpy-h₆)₂. Figure 2 shows the emission spectra of Pt-(2-thpy-d₆)₂ dissolved in *n*-octane, at 1.3 and 4.2 K. Only one dominating site occurs, and the compound can be excited nonselectively.

4.1.1. Electronic Origins. Figure 3 reproduces the region of the electronic origins for the three triplet sublevels in an enlarged scale. This figure shows, as expected for 0–0 transitions, that the electronic origins **II** and **III**, respectively, are clearly observed in emission and excitation at the same energies, at 17 199 and 17 208 cm^{–1}, respectively. An observation of an emission of origin **III** requires a temperature increase to >5 K to repopulate this state. However, the identification of origin **I** is not similarly straightforward, since the transition between the lowest triplet sublevel **I** and the ground state **0** is strongly forbidden and the corresponding transition does not occur. But it can be shown that the vibrational satellites observed in the 1.3 K emission (Figure 2a) fit only and exactly to the energy position of 17 192 cm^{–1}. This behavior is very similar to that found for Pt(2-thpy-h₆)₂,⁴⁵ for which the assignment of origin **I** could further be manifested by an application of a high magnetic field. (Due to the Zeeman interaction, the emission intensity of origin **I** strongly grows in.⁴⁵) The forbiddenness of the transition **I** → **0** is also displayed in the relatively long emission decay times of 110 and 140 μs for the perprotonated and the perdeuterated compounds, respectively. The increase of decay time upon deuteration can be understood on the basis of a decrease of nonradiative deactivation processes, as discussed in section 3.1. (See also section 4.2.)

A group-theoretical classification of the three triplet sublevels is not possible, since the orbital symmetry of the triplet is not yet known. Moreover, the crystal structure determination of Pt-(2-thpy-h₆)₂ showed that the symmetry of the complex in the crystal is only C₁.⁷⁰ In this group, a symmetry classification would not make sense. However, the result of this paper, showing that the three triplet sublevels are delocalized over both ligands, suggests that the effective symmetry is higher. This may also be a consequence of the specific site where the chromophore sits in the *n*-octane matrix. If it is assumed that Pt-(2-thpy)₂ can be described in the symmetry of the parent group C_{2v}, one may also offer an explanation for the very strict forbiddenness of the transition **I** ↔ **0**. In this situation, state **I** may be classified as an A₂ representation (ground state A₁). This implies that the corresponding transition is spin and symmetry forbidden. The states **II** and **III** will have A₁, B₁, or B₂ representations, but a more precise assignment is not yet possible.

(a) Deuteration-Induced Blue Shifts. Parts a and c of Figure 4 reproduce the splitting patterns of the two per-compounds. Interestingly, all three triplet sublevels are blue shifted upon

(69) Yersin, H.; Trümbach, D.; Wiedenhofer, H. *Inorg. Chem.* **1999**, *38*, 1411.

(70) Breu, J.; Range, K.-J.; von Zelewsky, A.; Yersin, H. *Acta Crystallogr.* **1997**, *C53*, 562.

(71) Shpol'skii, E. V. *Sov. Phys. Usp. (Engl. Transl.)* **1960**, *3*, 372.

(72) Wiedenhofer, H. Ph.D. Thesis, Universität Regensburg, 1994.

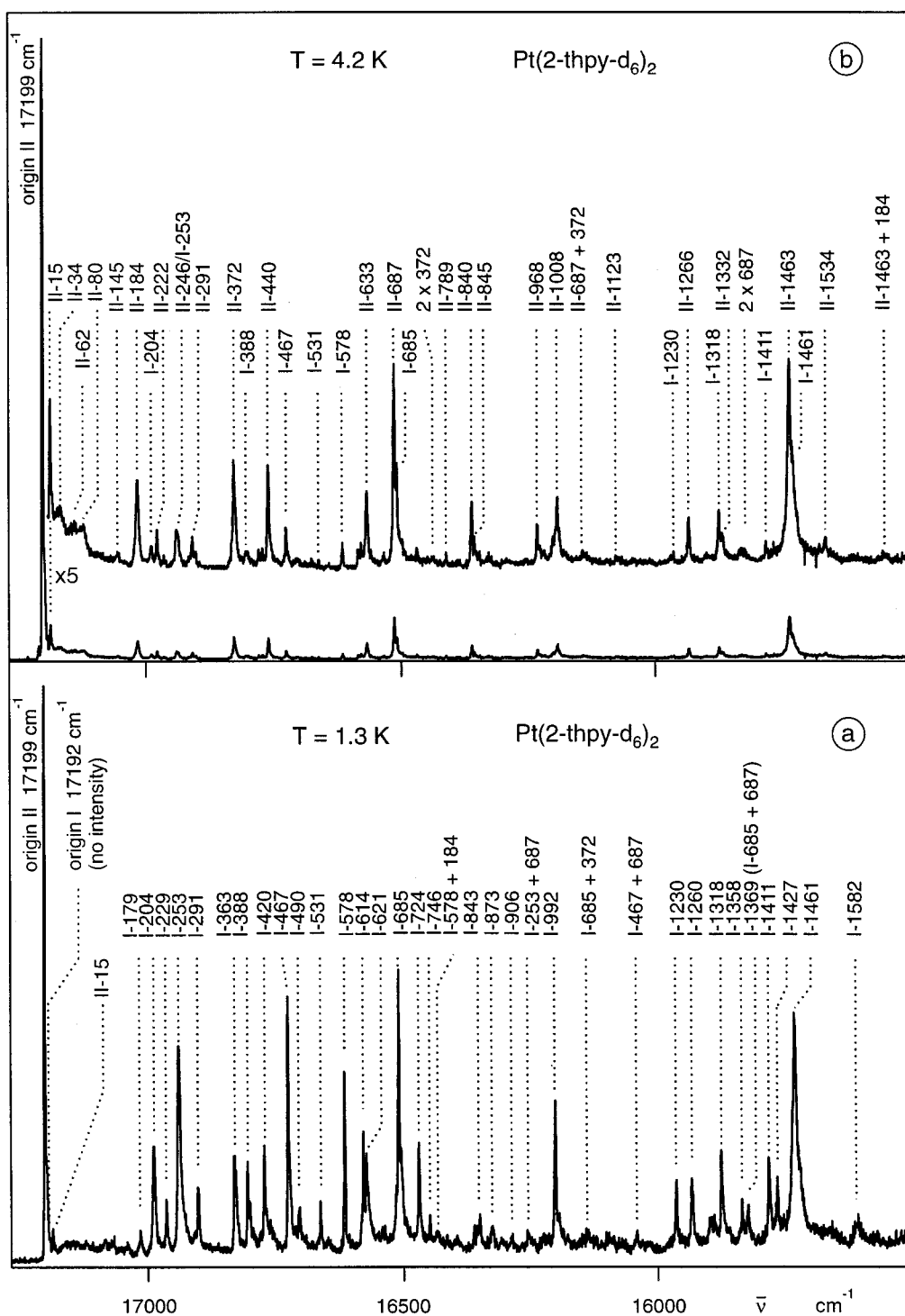


Figure 2. Emission spectra of $\text{Pt(2-thpy-d}_6)_2$ in *n*-octane at two different temperatures. $\lambda_{\text{exc}} = 457.9 \text{ nm}$. The energies of the vibrational satellites are given in cm^{-1} relative to the electronic origins I and II, respectively. The transition at the electronic origin I (at 17192 cm^{-1}) is strongly forbidden. Thus, all fundamentals, which occur at $T = 1.3 \text{ K}$ (a) represent "false origins" (vibronically induced satellites). At $T = 4.2 \text{ K}$ (b), origin II (at 17199 cm^{-1}) strongly dominates the spectrum. Two very weak Franck–Condon progressions (1×372 , $2 \times 372 \text{ cm}^{-1}$ and 1×687 , $2 \times 687 \text{ cm}^{-1}$) are observed.

deuteration by the same value of 36 cm^{-1} . Thus, the relative splittings are maintained. Further, the same blue shifts of 36 cm^{-1} with a maximum deviation of $\pm 2 \text{ cm}^{-1}$ were also found for all other investigated *n*-alkane sites (30 different sites in seven different *n*-alkane matrices). Thus, it can be concluded that the influence of the matrix or the individual site is of little importance for the amount of blue shift. This indicates that the blue shift represents largely a molecular property. It mainly displays the reduction of vibrational force constants in the trip-

let sublevels relative to those of the electronic ground state (section 3.1).

It is interesting to compare the amount of blue shift determined for Pt(2-thpy)_2 to the values found for the other compounds presented in Figure 1. Table 1 summarizes this series together with several other data, such as energy positions of the lowest triplet sublevels and the amounts of zero-field splittings, which characterize the strengths of the metal participation in these excited states.^{26,27,29,47} In particular, the blue shift

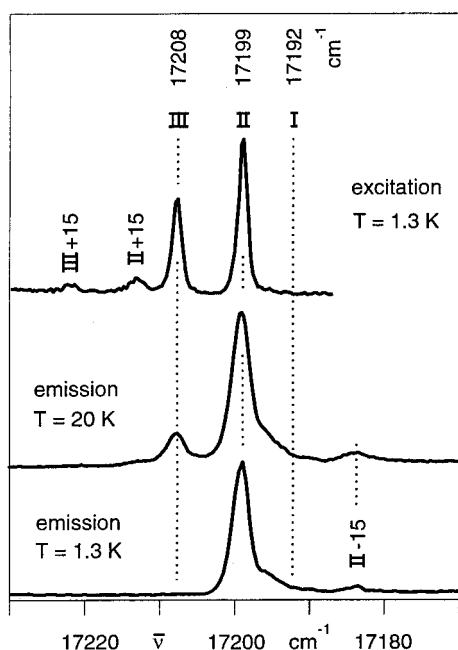


Figure 3. Emission and excitation spectra in the energy range of the electronic origins of the three triplet sublevels of $\text{Pt}(\text{2-thpy-d}_6)_2$ in *n*-octane at different temperatures. $\lambda_{\text{exc}} = 457.9$ nm (emission); $\bar{\nu}_{\text{det}} = 16\,507\text{--}16\,512\text{ cm}^{-1}$ ($\approx \text{I} - 685\text{ cm}^{-1}/\text{II} - 687\text{ cm}^{-1}$ satellites; see Figure 2) (excitation). Note: origin II cannot be frozen out with temperature reduction due to a slow spin–lattice relaxation (see section 4.1.1).

per proton displays (though indirectly) the trend that an increasing metal character leads to less different ground and excited state force constants. Indeed, this could also be shown directly, at least for $\text{Pt}(\text{2-thpy})_2^{45,46}$ and $[\text{Os}(\text{bpy})_3]^{2+,29}$ by determining the excited state vibrational frequencies from highly resolved excitation spectra.

(b) Spin–Lattice Relaxation. The emission from the second excited triplet sublevel II, lying 7 cm^{-1} above sublevel I, cannot be frozen out, even upon cooling to 1.3 K . The electronic origin II is still very strong. (See Figures 2a and 3.) This behavior is a consequence of a weak coupling of the triplet sublevels to the lattice. Thus, the excess energy can only slowly be transferred to the matrix. At $T = 1.3\text{ K}$, the relaxation time of the perprotonated compound is as long as $(710 \pm 10)\text{ ns}$.⁴⁶ The mechanism of relaxation has comprehensively been analyzed in refs 30, 46, and 75, and it can be ascribed to the process of a *direct* spin–lattice relaxation. Although this type of process has been known for a long time (e.g., see refs 76–78), its almost general importance for the low-temperature relaxation and emission behavior in metal–organic complexes has not yet been recognized, apart from a few recent investigations.^{25,27–30,46,75}

The spin–lattice relaxation time for the process of direct relaxation from state II to state I is determined from the emission decay of the transition from state II to the ground state 0. Interestingly, this relaxation time is not altered, when the chromophore is deuterated. For both per-compounds, and within

limits of experimental error also for the partially deuterated complex, one finds the same long relaxation time of $710 \pm 10\text{ ns}$. (Figure 4). Obviously, deuteration of the ligands does not influence (strongly) the coupling of the triplet sublevels to the lattice.

4.1.2. Vibrational Satellites. The vibrational satellites observed in the emission spectrum at $T = 1.3\text{ K}$ (Figure 2a) represent “false origins”, since they carry the emission intensity, while the purely electronic transition between I and 0 is forbidden. Thus, a transition at the electronic origin (0–0 transition) is not observed in the spectrum. Again, a similar behavior was found for $\text{Pt}(\text{2-thpy-h}_6)_2$,⁴⁵ as well as for several other transition metal complexes with organic ligands, such as $[\text{Ru}(\text{bpy})_3]^{2+}$,^{27,29} and $[\text{Os}(\text{bpy})_3]^{2+}$.^{29,79} The intensity mechanism, which induces the corresponding radiative deactivation process versus a “false origin”, is based on a vibrational coupling of a higher lying electronic state to state I. For this process—known as vibronic or Herzberg–Teller (HT) coupling (e.g., see refs 29, 68, and 79–82)—it is required that the transition between the higher lying state and the ground-state carries sufficient allowedness. In particular, all intense peaks seen in the spectrum of Figure 2a represent such HT satellites (e.g., 253 , 467 , 578 , 685 , 992 , and 1461 cm^{-1} ; Figure 2a and Table 2). Several of these couple with Franck–Condon (FC) active vibrations (see below) and lead to combinations which, however, are relatively weak (e.g., $253 + 687$, $467 + 687$, $578 + 184$, and $685 + 687\text{ cm}^{-1}$; Figure 2a).

In the discussed C_{2v} parent group, vibrational modes of a_2 , b_1 , and b_2 representations can induce this vibronic (Herzberg–Teller) coupling between triplet sublevel I of A_2 representation and higher lying A_1 , B_1 , and B_2 singlets, respectively. Such processes can induce intensities in the vibrational satellites, which then can occur as “false origins” in the emission spectrum from state I.

Hitherto, a normal-coordinate analysis is not available for $\text{Pt}(\text{2-thpy})_2$, but it is possible to assign the low-energy satellites (below $\approx 100\text{ cm}^{-1}$ relative to the electronic origin) to modes which are predominantly determined by the lattice (local phonon modes, e.g. at 15 , 34 , 62 , and 80 cm^{-1}). Phonon satellites with the same energies are also found for the perprotonated compound doped into *n*-octane.⁴⁵ In the energy range between ≈ 100 and $\approx 550\text{ cm}^{-1}$, one observes the metal–ligand (M–L) vibrations, and satellites corresponding to vibrational energies higher than $\approx 550\text{ cm}^{-1}$ are assigned to internal ligand vibrations.^{29,45,46} These are of particular importance in the scope of this investigation, since such vibrations do not exhibit any significant vibrational coupling between different ligands (see sections 3.2 and 4.2. and refs 26, 27, 29, 31, 33–35, and 64–68).

With temperature increase, state II is additionally repopulated, and according to the drastically higher radiative rate from state II to state 0 (compared to the forbidden transition from I to 0), the emission from state II grows in (Figure 2b). Further, the emission spectrum shows that the electronic origin strongly dominates, which is a consequence of a direct first-order spin–orbit coupling of a higher lying singlet state to triplet sublevel II.^{45,83} Moreover, in this situation, when the electronic origin carries high allowedness, it is expected that the vibrational

(73) Westra, J.; Glasbeek, M. *Chem. Phys. Lett.* **1991**, *180*, 41.

(74) Okabe, N.; Ikeyama, T.; Azumi, T. *Chem. Phys. Lett.* **1990**, *165*, 24.

(75) Strasser, J.; Homeier, H. H. H.; Yersin, H. *Chem. Phys.*, submitted for publication.

(76) Scott, P. L.; Jeffries, C. D. *Phys. Rev.* **1962**, *127*, 32.

(77) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Clarendon Press: Oxford, U.K., 1970; Chapter 10, p 541.

(78) Henderson, B.; Imbusch, G. F. *Optical Spectroscopy of Inorganic Solids*; Clarendon Press: Oxford, U.K., 1989.

(79) Braun, D.; Hensler, G.; Gallhuber, E.; Yersin, H. *J. Phys. Chem.* **1991**, *95*, 1067.

(80) Albrecht, A. C. *J. Chem. Phys.* **1963**, *38*, 354.

(81) Fischer, G. *Vibronic Coupling*; Academic Press: London, 1984.

(82) Flint, C. D., ed. *Vibronic Processes in Inorganic Chemistry*; NATO ASI Series C, Vol. 288; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989.

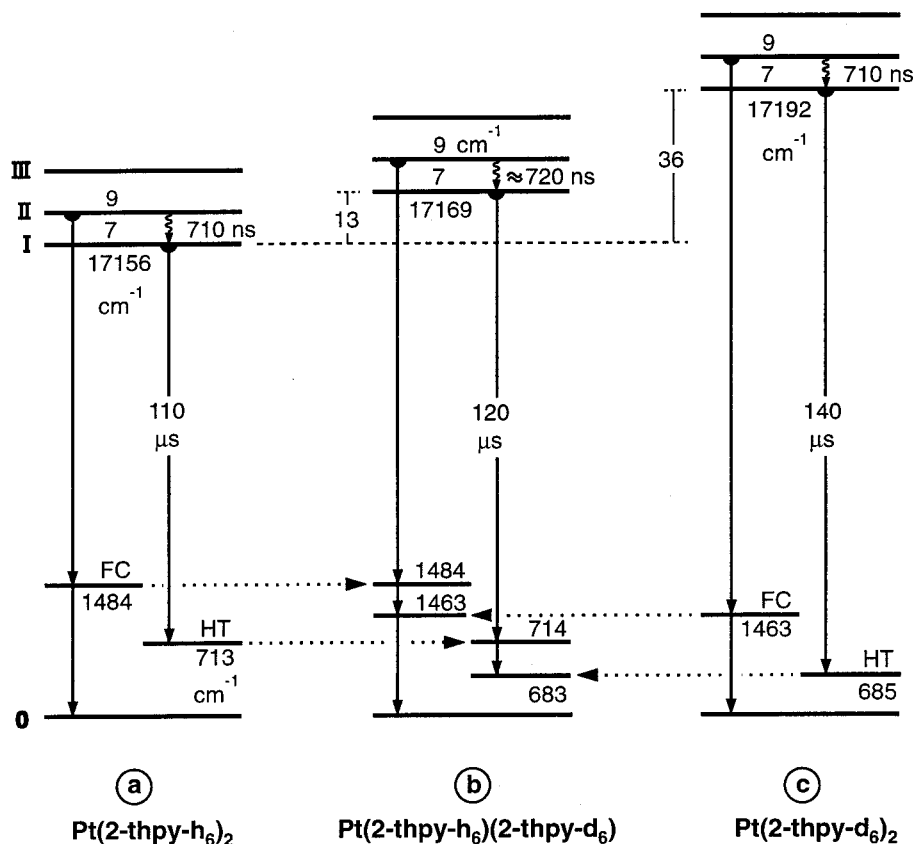


Figure 4. Splitting patterns of the lowest triplets of perprotonated, partially deuterated, and perdeuterated $\text{Pt}(\text{2-thpy})_2$ in *n*-octane. Emission decay times and spin–lattice relaxation times are given for $T = 1.3$ K. FC and HT modes represent Franck–Condon- and Herzberg–Teller-active vibrational modes, respectively. The energy of state **I** of $\text{Pt}(\text{2-thpy-h}_6)(\text{2-thpy-d}_6)$ refers to the lower lying site A.

Table 2. Prominent Satellites (cm^{-1}) of High-Energy Vibrational Ligand Modes Found in the 1.3 K Emission Spectra of $\text{Pt}(\text{2-thpy-h}_6)_2$, $\text{Pt}(\text{2-thpy-h}_6)(\text{2-thpy-d}_6)$, and $\text{Pt}(\text{2-thpy-d}_6)_2^a$

| $\text{Pt}(\text{2-thpy-h}_6)_2$ | $\text{Pt}(\text{2-thpy-h}_6)(\text{2-thpy-d}_6)$ site A | $\text{Pt}(\text{2-thpy-d}_6)_2$ |
|----------------------------------|---|----------------------------------|
| 17156 ^b | 17169 ^b | 17192 ^b |
| | 578 | 578 |
| | 614 | 614 |
| 631 | 631 | |
| | 685 | 685 |
| 713 | 713 | |
| | 724 | 724 |
| 1112 | 1114 | |
| | 1230 | 1230 |
| | 1260 | 1260 |
| 1293 | 1293 | |
| 1393 | 1393 | |
| | 1411 | 1411 |
| 1462 | 1462 | 1462 |
| 1484 | 1484 | |

^a All satellites belong to the respective lowest electronic origin **I**.

^b Electronic origin **I**. (Error: $\pm 1 \text{ cm}^{-1}$.)

satellites result mainly from Franck–Condon (FC) progressions with totally symmetric modes.^{29,79–83} Indeed, fundamentals at 372 and 687 cm^{-1} are accompanied by overtones at 2×372 and $2 \times 687 \text{ cm}^{-1}$, respectively. From the intensity distributions of these extremely weakly appearing progressions, one can still determine the corresponding Huang–Rhys factors S .^{84,85} One obtains very small values of $S \approx 0.1$. This result allows us to

conclude,^{26,27,29} as for the perprotonated compound,⁴⁵ that state **II** and the ground state **0** have very similar equilibrium positions of their potential surfaces. This conclusion may also be extended to states **I** and **III** with respect to the ground state **0**.⁴⁵

Most of the vibrational satellites, which grow in with increasing temperature together with origin **II** (Figure 2b), are presumably also assignable to FC-active modes, however, with even smaller Huang–Rhys factors. Thus, the corresponding overtones are expected to be hidden in the noise of the emission signal.

Moreover, the emission spectrum at $T = 4.2$ K exhibits a number of additional satellites, which do not grow in with temperature increase. These have to be assigned to an emission from state **I** induced by the HT activity. These satellites are also designated in Figure 2b.

The structure of the emission spectra with respect to the vibrational satellites and their intensities is somewhat altered upon perdeuteration, as expected (see the discussion in section 3.1). Nevertheless, it is possible, even without having normal-coordinate analyses, to correlate a large number of vibrational modes of the perdeuterated compound to those of the perprotonated compound. This is mainly achieved by comparing the intensity patterns in the emission spectra and by taking into account that the modes of the perdeuterated compound are shifted to lower energies. This correlation is carried out in Figure 5 for the nontotally symmetric HT-active modes (emission from state **I**) and in Figure 6 for the modes, which presumably are all totally symmetric FC-active modes (emission from state **II**).

(83) Hochstrasser, R. M. *Molecular Aspects of Symmetry*; W. A. Benjamin Inc.: New York, Amsterdam, 1966.

(84) Solomon, E. I. *Comments Inorg. Chem.* **1984**, *3*, 308.

(85) Denning, R. G. In *Vibronic Processes in Inorganic Chemistry*; Flint, C. D., Ed.; NATO ASI Series C: Mathematical and Physical Sciences, Vol. 288; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; p 111.

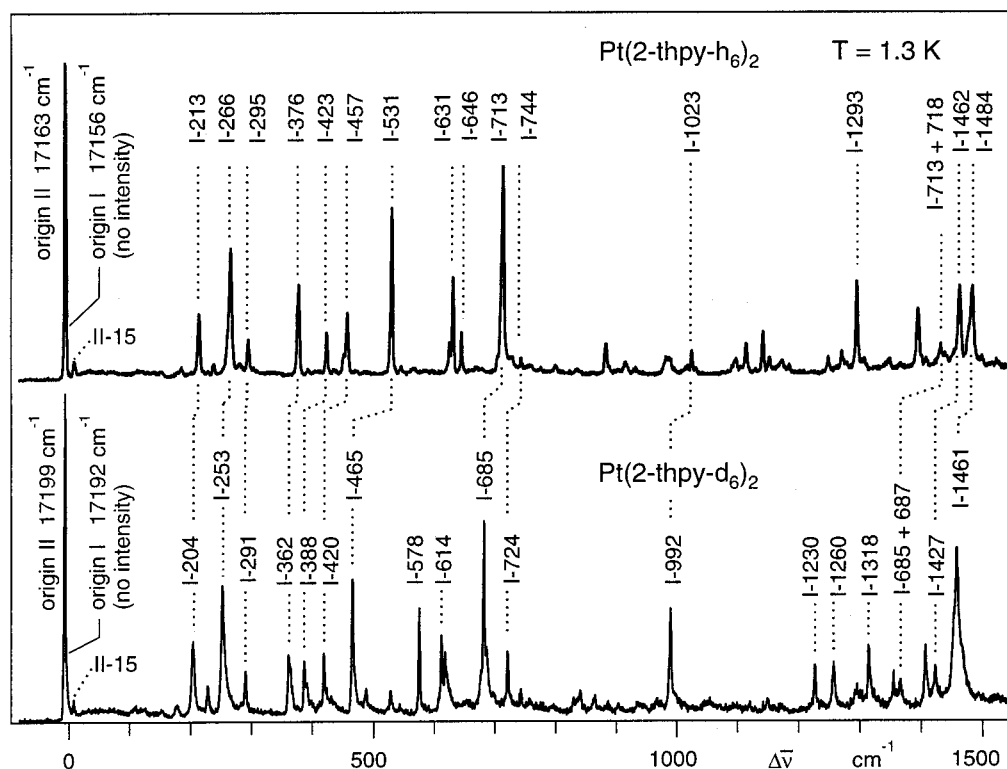


Figure 5. Emission spectra of $\text{Pt}(\text{2-thpy-}h_6)_2$ and $\text{Pt}(\text{2-thpy-}d_6)_2$ in *n*-octane at $T = 1.3$ K. $\lambda_{\text{exc}} = 457.9$ nm. The wavenumber scale gives the separation from the lowest triplet origins I, which are set to zero for both compounds. Several vibrational modes of the perprotonated compound may be correlated to those of the perdeuterated compound (connected by dotted lines). All satellites (fundamentals) are vibronically induced ("false origins").

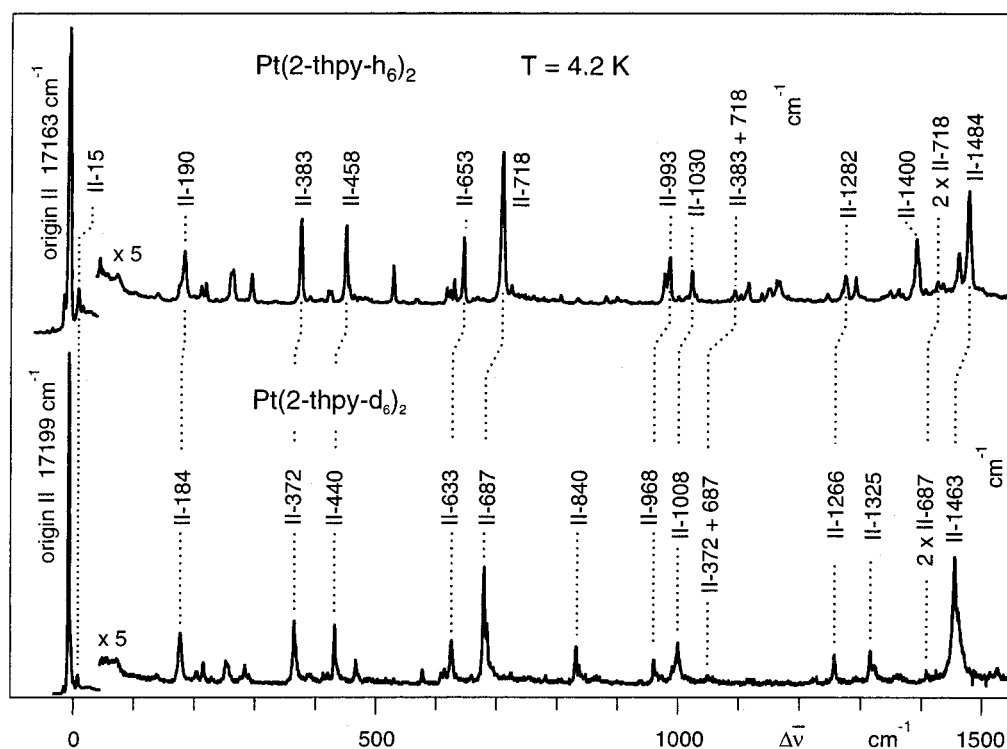


Figure 6. Emission spectra of $\text{Pt}(\text{2-thpy-}h_6)_2$ and $\text{Pt}(\text{2-thpy-}d_6)_2$ in *n*-octane at $T = 4.2$ K. $\lambda_{\text{exc}} = 457.9$ nm. The wavenumber scale gives the separation from the second triplet origins II, which are set to zero for both compounds. Several vibrational modes of the perprotonated compound may be correlated to those of the perdeuterated one (connected by dotted lines). The intense satellites are assigned to Franck–Condon-active modes.

(The symmetry message refers to the C_{2v} parent group of $\text{Pt}(\text{2-thpy})_2$.)

4.2. Delocalized Triplet in $\text{Pt}(\text{2-thpy-}h_6)(\text{2-thpy-}d_6)$. Deuteration of one ligand of $\text{Pt}(\text{2-thpy})_2$ leads to very characteristic

isotope effects, which will be studied in this section. The evaluation with respect to the spatial extension in the excited state(s) requires some detailed knowledge about the structure of the vibrational satellites observed, in particular, in the

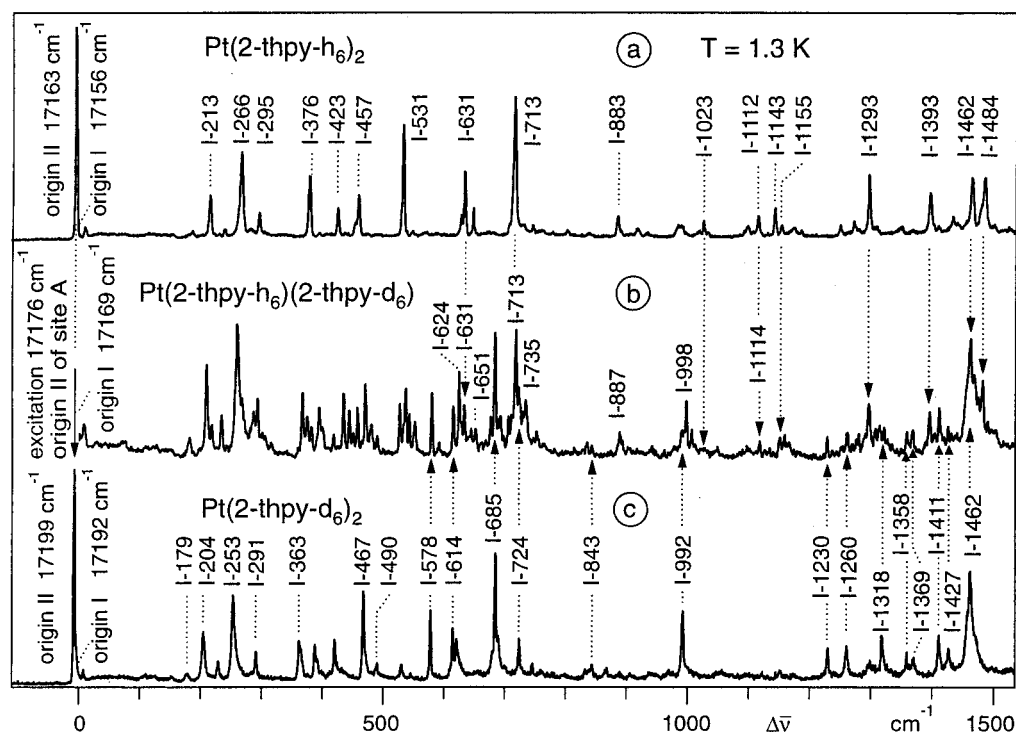


Figure 7. Emission spectrum of Pt(2-thpy- h_6)(2-thpy- d_6) (b) at $T = 1.3$ K (site A) compared to the emission spectra of the per-compounds (a, c). The compounds are dissolved in *n*-octane. Spectra a and c are excited at $\lambda_{\text{exc}} = 457.9$ nm ($\approx 21\,839$ cm^{-1}), while spectrum b is selectively excited at $17\,176$ cm^{-1} (origin II of site A). The wavenumber scales are set to zero with respect to the origins I of all three compounds. The emission spectrum of Pt(2-thpy- h_6)(2-thpy- d_6) (b) exhibits many satellites, which distinctly result from high-energy internal ligand vibrations of the protonated **and** the deuterated ligands (marked by arrows). Note, all satellites in spectrum b belong to the same electronic origin I at $17\,169$ cm^{-1} .

emission spectra. The basic information needed has already been worked out in the preceding section.

Fortunately, Pt(2-thpy- h_6)(2-thpy- d_6) can also be doped into an *n*-octane matrix like the two per-compounds, and one also obtains highly resolved spectra. However, due to slightly different chromophore–matrix interactions, the partially deuterated dopant is built in on two different chromophore sites, A and B, which are nearly equally important. The lowest electronic origin I of site A lies at $17\,169$ cm^{-1} , while the corresponding 0–0 transition of site B is found at 8 cm^{-1} higher energy. Similarly, as for the two per-compounds, the purely electronic transitions between states **I** and **0** are strongly forbidden for both sites. Again, the second electronic origins II(A) at $17\,176$ cm^{-1} and II(B) at $17\,184$ cm^{-1} , respectively, carry significant allowedness and can therefore directly and selectively be excited. Thus, one obtains well-separated site A emission spectra. In particular, this possibility of being able to selectively excite one specific site provides clear proof for the assignment of sites. In the subsequent discussion, we want to focus only on site A, since the properties of site B seem to be very similar.

It is an important result with respect to the criteria presented in section 3.2.2 that also Pt(2-thpy- h_6)(2-thpy- d_6) exhibits only one set of three triplet sublevels (criterion 1). The corresponding electronic origins of site A are equally blue shifted by 13 cm^{-1} relative to the energies of the perprotonated compound (Figure 4b). This value is somewhat smaller than half of the total blue shift of 36 cm^{-1} as found for the perdeuterated Pt(2-thpy) $_2$. Thus, the internal effect, which results from differences of the zero-point vibrational energies between excited state and ground state (section 3.1), is superimposed by a slight shift due to the chromophore–matrix interaction. Nevertheless, criterion 2 of Section 3.2.2 is also fulfilled.

The most important criterion (3) for the occurrence of a delocalized situation is illustrated by use of Figure 7. Figure 7b shows the emission spectrum of Pt(2-thpy- h_6)(2-thpy- d_6) measured at $T = 1.3$ K. The compound is excited selectively at the electronic origin II at $17\,176$ cm^{-1} of site A. For a better comparison of the vibrational satellite structures, the spectra of the two per-compounds are—as already shown in Figure 5—also reproduced in the same figure (Figure 7a,c). Further, the electronic origins I of all three compounds are set to zero on a wavenumber scale. Thus, Figure 7 demonstrates clearly that the partially deuterated compound exhibits a large number of vibrational satellites which have to be assigned to both ligands, the protonated **and** the deuterated ones. (See also Table 2) According to criterion 3 (section 3.2.2), this comparison is only carried out for the high-energy internal ligand modes ($\bar{\nu} > 550$ cm^{-1}), which—within limits of experimental error—do not couple vibrationally. It is stressed that all these vibrational satellites belong to one single electronic origin I, which lies at $17\,169$ cm^{-1} . In particular, this result requires the assignment to a delocalized situation.

According to the discussion in section 4.1.2, the vibrational satellites marked by arrows in Figure 7b have to be classified as vibronically induced (HT satellites) and may be assigned within the C_{2v} parent group to correspond to unsymmetric vibrational modes.

Figure 8 demonstrates that an equivalent conclusion can also be drawn from the 4.2 K emission spectrum. In this case, one observes mainly the emission from state **II**. The corresponding vibrational satellites of Pt(2-thpy- h_6)(2-thpy- d_6) are probably all assignable to totally symmetric Franck–Condon-active modes (at least the intense satellites; see also section 4.1.2). Again, vibrational satellites corresponding to both ligands are observed, and they belong only to one single origin II at $17\,176$ cm^{-1} .

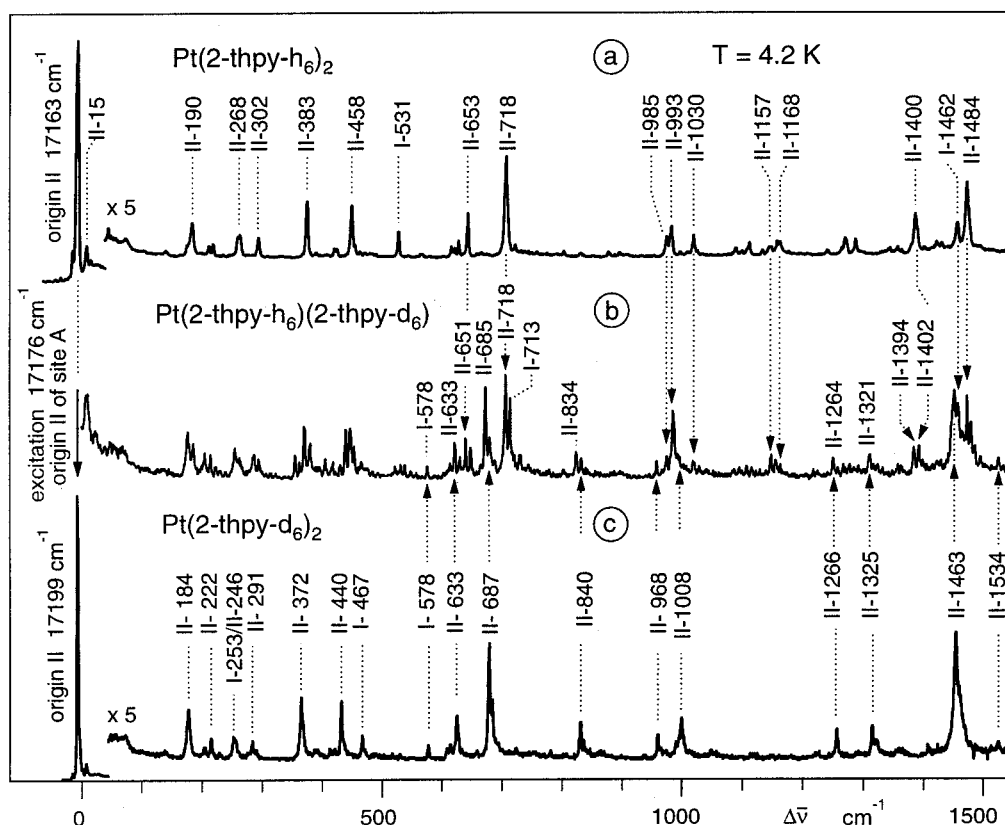


Figure 8. Emission spectrum of $\text{Pt}(\text{2-thpy-}h_6)(\text{2-thpy-}d_6)$ (b) at $T = 4.2$ K (site A) compared to the emission spectra of the per-compounds (a, c). The wavenumber scales are set to zero with respect to the electronic origins II of all three compounds. The emission spectrum of $\text{Pt}(\text{2-thpy-}h_6)(\text{2-thpy-}d_6)$ (b) exhibits many vibrational satellites in the high-energy range of internal ligand vibrations, which have to be assigned to **both** ligands (see the arrows). Note: all these satellites belong to the same electronic origin II at $17\,176\text{ cm}^{-1}$ of site A. For further data, see the caption to Figure 7.

(site A). (See Table 3.) It follows that also the triplet sublevel **II** is delocalized over the two ligands.

Interestingly, the information with respect to an involvement of the two ligands is manifested by different vibrational coupling mechanisms, by Herzberg–Teller activity, and by Franck–Condon activity for emissions of state **I** and state **II**, respectively. Obviously, the coupling mechanisms are not significantly altered due to the partial deuteration (see also section 4.2.1).

Finally, the emission decay behavior also fits well to the model described. At $T = 1.3$ K, the emission decay time is mainly determined by the radiative and nonradiative processes of state **I**. For $\text{Pt}(\text{2-thpy-}h_6)(\text{2-thpy-}d_6)$, one finds a value of $120 \pm 3\text{ }\mu\text{s}$, which thus lies between $110 \pm 3\text{ }\mu\text{s}$ and $140 \pm 3\text{ }\mu\text{s}$ of the protonated and perdeuterated compounds, respectively. (See also Figure 4.) Apart from the effects of spin–lattice relaxation occurring in about the first microsecond (section 4.1.1 and refs 30 and 46), the decay is strictly monoexponential, at least over 5 lifetimes. It is important that the decay is exactly equal when measured on a vibrational satellite which is related to the protonated part of the molecule (e.g., the 713 cm^{-1} satellite) and to the deuterated part (e.g., the 685 cm^{-1} satellite), respectively (Figure 7b, Table 2). Also, this result strongly supports the assignment to a delocalized excited state. (Compare also ref 34.)

In summary, the spectroscopic properties of $\text{Pt}(\text{2-thpy-}h_6)(\text{2-thpy-}d_6)$ doped into *n*-octane can only be explained on the basis of a delocalized situation. All criteria developed for this situation are fulfilled as could be shown directly for the triplet sublevels **I** and **II**, while the fingerprints for the localized situation (section

Table 3. Prominent Satellites (cm^{-1}) of High-Energy Vibrational Ligand Modes Found in the 4.2 K Emission Spectra of $\text{Pt}(\text{2-thpy-}h_6)_2$, $\text{Pt}(\text{2-thpy-}h_6)(\text{2-thpy-}d_6)$, and $\text{Pt}(\text{2-thpy-}d_6)_2$ ^a

| $\text{Pt}(\text{2-thpy-}h_6)_2$ | $\text{Pt}(\text{2-thpy-}h_6)(\text{2-thpy-}d_6)$ site A | $\text{Pt}(\text{2-thpy-}d_6)_2$ |
|----------------------------------|---|----------------------------------|
| 17 163 ^b | 17 176 ^b | 17 199 ^b |
| | 633 | 633 |
| 653 | 651 | |
| | 687 | 687 |
| 718 | 718 | |
| | 968 | 968 |
| 993 | 993 | |
| 1157 | 1157 | |
| | 1264 | 1266 |
| 1400 | 1402 | |
| | 1463 | 1463 |
| 1484 | 1484 | |
| | 1534 | 1534 |

^a All satellites belong to the respective second electronic origin II.

^b Electronic origin II. (Error: $\pm 1\text{ cm}^{-1}$.)

3.2.1) do not fit to the experimental situation. In an additional experiment, it was also possible to demonstrate that, after application of a high magnetic field of $B = 12$ T, the lowest excited state is still delocalized, as is evidenced again by the occurrence of vibrational satellites corresponding to both ligands in the emission of this magnetically distorted state **I**. (A similar situation has already been described for $[\text{Os}(\text{bpy-}h_8)_2(\text{bpy-}d_8)]^{2+}$; see also ref 34.) According to the fact that state **I** exhibits a very strong Zeeman interaction with state **III** (e.g., compare refs 29, 47, 86, and 87), we can conclude that sublevel **III** is delocalized, too.

5. Conclusion

Highly resolved emission spectra of compounds with isotopically labeled ligands display distinct fingerprints with respect to the spatial extension of excited states. Using these relatively simple and distinct fingerprints, which are based mainly on a comparison of emission properties of the perprotonated, perdeuterated, and partially deuterated compounds, one can decide whether an excited state is localized or delocalized. This procedure was applied to $\text{Pt}(\text{2-thpy})_2$. It could be shown that the three sublevels of the lowest excited triplet of $\text{Pt}(\text{2-thpy-}h_6)(\text{2-thpy-}d_6)$ are delocalized over the two different ligands. Although, the partial deuteration induces a slight distortion, this effect is not large enough to induce a localization. From this result it can also be concluded that the triplets of the homoleptic, more symmetric per-compounds $\text{Pt}(\text{2-thpy-}h_6)_2$ and $\text{Pt}(\text{2-thpy-}d_6)_2$ are delocalized, too.

With regard to the sequence of compounds shown in Figure 1, the result obtained in the present investigation is of particular interest, since $\text{Pt}(\text{2-thpy})_2$ represents a compound with a significantly smaller MLCT contribution in the lowest excited states than is found for $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Os}(\text{bpy})_3]^{2+}$. For example, the amount of zero-field splitting of the triplet, being characteristic for the metal admixture, is smaller by a factor of about 4 for $\text{Pt}(\text{2-thpy})_2$ than for $[\text{Ru}(\text{bpy})_3]^{2+}$. Nevertheless, one still finds a delocalized situation. From this behavior, we may come to the conclusion that, for homoleptic compounds (with symmetry-related ligands) doped into rigid matrices, already a moderate metal character couples the different ligands sufficiently and induces a delocalized situation.

Although the results presented in this investigation clearly show that the interaction between the ligands is metal mediated, alternative models are briefly addressed. For example, an intramolecular "triplet exciton coupling" can be ignored due to the extremely small interaction energy, which is—according to

the Davydov model (compare refs 88 and 89)—approximately proportional to the square of the corresponding transition matrix element. Since, for example the 0–0 transition between states **I** and **0** is strongly forbidden (section 4.1.1), the matrix element and thus this coupling contribution are negligible. Moreover, also a direct ligand–ligand coupling (if the metal is ignored) does not seem to be very important. In particular, $[\text{Rh}(\text{bpy})_3]^{3+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ should exhibit nearly the same ligand–ligand couplings due to very similar molecular structures. However, the localization/delocalization behavior is totally different, as is discussed in section 1 and in refs 27, 29, and 33. This distinctly different behavior represents strong support for the metal-mediated ligand–ligand coupling. Nevertheless, it is still of interest to investigate the importance of a direct ligand–ligand coupling for a nearly planar compound, like $\text{Pd}(\text{2-thpy})_2$. For this compound, the metal character in the lowest excited state is small, as is, for example, displayed in the small zfs value of 0.0962 cm^{-1} ⁹⁰ ($2E$ parameter). (Compare also refs 47 and 87.) Thus, it is currently planned to study the spatial extension of the excited triplet also for this $\text{Pd}(\text{II})$ compound. For future investigations, it is further of interest to find a compound with an intermediate metal character in the lowest excited state. Possibly, in this situation changes of *physical* parameters, like external magnetic fields, high pressure, etc., might allow us to tune between a localized and a delocalized situation.

Acknowledgment. Financial support from the Deutsche Forschungsgemeinschaft and the Verband der Chemischen Industrie is gratefully acknowledged. We also thank Degussa AG (Haunau, Germany) for a donation of $\text{K}_2[\text{PtCl}_4]$.

IC990582P

(86) Gallhuber, E.; Hensler, G.; Yersin, H. *J. Am. Chem. Soc.* **1987**, *109*, 4818.

(87) Schmidt, J.; Wiedenhofer, H.; von Zelewsky, A.; Yersin, H. *J. Phys. Chem.* **1995**, *99*, 226.

(88) Craig, D. P.; Walmsley, S. H. *Excitons in Molecular Crystals*; W. A. Benjamin, Inc.: New York, 1968.

(89) Yersin, H.; Hensler, G.; Gallhuber, E. *Inorg. Chim. Acta* **1987**, *132*, 187.

(90) Glasbeek, M.; Sitters, R.; van Veldhoven, E.; von Zelewsky, A.; Humbs, W.; Yersin, H. *Inorg. Chem.* **1998**, *37*, 5159.