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Author(s)	Akagi, Soichiro; Fujii, Sho; Kitamura, Noboru
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A ^{195}Pt NMR Study on Zero-Magnetic-Field Splitting and the Phosphorescence Properties in the Excited Triplet States of Cyclometalated Platinum(II) Complexes

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

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We report the factor governing zero-magnetic-field splitting (zfs) in the lowest-energy electronically excited triplet (T_1) states of cyclometalated platinum(II) complexes, whose zfs energies between the lowest- (φ_1) and highest-energy spin-sublevels (φ_3) in the T_1 states (ΔE_{zfs}) have been already known: [Pt(bhq)(dpm)] (**1Pt**), [Pt(thpy)(acac)] (**2Pt**), [Pt(ppy)(acac)] (**3Pt**), *cis*-[Pt(thpy)₂] (**4Pt**), and *cis*-[Pt(ppy)₂] (**5Pt**) where bhq, dpm, thpy, acac, and ppy are benzo[*h*]quinoline, dipivaloilmethanone, 2-(2-thienyl)pyridine, acetylacetone, and 2-phenylpyridine, respectively. As one of the important findings, we show the relationship between ΔE_{zfs} and ^{195}Pt NMR chemical shifts of the five Pt(II) complexes. The implications of the ΔE_{zfs} 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 ΔE_{zfs} and ^{195}Pt NMR chemical shifts.

Introduction

The spin-sublevels in the emissive excited triplet state (φ_n , $n = 1 - 3$ in general) of a molecule possess own emission parameters (maximum energy ($\tilde{\nu}_{em}$), lifetime (τ_{em}), quantum yield (Φ_{em}), radiative (k_r) and nonradiative rate constants (k_{nr})) and, therefore, the observed emission properties become the average of the Boltzmann weighed sum of the emission properties of φ_n at a given temperature (T).¹ In particular, since the splitting energy between the lowest-energy φ_1 and higher-energy φ_2 or φ_3 (ΔE_{zfs} , 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 ($\Delta E_{zfs} \ll 1 \text{ cm}^{-1}$), the emission properties show sometimes relatively large T -dependences depending on ΔE_{zfs} . As an example, the ΔE_{zfs} value between φ_1 and φ_3 in the lowest-energy excited triplet (T_1) state (ΔE_{13}) of [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) is as large as $\sim 62 \text{ cm}^{-1}$.² Reflecting such large ΔE_{zfs} , [Ru(bpy)₃]²⁺ shows large T -dependences of τ_{em} and Φ_{em} in $3 < T < 300 \text{ K}$.² Such results indicate that the ΔE_{zfs} 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 ΔE_{13} values of a variety of Pt(II), Ir(III), Ru(II), Os(II), and Re(III) complexes are governed by nature of the emissive T_1 state and increase in the sequence, the ligand-

centered (LC) < LC/metal-to-ligand charge transfer (MLCT) < MLCT excited state with ΔE_{zfs} being varied from < 1 (LC, [Rh(bpy)₃]³⁺) to $\sim 180 \text{ cm}^{-1}$ (MLCT, [Ir(4-phenylpyridine)₃]).³ They have also demonstrated that the k_r value of the complex increases in this sequence. It is worth emphasizing that the increasing order of ΔE_{zfs} mentioned above agrees with that of the d-electron character in the T_1 state. Nevertheless, prediction of ΔE_{zfs} or d-electron character in the T_1 state of a transition metal complex is a very difficult task in the present stage of the investigations.

We reported recently that the ΔE_{zfs} ($= \Delta E_{1n}$ ($n = 3$ or 4))^{1,3} values of a series of nine octahedral hexanuclear molybdenum(II) complexes, $\{[\text{Mo}_6\text{X}_8\text{Y}_6]^{2-}$ ($\text{X} = \text{Y} = \text{Cl}, \text{Br}, \text{or I}$), correlated with the ^{95}Mo NMR chemical shifts of $\{[\text{Mo}_6\text{X}_8\text{Y}_6]^{2-}; \delta(^{95}\text{Mo})\}$.⁴ The correlation between ΔE_{1n} and $\delta(^{95}\text{Mo})$ observed for $\{[\text{Mo}_6\text{X}_8\text{Y}_6]^{2-}$ is very important, since the NMR chemical shift of the metal center ($\delta(\text{M})$) 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 ΔE_{zfs} and $\delta(\text{M})$ of a transition metal (M) complex is limited to that of $\{[\text{Mo}_6\text{X}_8\text{Y}_6]^{2-}$ alone.⁴ An experimental study on the generality of the relationship between ΔE_{zfs} and $\delta(\text{M})$ other than $\{[\text{Mo}_6\text{X}_8\text{Y}_6]^{2-}$ is thus worth conducting in detail.

^a Department of Chemical Sciences and Engineering, Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-0810, Japan. E-mail: sfujii@sci.hokudai.ac.jp, kitamura@sci.hokudai.ac.jp

^b Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan

^c Toyota Physical and Chemical Research Institute, Nagakute 480-1192, Aichi, Japan

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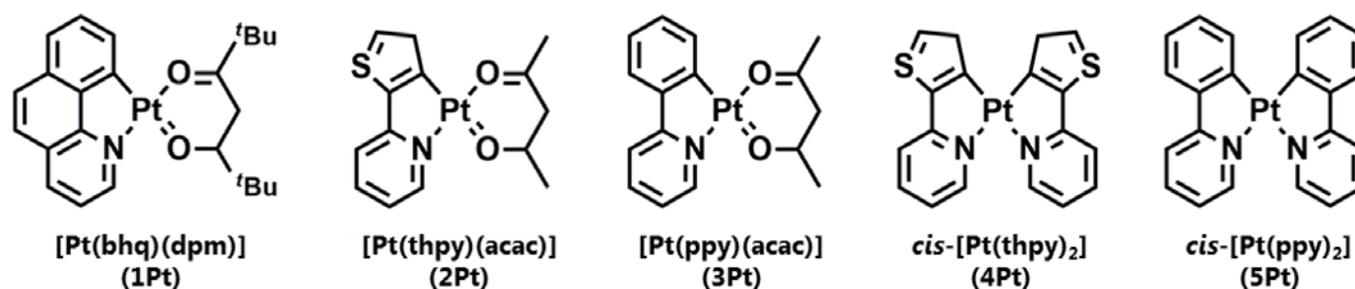


Chart 1. Structures and abbreviations of the Pt(II) (**1Pt–5Pt**). bhq = benzo[*h*]quinoline; thpy = 2-(2-thienyl)pyridine; ppy = 2-phenylpyridine; dpm = dipivaloylmethane; acac = acetylacetonate.

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- (φ_1) and highest-energy spin-sublevels (φ_3) ($\Delta E_{13} = \Delta E_{zfs}$) in the T_1 states have been reported by Yersin et al.: $\Delta E_{zfs} = 1–32$.³ In particular, we have paid special attention to the ^{195}Pt NMR chemical shifts ($\delta(^{195}\text{Pt})$) of *nPt* to check the relationship between ΔE_{zfs} and $\delta(^{195}\text{Pt})$. In order to pursue such a study, we prepared **1Pt–3Pt** to conduct ^{195}Pt NMR spectroscopy in the present study, while we employed the reported $\delta(^{195}\text{Pt})$ data on **4Pt** and **5Pt**.⁵ Implications of $\delta(^{195}\text{Pt})$ and ΔE_{zfs} values of *nPt* to the emission properties of the complexes in acetonitrile at 293 K are also reported.

Experimental

Pt(II) Complexes. [Pt(C[^]N)(O[^]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}Pt NMR spectroscopy was conducted by using a 400 MHz JNM-ECZ spectrometer (JEOL Ltd). For ^{195}Pt NMR spectroscopy, potassium tetrachloroplatinate (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 C5094 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.

Results and discussion

ΔE_{zfs} and ^{195}Pt NMR Spectroscopy of Luminescent Platinum(II) Complexes. The ΔE_{zfs} ($= \Delta E_{13}$) values in the T_1 states of **1Pt–5Pt** reported by Yersin et al. are summarized in Table 1.³ The ΔE_{zfs} values of **1Pt–5Pt** are sensitive to the ligand structures and vary in $1–36$ cm^{-1} . In general, the combination of an $O^{\wedge}O$ (dpm or acac) or $C^{\wedge}N$ ligand (bhq, thpy, or ppy) with a Pt(II) ion (**1Pt–3Pt**) gives rise to small ΔE_{zfs} ($1–11.5$ cm^{-1}) compared to that of the complex having two $C^{\wedge}N$ ligands (i.e., homoleptic complex, **4Pt** or **5Pt**, $16–32$ cm^{-1}) as seen in Table 1.³ For a given ligand in the heteroleptic $O^{\wedge}O$ - $C^{\wedge}N$ and homoleptic $C^{\wedge}N$ - $C^{\wedge}N$ Pt(II) complexes shown in Chart 1, furthermore, the ΔE_{zfs} 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}Mo NMR chemical shifts of the clusters⁴ as described above. In order to check the generality of the relationship between ΔE_{zfs} and $\delta(\text{M})$ of a complex, therefore, we evaluated the $\delta(^{195}\text{Pt})$ values of *nPt*.

Figure 1a shows the ^{195}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 $O^{\wedge}O$ - $C^{\wedge}N$ Pt(II) complexes

(**1Pt–3Pt**) show $\delta(^{195}\text{Pt})$ in the lower magnetic field side ($\delta(^{195}\text{Pt}) = -(1148-1219)$ ppm) compared to that of the homoleptic $C^{\wedge}N-C^{\wedge}N$ Pt(II) complex (**4Pt** or **5Pt**, $\delta(^{195}\text{Pt}) = -1524$ or -1518 ppm, respectively), though **4Pt** or **5Pt** possesses the same $C^{\wedge}N$ ligand with that in **2Pt** or **3Pt**, respectively. For a given ligand in the heteroleptic $O^{\wedge}O$ or homoleptic $C^{\wedge}N$ Pt(II) complex, furthermore, the $\delta(^{195}\text{Pt})$ values of **1Pt–5Pt** decrease in the sequence, bhq (**1Pt**) > thpy (**2Pt**, **4Pt**) > ppy (**3Pt**, **5Pt**). It is worth noting that the increasing order of ΔE_{zfs} of the complex with the ligand correlates with the decreasing order of $\delta(^{195}\text{Pt})$. Thus, the $\delta(^{195}\text{Pt})$ values of **1Pt–5Pt** were plotted against the relevant ΔE_{zfs} values. Figure 1b demonstrates that a decrease in $\delta(^{195}\text{Pt})$ (i.e., to the more negative direction) gives rise to an increase in the ΔE_{zfs} value: negative relationship between ΔE_{zfs} and $\delta(^{195}\text{Pt})$. This is contrasted to the results on $[\{\text{Mo}_6\text{X}_8\}\text{Y}_6]^{2-}$, where ΔE_{zfs} increases with an increase in $\delta(^{95}\text{Mo})$ (i.e., to the more positive direction).⁴ In $^1\text{H-NMR}$ spectroscopy, a negative shift of the chemical shift (in ppm) implies an increase in the electron density on the H atom, while the NMR chemical shift of a metal ion is influenced by other electronic environments around the metal atom: strength of ligand-field splitting, degree of covalency of a metal-ligating atom bond, and so forth. The opposite trend of the relationship between ΔE_{zfs} and $\delta(\text{M})$ observed for $n\text{Pt}$ and $[\{\text{Mo}_6\text{X}_8\}\text{Y}_6]^{2-}$ mentioned above would be due to the different electronic origin in the T_1 states of $n\text{Pt}$ (LC/MLCT characters) and $[\{\text{Mo}_6\text{X}_8\}\text{Y}_6]^{2-}$ (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 T_1 state as reported by Yersin et al.³ We suppose that since the relationship between ΔE_{zfs} and $\delta(^{195}\text{Pt})$ observed for **4Pt** and **5Pt** (homoleptic complexes) will be different from that observed for **1Pt–3Pt** (heteroleptic complexes) owing to the differences in the ligand electronic structures, the $\delta(^{195}\text{Pt})$ 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 $\delta(\text{M})$ of a transition metal complex is absolutely necessary.

Table 1. ΔE_{zfs} (determined in *n*-alkane matrices by high-resolution emission spectroscopy) and $\delta(^{195}\text{Pt})$ values (in ppm, determined in CDCl_3 relative to that of K_2PtCl_4 in D_2O) of **1Pt–5Pt**.

Complexes	1Pt	2Pt	3Pt	4Pt	5Pt
ΔE_{zfs} / cm^{-1}	~1 ^{a)}	4.3 ^{a)}	11.5 ^{a)}	16 ^{a)}	32 ^{a)}
$\delta(^{195}\text{Pt})$ / ppm	-1148	-1165	-1219	-1524 ^{b)}	-1518 ^{b)}

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

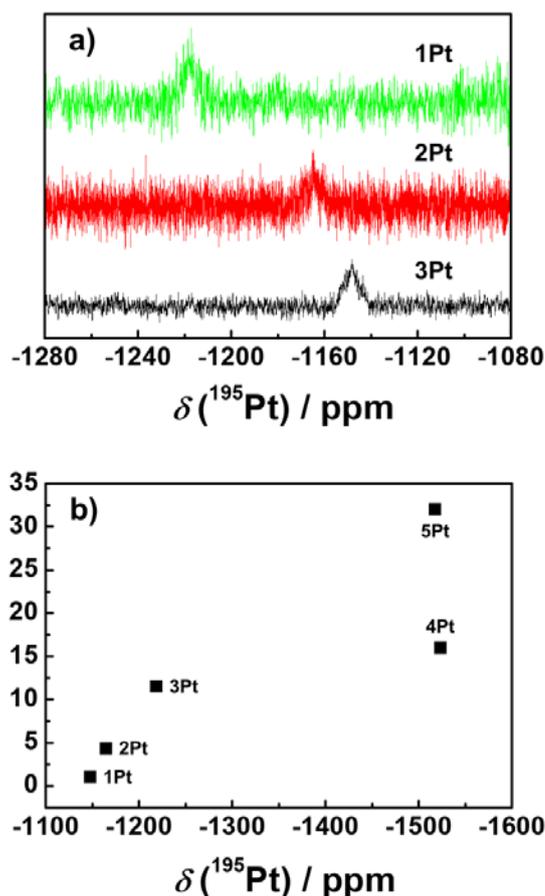


Figure 1. a) ^{195}Pt NMR spectra of **1Pt** (black), **2Pt** (red), and **3Pt** (green) in CDCl_3 at 293 K. b) Relationship between $\delta(^{195}\text{Pt})$ and ΔE_{zfs} of **1Pt–5Pt**. $\delta(^{195}\text{Pt})$ in ppm is relative to that of K_2PtCl_4 in D_2O at 293 K.

Implications of ΔE_{zfs} to the Phosphorescence Properties of the Platinum(II) Complexes in Acetonitrile at 293 K. In the case of $[\{\text{Mo}_6\text{X}_8\}\text{Y}_6]^{2-}$ ($\text{X}, \text{Y} = \text{Cl}, \text{Br}, \text{or I}$),³ $[\{\text{Mo}_6\text{X}_8\}(n\text{-C}_3\text{F}_7\text{COO})_6]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$),⁷ and $[\{\text{Mo}_6\text{Br}_8\}\text{L}_6]^{2-}$ ($\text{L} = \text{aromatic carboxylates}$),⁸ we have reported that the ΔE_{zfs} ($= \Delta E_{14}$) values in the T_1 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 ($\tilde{\nu}^{\text{em}}$) through the energy gap dependence of k_{nr} : $\ln(k_{nr}) \propto \tilde{\nu}^{\text{em}}$.^{3,7,8–11} We also reported that the Φ_{em} and τ_{em} values of $[\{\text{Mo}_6\text{X}_8\}\text{Y}_6]^{2-}$ were correlated with ΔE_{14} , demonstrating that the ΔE_{14} value of the cluster governed the k_{nr} value as expected from the relation, $\Phi_{\text{em}} = k_r / (k_r + k_{nr}) = k_r \tau_{\text{em}}$ where $k_r < k_{nr}$.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 $\delta(^{195}\text{Pt})$ values, which is worth discussing further in detail.

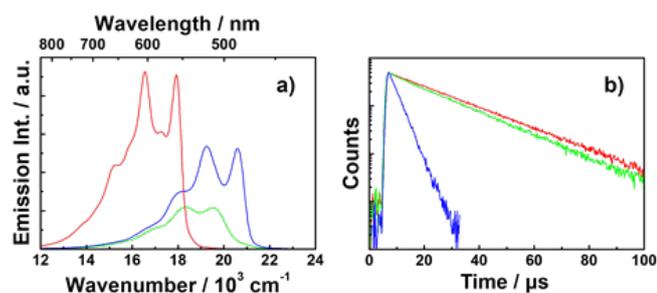


Figure 2. Emission spectra (a) and decay profiles (b) of **1Pt** (green), **2Pt** (red), and **3Pt** (blue) in acetonitrile at 293 K. The areas of the emission spectra correspond to the relative emission quantum yields.

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 $\tilde{\nu}_{em}$, τ_{em} , and Φ_{em} values of **1Pt–4Pt** vary in $\tilde{\nu}_{em} = (17.30\text{--}20.62) \times 10^3 \text{ cm}^{-1}$, $\tau_{em} = 2.2\text{--}20.3 \text{ }\mu\text{s}$, and $\Phi_{em} = 0.095\text{--}0.305$, and the values decrease in the sequences, $\tilde{\nu}_{em} = \mathbf{3Pt} > \mathbf{1Pt} > \mathbf{2Pt} > \mathbf{4Pt}$, $\tau_{em} = \mathbf{2Pt} > \mathbf{1Pt} > \mathbf{3Pt} > \mathbf{4Pt}$, and $\Phi_{em} = \mathbf{2Pt} > \mathbf{4Pt} > \mathbf{3Pt} > \mathbf{1Pt}$. In these data, one cannot find any common tendency in the ΔE_{zfs} dependences of $\tilde{\nu}_{em}$, τ_{em} , or Φ_{em} of the complex. In particular, the k_{nr} values of the complexes cannot be explained by the energy gap ($\tilde{\nu}_{em}$) 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 ΔE_{zfs} values of **1Pt–3Pt** ($1 \sim 11.5 \text{ cm}^{-1}$) 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 $\delta(^{195}\text{Pt})$ 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_r value of the complex increases with an increase in ΔE_{zfs} in the sequence, $k_r (\times 10^3 \text{ s}^{-1})$: **1Pt** = 0.52 ($\Delta E_{zfs} = \sim 1 \text{ cm}^{-1}$) < **2Pt** = 1.50 (4.3) < **3Pt** = 6.06 (11.5) < **4Pt** = 6.06 (16). In practice, the k_r values of **1Pt–4Pt** show the correlation with the relevant ΔE_{zfs} values as shown in Figure 3a. Interestingly, furthermore, Figure 3b demonstrates that the $\delta(^{195}\text{Pt})$ value also correlate with the k_r values of **1Pt–4Pt** and, therefore, with ΔE_{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.

	1Pt ^{a)}	2Pt ^{a)}	3Pt ^{a)}	4Pt ^{b)}
$\tilde{\nu}_{em} / 10^3 \text{ cm}^{-1}$	19.53	17.92	20.62	17.30
$(\lambda_{em} / \text{nm})$	(512)	(558)	(485)	(578)
$\tau_{em} / \mu\text{s}$	18.4	20.3	3.3	2.2
Φ_{em}	0.095	0.305	0.200	0.30
$k_r / 10^3 \text{ s}^{-1}$	0.52	1.50	6.06	13.6
$k_{nr} / 10^3 \text{ s}^{-1}$	4.92	3.42	24.2	31.8

a) Measured in deaerated acetonitrile at 293 K in the present study.

b) Data in a deaerated propionitrile/butyronitrile mixture taken from ref. 12.

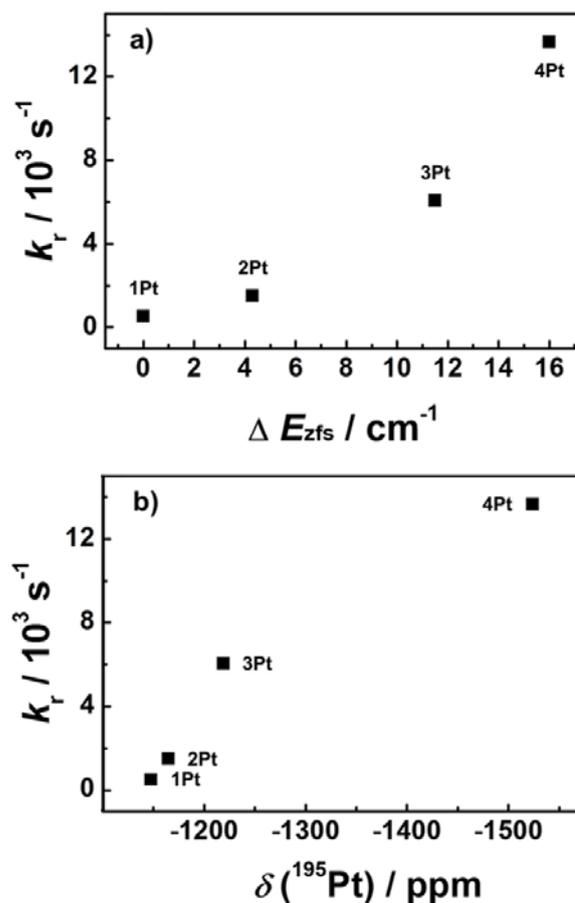


Figure 3. ΔE_{zfs} (a) and $\delta(^{195}\text{Pt})$ dependences (b) of the k_r values of **1Pt–4Pt** in acetonitrile at 293 K.

Conclusions

In this paper, we reported the relationship between the ΔE_{zfs} and $\delta(^{195}\text{Pt})$ values of the five cyclometalated Pt(II) complexes (**1Pt–5Pt**). It is worth emphasizing that the relationship between ΔE_{zfs} and $\delta(^{95}\text{Mo})$ of $[\{\text{Mo}_6\text{X}_8\}\text{Y}_6\}^{2-}$ (X, Y = Cl, Br, or I) has been also confirmed by our research group.³ However, the ΔE_{zfs} values of **nPt** increased by shifting of $\delta(^{195}\text{Pt})$ to a more negative direction, while those of $[\{\text{Mo}_6\text{X}_8\}\text{Y}_6\}^{2-}$ showed an opposite trend to that observed for **nPt**: increase in ΔE_{zfs} by a positive shift of $\delta(^{95}\text{Mo})$. 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 ΔE_{zfs} and $\delta(M)$ has not been observed for the results on **nPt** and $\{[Mo_6X_8]Y_6\}^{2-}$. 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 **1Pt–4Pt** complexes in acetonitrile at 293 K correlate with the relevant $\delta(^{195}Pt)$ values, probably due to the importance of the k_r value and the Boltzmann population of the highest-energy spin-sublevel (ϕ_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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