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A 195Pt NMR Study on Zero-Magnetic-Field Splitting and the Phosphorescence Properties in the Excited Triplet States of Cyclometalated Platinum(II) Complexes

Soichiro Akagi,a Sho Fujii*a,b and Noboru Kitamura*a,b,c

We report the factor governing zero-magnetic-field splitting (zfs) in the lowest-energy electronically excited triplet (T1) states of cyclometalated platinum(II) complexes, whose zfs energies between the lowest- (zfs) and highest-energy spin-sublevels (zfs) in the T1 states (∆Ezfs) have been already known: [Pt(bhp)(dpm)] (1Pt), [Pt(thpy)(acac)] (2Pt), [Pt(ppy)(acac)] (3Pt), cis-[Pt(thpy)(acac)] (4Pt), and cis-[Pt(ppy)(acac)] (5Pt) where bhp, dpm, thpy, acac, and ppy are benzo[h]quinoline, dipivaloilmethanone, 2-[2-thienyl]pyridine, acetylacetone, and phenylpyridine, respectively. As one of the important findings, we show the relationship between ∆Ezfs and 195Pt NMR chemical shifts of the five Pt(II) complexes. The implications of the ∆Ezfs values to the emission properties of the Pt(II) complexes in acetonitrile at 293 K are also discussed. In particular, we demonstrate the radiative rate constants of the Pt(II) complexes correlate with both ∆Ezfs and 195Pt NMR chemical shifts.

Introduction

The spin-sublevels in the excited emission triplet state (∆Ezfs) of a molecule possess own emission parameters (maximum energy (∧em), lifetime (τem), quantum yield (Φem), radiative (kθ) and nonradiative rate constants (kν)) and, therefore, the observed emission properties become the average of the Boltzmann weighted sum of the emission properties of ∆Ezfs. In particular, since the splitting energy between the lowest-energy zfs and higher-energy zfs or zfs (ΔEzfs, zfs: zero-magnetic field splitting) of a transition metal complex is large compared to that of an ordinary organic molecule without a heavy atom element (ΔEzfs << 1 cm⁻¹), the emission properties show sometimes relatively large T-dependences depending on ΔEzfs. As an example, the ΔEzfs value between zfs and zfs in the lowest-energy excited triplet (T1) state (∆Ezfs) of [Ru(bpy)3]²⁺ (bpy = 2,2'-bipyridine) is as large as ~62 cm⁻¹. Reflecting such large ΔEzfs, [Ru(bpy)3]²⁺ shows large T-dependences of τem and Φem in 3 < T < 300 K. Such results indicate that the ∆Ezfs value of a transition metal complex plays decisive roles in determining the emission properties of the complex. Importantly, Yersin et al. have reported that the ∆Ezfs values of a variety of Pt(II), Ir(III), Ru(II), Os(II), and Re(III) complexes are governed by nature of the emissive T1 state and increase in the sequence, the ligand-centered (LC) < LC/metal-to-ligand charge transfer (MLCT) < MLCT excited state with ∆Ezfs being varied from < 1 (LC, [Rh(bpy)3]³⁺) to ~180 cm⁻¹ (MLCT, [Ir(4-phenylpyridine)3]).³ They have also demonstrated that the kθ value of the complex increases in this sequence. It is worth emphasizing that the increasing order of ΔEzfs mentioned above agrees with that of the d-electron character in the T1 state. Nevertheless, prediction of ΔEzfs or d-electron character in the T1 state of a transition metal complex is a very difficult task in the present stage of the investigations.

We reported recently that the ΔEzfs (∆Ezfs (n = 3 or 4)) values of a series of nine octahedral hexanuclear molybdenum(II) complexes, [(Mo5X8)Y2]²⁻ (X = Y = Cl, Br, or I), correlated with the 95Mo NMR chemical shifts of [(Mo5X8)Y2]²⁻:δ95Mo).⁴ The correlation between ∆Ezfs and δ95Mo observed for [(Mo5X8)Y2]²⁻ is very important, since the NMR chemical shift of the metal center (δ(M)) in an any transition metal complex might predict the zfs energy, although one cannot predict its absolute value. In the present stage of the investigations, nevertheless, the experimental study on the relationship between ∆Ezfs and δ(M) of a transition metal (M) complex is limited to that of [(Mo5X8)Y2]²⁻ alone.⁴ An experimental study on the generality of the relationship between ∆Ezfs and δ(M) other than [(Mo5X8)Y2]²⁻ is thus worth conducting in detail.

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Chart 1. Structures and abbreviations of the Pt(II) (1Pt–5Pt). bhq = benzo[h]quinoline; thpy = 2-(2-thienyl)pyridine; ppy = 2-phenylpyridine; dpm = dipivaloylmethane; acac = acetylacetone.

In the present study, we focus on luminescent mononuclear cyclometalated square-planar Pt(II) complexes (nPt, 1Pt–5Pt) shown in Chart 1, whose zfs energies between the lowest- ($\phi_1$) and highest-energy spin-sublevels ($\phi_3$) ($\Delta E_{\text{zfs}} = \Delta E_{13}$) in the T_1 states have been reported by Yersin et al.: $\Delta E_{13} = 1–32$. In particular, we have paid special attention to the $\delta^{195}\text{Pt}$ NMR chemical shifts ($\delta(195\text{Pt})$) of $nPt$ to check the relationship between $\Delta E_{13}$ and $\delta^{195}\text{Pt}$. In order to pursue such a study, we prepared $1Pt–3Pt$ to conduct $^{195}\text{Pt}$ NMR spectroscopy in the present study, while we employed the reported $\delta^{195}\text{Pt}$ data on $4Pt$ and $5Pt$. Implications of $\delta^{195}\text{Pt}$ and $\Delta E_{13}$ values of $nPt$ to the emission properties of the complexes in acetonitrile at 293 K are also reported.

Results and discussion

$\Delta E_{13}$ and $^{195}\text{Pt}$ NMR Spectroscopy of Luminescent Platinum(II) Complexes. The $\Delta E_{13} (= \Delta E_{13})$ values in the T_1 states of $1Pt–5Pt$ reported by Yersin et al. are summarized in Table 1. The $\Delta E_{13}$ values of $1Pt–5Pt$ are sensitive to the ligand structures and vary in 1–36 cm$^{-1}$. In general, the combination of an O$^\text{O}$ (dpm or acac) or C$^\text{N}$ ligand (bhq, thpy, or ppy) with a Pt(II) ion ($1Pt–3Pt$) gives rise to small $\Delta E_{13}$ (1–11.5 cm$^{-1}$) compared to that of the complex having two C$^\text{N}$ ligands (i.e., homoleptic complex, $4Pt$ or $5Pt$, 16–32 cm$^{-1}$) as seen in Table 1. For a given ligand in the heteroleptic O$^\text{O}$-C$^\text{N}$ and homoleptic C$^\text{N}$-C$^\text{N}$ Pt(II) complexes shown in Chart 1, furthermore, the $\Delta E_{13}$ value increases in the sequence, benzo[h]quinoline (bhq) < 2-(2-thienyl)pyridine (thpy) < 2-phenylpyridine (ppy). In the case of ${\text{[Mo}_6\text{X}_8\text{Y}_6]}^{2–}$, we have reported that the zfs energies ($\Delta E_{13}/\Delta E_{14}$) in the T_1 states of the complexes correlate with the $^{95}\text{Mo}$ NMR chemical shifts of the clusters as described above. In order to check the generality of the relationship between $\Delta E_{13}$ and $\delta(M)$ of a complex, therefore, we evaluated the $\delta^{195}\text{Pt}$ values of $nPt$.

Figure 1a shows the $^{195}\text{Pt}$ NMR spectra of $1Pt–3Pt$ in CDCl_3 at 293 K, and the relevant $\delta^{195}\text{Pt}$ values are included in Table 1, together with those of $4Pt$ and $5Pt$ reported by Chassot et al.$^5$

As seen in Table 1, the heteroleptic O$^\text{O}$-C$^\text{N}$ Pt(II) complexes

Experimental

Pt(II) Complexes. [Pt(C$^\text{N}$)(O$^\text{O}$)] complexes (1Pt–3Pt) were synthesized according to the literature.$^6$ The details of the synthesis and characterizations of the complexes are reported in Supporting Information.

Physical Measurements. $^{195}\text{Pt}$ NMR spectroscopy was conducted by using a 400 MHz JNM-ECZ spectrometer (JEOL Ltd). For $^{195}\text{Pt}$ NMR spectroscopy, potassium tetrachloro-platinate (in D_2O, ~1618 ppm with respect to hexachloroplatinate) was used as an external standard for determining the chemical shifts of the NMR signals in ppm.

Spectroscopic grade acetonitrile, supplied from Wako Pure Chemicals Co. Ltd., was used for emission spectroscopy under deaerated conditions at 293 K. Corrected emission spectra of the Pt(II) complexes were recorded on a PMA-11 multichannel photodetector (Hamamatsu Photonics K.K.). For emission lifetime measurements, 355 nm laser pulses (LS-2137, LOTIS TII Ltd., pulse width = ~10 ns) and a C4334 streak camera (Hamamatsu Photonics K.K.) equipped with a CS094 imaging spectrograph (Hamamatsu Photonics K.K.) were used as an excitation light source and a photodetector, respectively. The absolute emission quantum yields of the Pt(II) complexes in acetonitrile at 293 K were determined by a C9920-02 system equipped with an integrating sphere and a red-sensitive PMA-12 photodetector (Hamamatsu Photonics K.K.) at 400 nm excitation.


Furthermore, the δ(195Pt) values of δ observed for δ ligand correlates with the decreasing order of opposite trend of the relationship between Δ covalency of a metal-ligating atom bond, and so forth. The density on the H atom, while the NMR chemical shift of a metal chemical shift (in ppm) implies an increase in the electron metal atom: strength of ligand-field splitting, degree of largely by the d-electron character and, thus, by the electronic structures, the in D2O) of to the more negative direction) gives rise to an increase in the δ(195Pt) values. Figure 1b demonstrates that a decrease in δ(195Pt) (i.e., to the more negative direction) gives rise to an increase in the ΔE_zfs value: negative relationship between ΔE_zfs and δ(195Pt). This is contrasted to the results on [(Mo6X8)Y6]2– (purely metal-centered complexes) owing to the differences in the ligand electronic structures in the emissive T1 state as reported by Yersin et al.3 We suppose that since the relationship between ΔE_zfs and ΔE_zfs or δ(M) observed for nPt and [(Mo6X8)Y6]2– mentioned above would be due to the different electronic origin in the T1 states of nPt (LC/MLCT characters) and [(Mo6X8)Y6]2– (purely metal-centered characters): discussed later again. It is worth noting, furthermore, that the ΔE_zfs value of a Pt(II) complex is influenced largely by the d-electron character and, thus, by the electronic structures in the emissive T1 state as reported by Yersin et al.3 We suppose that since the relationship between ΔE_zfs and ΔE_zfs observed for 4Pt and 5Pt (heteroleptic complexes) will be different from that observed for 1Pt–3Pt (heteroleptic complexes) owing to the differences in the ligand electronic structures, the ΔE_zfs(195Pt) dependence of ΔE_zfs or d-electron character will be valid for a series of the complexes having similar ligand electronic structures. Further systematic study on the relationship between ΔE_zfs and δ(M) of a transition metal complex is absolutely necessary.

Table 1. ΔE_zfs (determined in n-alkane matrices by high-resolution emission spectroscopy) and δ(195Pt) values (in ppm, determined in CDCl3 relative to that of K2PtCl4 in D2O) of 1Pt–5Pt.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>1Pt</th>
<th>2Pt</th>
<th>3Pt</th>
<th>4Pt</th>
<th>5Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE_zfs</td>
<td>–1</td>
<td>4.3</td>
<td>11.5</td>
<td>16</td>
<td>32</td>
</tr>
<tr>
<td>/ cm⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ(195Pt)</td>
<td>–1148</td>
<td>–1165</td>
<td>–1219</td>
<td>–1524</td>
<td>–1518</td>
</tr>
<tr>
<td>/ ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a), b) The data taken from ref. 3 and 5, respectively.

Figure 1. a) 195Pt NMR spectra of 1Pt (black), 2Pt (red), and 3Pt (green) in CDCl3 at 293 K. b) Relationship between ΔE_zfs and ΔE_zfs of 1Pt–5Pt. δ(195Pt) in ppm is relative to that of K2PtCl4 in D2O at 293 K.

Implications of ΔE_zfs to the Phosphorescence Properties of the Platinum(II) Complexes in Acetonitrile at 293 K. In the case of [(Mo6X8)Y6]2– (X = Cl, Br, or I),3 [(Mo6X8)(n-C12H23COO)4]2– (X = Cl, Br, or I),7 and [(Mo6Br8)L6]2– (L = aromatic carboxylates),8 we have reported that the ΔE_zfs (= ΔE_14) values in the T1 states determine the emission characteristics of the clusters in the crystalline phases at 293 K. Furthermore, the photophysical properties of these clusters at 293 K are determined primarily by the relevant emission maximum energies (ṽ_em) through the energy gap dependence of k_int: ln(k_int) ∝ ṽ_em.3,7,8–11 We also reported that the ṽ_em and t_em values of [(Mo6X8)Y6]2– were correlated with ΔE_14, demonstrating that the ΔE_14 value of the cluster governed the k_int value as expected from the relation, ṽ_em = k_r / (k_r + k_int) = k_r t_em, where k_r < k_int.4 These results suggest that the photophysical properties of the present Pt(II) complexes in solution at room temperature might be also governed and explained by the relevant ΔE_zfs or δ(195Pt) values, which is worth discussing further in detail.
The emission spectra and decay profiles of 1Pt–3Pt in acetonitrile at 293 K are shown in Figure 2, while the photophysical properties of the complexes are summarized in Table 2 together with those of 4Pt reported by Maestri et al.12 Unfortunately, the emission data on 5Pt have not been collected since the complex is non-emissive in solution at ambient temperature.12 As seen in Table 2, the \( \bar{v}_{\text{em}}, \tau_{\text{em}}, \text{ and } \Phi_{\text{em}} \) values of 1Pt–4Pt vary in \( \bar{v}_{\text{em}} = (17.30–20.62) \times 10^3 \text{ cm}^{-1}, \tau_{\text{em}} = 2.2–20.3 \mu\text{s}, \text{ and } \Phi_{\text{em}} = 0.095–0.305, \) and the values decrease in the sequences, \( \bar{v}_{\text{em}} = 3Pt > 1Pt > 2Pt > 4Pt, \tau_{\text{em}} = 2Pt > 1Pt > 3Pt > 4Pt, \text{ and } \Phi_{\text{em}} = 2Pt > 4Pt > 3Pt > 1Pt. \) In these data, one cannot find any common tendency in the \( \Delta E_{\text{zfs}} \) dependences of \( \bar{v}_{\text{em}}, \tau_{\text{em}}, \text{ or } \Phi_{\text{em}} \) of the complex. In particular, the \( k_{\text{nr}} \) values of the complexes cannot be explained by the energy gap (\( \bar{v}_{\text{em}} \)) law, probably due to the large differences in the ligand electronic structures in the series of the complexes. In practice, it has been reported that the emissive \( T_1 \) states of 1Pt–3Pt are characterized by LC in nature, while those of 4Pt and 5Pt will possess MLCT characters.3 The LC characters in the \( T_1 \) states of 1Pt–3Pt are confirmed by the structured emission spectra in acetonitrile at 293 K: Figure 2. The small \( \Delta E_{\text{zfs}} \) values of 1Pt–3Pt (1–11.5 cm\(^{-1}\)) relative to that of 4Pt (16 cm\(^{-1}\)) or 5Pt(32 cm\(^{-1}\)) will be also accounted by the smaller d-electron characters in the \( T_1 \) states of 1Pt–3Pt compared to that of 4Pt or 5Pt. Reflecting the stronger MLCT characters, we suppose the \( \delta(195Pt) \) values of 4Pt and 5Pt are observed at a more negative direction (stronger covalency between Pt and the ligating C/N atoms) compared to those of 1Pt–3Pt.

A close inspection of the data in Tables 1 and 2 indicate that the \( k_{\text{nr}} \) value of the complex increases with an increase in \( \Delta E_{\text{zfs}} \) in the sequence, \( k_{\text{nr}} (\times 10^3 \text{ s}^{-1}) \): 1Pt = 0.52 (\( \Delta E_{\text{zfs}} \approx 1 \text{ cm}^{-1} \)) < 2Pt = 1.50 (4.3) < 3Pt = 6.06 (11.5) < 4Pt = 6.06 (16). In practice, the \( k_{\text{nr}} \) values of 1Pt–4Pt show the correlation with the relevant \( \Delta E_{\text{zfs}} \) values as shown in Figure 3a. Interestingly, furthermore, Figures 3b demonstrates that the \( \delta(195Pt) \) value also correlate with the \( k_{\text{nr}} \) values of 1Pt–4Pt and, therefore, with \( \Delta E_{\text{zfs}} \). The results demonstrate clearly that zfs in the \( T_1 \) state plays the decisive roles in determining the emission properties of 1Pt–4Pt in acetonitrile at 293 K. We convince that the present study will offer a novel guideline for developments of new luminescent materials in near future.

**Table 2. Emission properties of 1Pt–4Pt in the \( T_1 \) states at room temperature.**

<table>
<thead>
<tr>
<th></th>
<th>1Pt(^{a})</th>
<th>2Pt(^{a})</th>
<th>3Pt(^{a})</th>
<th>4Pt(^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{v}_{\text{em}} / 10^3 \text{ cm}^{-1} )</td>
<td>19.53</td>
<td>17.92</td>
<td>20.62</td>
<td>17.30</td>
</tr>
<tr>
<td>( \lambda_{\text{em}} / \text{nm} )</td>
<td>(512)</td>
<td>(558)</td>
<td>(485)</td>
<td>(578)</td>
</tr>
<tr>
<td>( \tau_{\text{em}} / \mu\text{s} )</td>
<td>18.4</td>
<td>20.3</td>
<td>3.3</td>
<td>2.2</td>
</tr>
<tr>
<td>( \Phi_{\text{em}} )</td>
<td>0.095</td>
<td>0.305</td>
<td>0.200</td>
<td>0.30</td>
</tr>
<tr>
<td>( k_{\text{nr}} / 10^3 \text{ s}^{-1} )</td>
<td>0.52</td>
<td>1.50</td>
<td>6.06</td>
<td>13.6</td>
</tr>
<tr>
<td>( k_{\text{nr}} / 10^5 \text{ s}^{-1} )</td>
<td>4.92</td>
<td>3.42</td>
<td>24.2</td>
<td>31.8</td>
</tr>
</tbody>
</table>

\(^{a}\) Measured in deaerated acetonitrile at 293 K in the present study.

\(^{b}\) Data in a deaerated propionitrile/buryronitrile mixture taken from ref. 12.

**Figure 3.** \( \Delta E_{\text{zfs}} \) (a) and \( \delta(195Pt) \) (b) of the \( k_{\text{nr}} \) values of 1Pt–4Pt in acetonitrile at 293 K.

**Conclusions**

In this paper, we reported the relationship between the \( \Delta E_{\text{zfs}} \) and \( \delta(195Pt) \) values of the five cyclometalated Pt(II) complexes (1Pt–5Pt). It is worth emphasizing that the relationship between \( \Delta E_{\text{zfs}} \) and \( \delta(95Mo) \) of \( \{[Mo_{6}X_{8}Y_{6}]^{2+} \} \) (X = Cl, Br, or I) has been also confirmed by our research group.3 However, the \( \Delta E_{\text{zfs}} \) values of nPt increased by shifting of \( \delta(195Pt) \) to a more negative direction, while those of \( \{[Mo_{6}X_{6}Y_{6}]^{2+} \} \) showed an opposite trend to that observed for nPt: increase in \( \Delta E_{\text{zfs}} \) by a positive shift of \( \delta(95Mo) \). Since the NMR chemical shift of the metal atom in a transition metal complex is influenced by several factors...
represented by a ligand-field-splitting energy, covalency of a metal-ligating atom bond, presence/absence of a π-chromophoric ligand, and so forth, a common trend between $\Delta E_{zz}$ and $\delta(M)$ has not been observed for the results on $\text{nPt}$ and $[\text{Mo}_6\text{X}_8\text{Y}_6]^{2-}$. In the case of a series of the complexes for a given metal center(s), nonetheless, we suppose the $\delta(M)$ value of a transition metal complex will be very important factor to discuss zfs in the $T_1$ state of the complex. The present study has also demonstrated that the $k_r$ values of the $1\text{Pt}–4\text{Pt}$ complexes in acetonitrile at 293 K correlate with the relevant $\delta^{195}\text{Pt}$ values, probably due to the importance of the $k_r$ value and the Boltzmann population of the highest-energy spin-sublevel ($\phi_3$) in the $T_1$ state of the complex at 293 K. In conclusion, we have succeeded in showing the importance of $\delta(M)$ to discuss the photophysical properties ($k_r$) in the $T_1$ state of a transition metal complex, which will contribute to further development and synthetic designs of highly-intense luminescent transition metal complexes.

Conflicts of interest
There are no conflicts to declare.

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Notes and references