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Temperature Dependence of the Luminescence of Cyclometalated Palladium(II), Rhodium(III), Platinum(II), and Platinum(IV) Complexes

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The luminescence lifetimes of the cyclometalated complexes $Pd(thpy)_2$, $Rh(thpy)_2(bpy)^+$, $Rh(phpy)_2(bpy)^+$, $Pt(thpy)_2$, and $Pt(thpy)_2(CHCl_2)Cl$ (where $thpy^-$ and $phpy^-$ are the ortho-C-deprotonated forms of 2-(2-thienyl)pyridine and 2-phenylpyridine and bpy is 2,2′-bipyridine) have been measured in a propionitrile–butyronitrile solution in the temperature range 77–310 K. Activation energies and preexponential factors for the deactivation processes have been obtained from the experimental $\ln (1/\tau)$ vs $1/T$ plots. The analysis of the results obtained shows that for $Pd(thpy)_2$, $Rh(thpy)_2(bpy)^+$, $Rh(phpy)_2(bpy)^+$, and $Pt(thpy)_2$ increasing temperature opens efficient deactivation channels related to the presence of thermally accessible metal-centered excited states. Comparisons with the previously reported behavior of $Rh(bpy)_3^{2+}$ and other Rh(III)–polypyridine complexes support this hypothesis. In the case of $Pt(thpy)_2(CHCl_2)Cl$ the luminescence lifetime is only slightly affected by temperature, presumably because of the thermal inaccessibility of metal-centered levels. Elaboration of the spectroscopic results and activation parameters allows one to establish the relative energy order of the lowest ^3MC excited states of structurally related complexes containing the same metal and different ligands or vice versa.

Introduction

Cyclometalated complexes that contain ligands structurally similar to diimines are presently the object of much interest because they exhibit strong luminescence[2–15] and, at least in some cases, a peculiar photoreactivity.[15,16] The absorption spectra of these complexes are dominated by intense ligand-centered (LC) or metal-to-ligand charge-transfer (MLCT) bands, and their luminescence spectra show only one band, related to emission from the lowest lying excited state that is a LC or MLCT state (or a mixture of them). As in the case of the Ru(II)–polypyridine complexes,[17,18] metal-centered (MC) excited states (also called ligand field excited states) do not appear in the absorption and emission spectra of cyclometalated complexes. However, it is known that in transition-metal complexes the low-lying MC levels can play important roles in determining the photochemical and photophysical behavior since they (i) are usually responsible for photochemical ligand labilization processes[17–21] and (ii) can provide efficient paths for the radiationless decay.[17–22]

Important pieces of information on the presence of MC levels at low energies can be obtained from systematic temperature dependence studies of the luminescence lifetime since thermal accessibility to MC levels, which are strongly distorted with respect to the ground state, results in a faster deactivation of the luminescent excited state.

In an attempt to obtain information on the factors that govern the excited-state lifetime of cyclometalated complexes and particularly on the role played by MC levels, we have measured the luminescence lifetime of the following complexes in a propionitrile–butyronitrile mixture between 77 and 310 K: $Pd(thpy)_2$, $Rh(thpy)_2(bpy)^+$, $Rh(phpy)_2(bpy)^+$, $Pt(thpy)_2$, and $Pt(thpy)_2(CHCl_2)Cl$ ($thpy^-$ and $phpy^-$ are the ortho-C-deprotonated forms of 2-(2-thienyl)pyridine and 2-phenylpyridine, and bpy is 2,2′-bipyridine). The results obtained are discussed together with those previously available for $Rh(bpy)_3^{3+}$ [23] and other Rh(III)–polypyridine complexes.[24,25] The structural formulas of the ligands are shown in Figure 1.

Experimental Section

The preparations and characterizations of *cis*-$Pd(thpy)_2$,[26] $Rh(thpy)_2(bpy)^+$,[27] $Rh(phpy)_2(bpy)^+$,[27,28] *cis*-$Pt(thpy)_2$,[29] and one of the C,C,C facial isomers of $Pt(thpy)_2(CHCl_2)Cl$[15,30] have been previously reported. The experiments were carried out in a 4:5 v/v mixture of freshly distilled propionitrile and butyronitrile. Diluted solutions (10^{-5}–10^{-4} M) were sealed under vacuum in 1-cm quartz cells after repeated freeze–pump–thaw cycles. The cells were placed inside a modified C 600 Thor cryostat, equipped with a 3050 Thor temperature controller. The absolute error for the temperature is estimated to be ±2 K. Uncorrected emission spectra were obtained by a Perkin-Elmer MPF-44B spectrofluorometer equipped with a Hamamatsu R928 phototube. Emission lifetimes were measured by a Lambda Physik nitrogen laser. The error for τ is estimated to be <8%. The curves obtained were analyzed according to a single exponential decay. Excitation was carried

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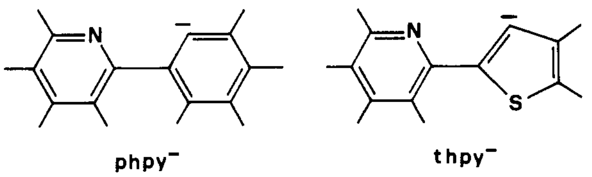

Figure 1. Structural formulas of the ligands.

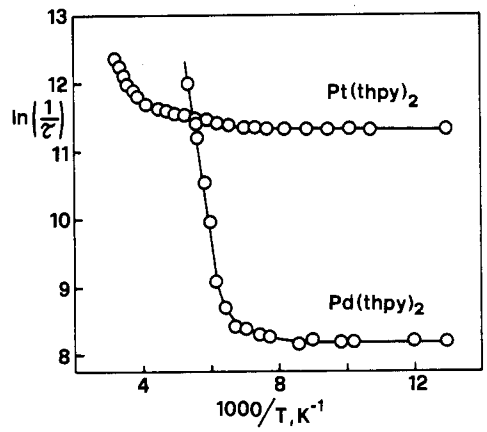

Figure 2. Temperature dependence of the luminescence lifetimes for $Pd(thpy)_2$ and $Pt(thpy)_2$. Full lines result from the best fitting of eq 1 to the experimental points (see text).

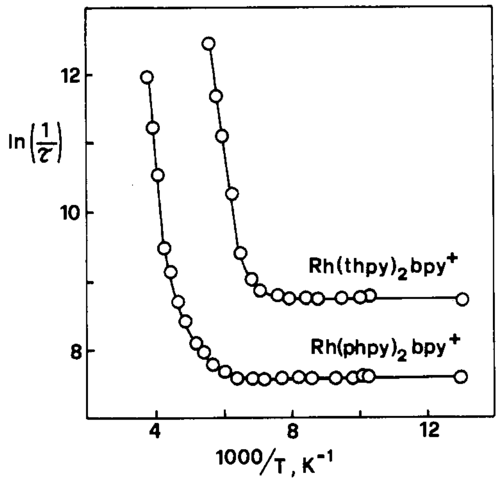

Figure 3. Temperature dependence of the luminescence lifetimes for $Rh(thpy)_2bpy^+$ and $Rh(phpy)_2bpy^+$. Full lines result from the best fitting of eq 1 to the experimental points (see text).

out at 337 nm, and emission was monitored at the wavelength corresponding to the maxima of the emission spectra. The single-exponential analysis was performed with nonlinear iterative programs,[31] and the quality of the fit was assessed by the χ^2 value close to unity and the residuals regularly distributed along the time axis. Standard iterative nonlinear programs[31] were employed to extract the parameters for the temperature dependence of the lifetime. Data treatment was carried out with a PDP/11 microcomputer.

Results

The absorption and emission spectra of the complexes examined were in agreement with those previously reported in acetonitrile or in a propionitrile–butyronitrile mixture.[5,10,11,14,15] The temperature dependences of the luminescence lifetimes for $Pd(thpy)_2$, $Pt(thpy)_2$, $Rh(thpy)_2(bpy)^+$, $Rh(phpy)_2(bpy)^+$, and $Pt(thpy)_2(CHCl_2)Cl$ are shown in Figures 2–4. The changes in the luminescence intensities with temperature were qualitatively similar to but not identical with the changes in lifetime. Since intensity may be affected by changes in the absorption spectrum and refraction index with temperature, we preferred to consider the lifetime data to obtain kinetic parameters (vide infra).

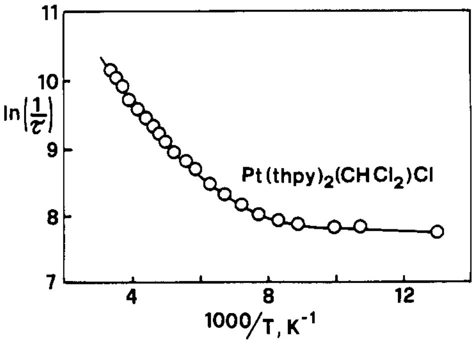

Figure 4. Temperature dependence of the luminescence lifetime for $Pt(thpy)_2(CHCl_2)Cl$. Full line results from the best fitting of eq 1 to the experimental points (see text).

Table I. Kinetic Parameters for the Decay of the Luminescent Excited State Obtained from the Fitting of the Experimental Results[a]

complex	k_0, s^{-1}	A_1, s^{-1}	ΔE_1, cm^{-1}	A_2, s^{-1}	ΔE_2, cm^{-1}
$Pd(thpy)_2$	3.4×10^3			8×10^{12}	2300
$Rh(thpy)_2bpy^+$	1.9×10^3	9×10^5	900	2×10^{13}	3500
$Rh(phpy)_2bpy^+$	6.1×10^3			2×10^{14}	2600
$Pt(thpy)_2$	8.5×10^4	1×10^6	600	3×10^{12}	3700
$Pt(thpy)_2(CHCl_2)Cl$	2.3×10^3	3×10^5	500		
$Rh(bpy)_3^{3+}$ [b]	4.5×10^2			6×10^{12}	2200

[a] Propionitrile–butyronitrile mixture (4:5 v/v), unless otherwise noted. [b] Ethanol–methanol mixture (4:1 v/v).[23]

Discussion

In general, the changes in $1/\tau$ vs $1/T$ over a large temperature range can be explained by considering additional contributions to the radiatonless decay process of the emitting excited state(s) as the temperature increases.

$$1/\tau = k_0 + \sum_i k_i \tag{1}$$

In eq 1, k_0 is a temperature-independent term and k_i is the rate constant of the ith step that contributes to the decay process. Previous work has shown that the k_i terms can take either the form of an Arrhenius equation[18,22,32-36]

$$k_i = A_i \exp(-\Delta E_i/RT) \tag{2}$$

where A_i is a frequency factor and ΔE_i an activation energy or, in some peculiar cases, the form of an empirical equation[18,35] that describes a stepwise behavior in the melting region of the matrix. For the complexes examined, the ln $(1/\tau)$ vs $1/T$ plots (Figures 2–4) do not show any step, so that only Arrhenius terms (eq 2) are needed to fit the experimental behavior.

Least-squares analysis was employed to fit the ln $(1/\tau)$ vs $1/T$ data. While for $Pd(thpy)_2$ (Figure 2) and $Pt(thpy)_2(CHCl_2)Cl$ (Figure 4) one Arrhenius term gave a satisfactory fit, for $Pt(thpy)_2$ (Figure 2), $Rh(thpy)_2(bpy)^+$ (Figure 3), and $Rh(phpy)_2(bpy)^+$ (Figure 3) the use of two Arrhenius terms resulted in a significant

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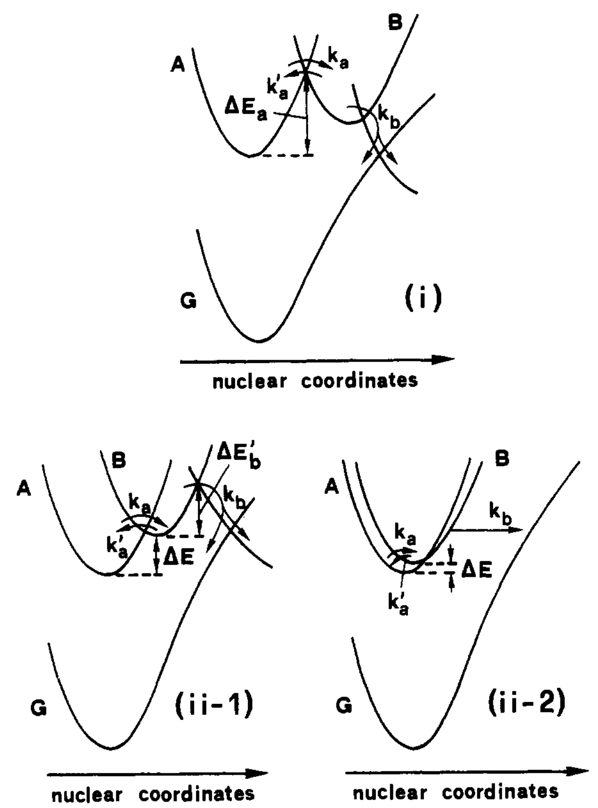

Figure 5. Schematic representation of the potential energy surfaces for the three limiting kinetic regimes described in the text.

improvement of the fit. The kinetic parameters corresponding to the best fitting curves are gathered in Table I. For comparisons purposes, the parameters previously obtained[23] for $Rh(bpy)_3^{3+}$ are also given.

In order to discuss the meaning of the values of the observed kinetic parameters, a kinetic model is needed. Following a previously reported treatment,[33,35] we may assume that on increasing temperature upper lying excited states begin to be populated. If such states exhibit fast radiationless decay channels, the lifetime of the luminescent state will decrease. When only the ground state G, the luminescent excited state A, and the upper excited state B, which decays to G or to a product, are considered, the following kinetic scheme can be used:

$$G \xleftarrow{k_0} A \underset{k'_a}{\overset{k_a}{\rightleftarrows}} B \xrightarrow{k_b} G \text{ or products} \tag{3}$$

If we assume a steady-state concentration for B, the experimental rate constant k_i that comes into play on increasing temperature (eq 1) can be expressed as

$$k_i = \frac{k_b k_a}{k'_a + k_b} \tag{4}$$

Equation 4 can give rise to two limiting cases (Figure 5):

(i) When $k_b \gg k'_a$, the decay of B is rapid and eq 4 becomes

$$k_i = k_a \tag{5}$$

It follows that

$$A_i \exp(-\Delta E_i/RT) = A_a \exp(-\Delta E_a/RT) \tag{6}$$

In this limit the A_i and ΔE_i parameters obtained from the fitting correspond to the preexponential factor and activation energy for the A → B transition (Figure 5(i)).

(ii) When $k'_a \gg k_b$, the decay of B is slow compared to the back-transition to A. In such a case, A and B are in equilibrium and eq 4 becomes

$$k_i = (k_a/k'_a)k_b \tag{7}$$

since $k_a/k'_a = K = \exp(-\Delta E/RT) \exp(\Delta S/R)$, where ΔE and ΔS are the internal energy and entropy differences between A and B, it follows that

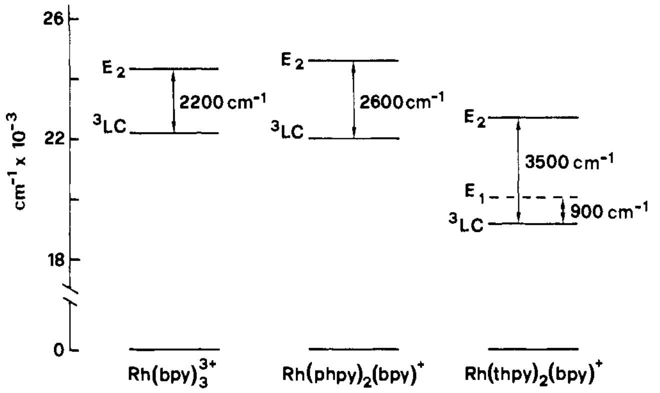

Figure 6. Energy levels for the Rh compounds. ^3LC is the luminescent excited state. E_1 is likely another LC state. E_2 is an upper limiting value for the energy of the ^3MC excited state. The relative energy positions of the E_2 levels are thought to reflect those of the corresponding ^3MC states. For more details, see text.

$$A_i \exp(-\Delta E_i/RT) = k_b \exp(-\Delta E/RT) \exp(\Delta S/R) \tag{8}$$

Neglecting the entropic difference between the two states, which is expected to be small, one can rewrite eq 8 as

$$A_i \exp(-\Delta E_i/RT) = k_b \exp(-\Delta E/RT) \tag{9}$$

The meaning of the experimental quantities A_i and ΔE_i depends on the nature of the processes that contribute to k_b. The following limiting kinetic regimes are of interest:

(ii-1) When the major contribution to k_b comes from a chemical reaction or a deactivation process (k'_b) that can be described by an Arrhenius-type equation, eq 9 can be written as

$$A_i \exp(-\Delta E_i/RT) = A'_b \exp[-(\Delta E'_b + \Delta E)/RT] \tag{10}$$

In such case the A_i and ΔE_i parameters obtained from the fitting of the ln $(1/\tau)$ vs $1/T$ plot correspond to the preexponential factor of the decay process of B and to the sum of the B–A energy gap, ΔE, and the activation energy of the decay process of B, $\Delta E'_b$ (Figure 5(ii-1)).

(ii-2) When the main contribution to k_b comes from a nonactivated process (k''_b), from eq 8 it follows that the preexponential parameter A_i corresponds to the rate of the nonactivated B decay, k''_b, and the activation energy ΔE_i corresponds to the B–A energy gap, ΔE (Figure 5(ii-2)).

In the frame of the above kinetic model, if the electronic interaction is large enough to give an adiabatic regime,[37] it can be expected that A_a and A_b are vibrational frequencies (10^{12}–10^{14} s^{-1}) whose activation leads to a surface-crossing region (Figure 5(i, ii-1)). By contrast, k''_b can be much smaller because it represents the rate constant of a radiationless transition having a poor Franck–Condon factor (Figure 5(ii-2)). Note that the radiationless decay of the luminescent state to the ground state, whose temperature-independent rate constant is included in k_0, is a typical example of such Franck–Condon "forbidden" transitions. It should also be noted that in all kinetic regimes ΔE_i contains ΔE and that for structurally similar complexes an increase in ΔE will correspond to an increase of ΔE_i.

We can now try to examine the behavior of each complex in the light of the above model, making reference to Figures 6 and 7, which report the energies of the luminescent excited states, and the experimental activation energies taken from Table I. The weakly activated processes that come into play for $Pt(thpy)_2$, $Rh(thpy)_2(bpy)^+$, and $Pt(thpy)_2(CHCl_2)Cl$ at low temperature are characterized by a very low value of the preexponential factor A_1 (Table I). According to the model described above, these processes correspond to Franck–Condon forbidden transitions as

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(37) In the cyclometalated complexes the mixing among formally MC, LC, and CT levels is expected to be rather large because of the substantial degree of covalency of the M–C⁻ bonds.

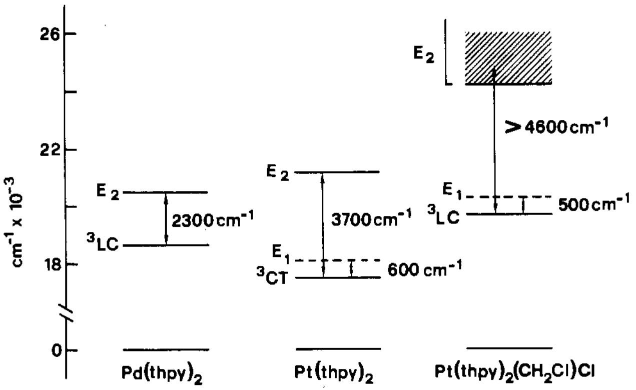

Figure 7. Energy levels for the Pd and Pt complexes. ^{3}LC and ^{3}CT are the luminescent excited states. E_1 is likely a LC or MC level. E_2 is an upper limiting value for the energy of the ^{3}MC excited state. The relative energy positions of the E_2 levels are thought to reflect those of the corresponding ^{3}MC states. For more details, see text.

indicated in Figure 5(ii-2). This suggests that the upper excited level E_1 coming into play (Figures 6 and 7) is not strongly distorted compared to the luminescent level, typical for LC or CT levels. A similar situation of relatively closely spaced MLCT levels is common for Ru(II)–polypyridine complexes[38] and does not merit further discussion. We only wish to note that the lack of kinetic evidence for levels closely spaced from the lowest one for Pd(thpy)$_2$ and Rh(phpy)$_2$(bpy)$^+$ does not mean that such levels are not present. Simply, their appearance from the ln $(1/\tau)$ vs $1/T$ plots may be precluded because of one or more of the following conditions: (a) ΔE_1 is too small; (b) A_1 is too small; (c) ΔE_1 is too close to ΔE_2.

The strongly activated processes are characterized by high values of the preexponential factor A_2 (Table I). This suggests that the excited level E_2 coming into play (Figures 6 and 7) is either the crossing point between the ^{3}LC and ^{3}MC levels (case i, Figure 5) or an upper limiting value for the energy difference between the minima of the ^{3}LC and ^{3}MC surfaces (case ii-1, Figure 5). For Rh(thpy)$_2$(bpy)$^+$ and Rh(phpy)$_2$(bpy)$^+$ the obvious comparisons are with recently studied Rh(III) complexes of the polypyridine family. For Rh(bpy)$_3^{3+}$,[23] Rh(3,3′-dmbpy)$_3^{3+}$,[39] Rh(phen)$_3^{3+}$,[24,25,40] and Rh(4,7-dmphen)$_3^{3+}$[25] (dm indicates dimethyl substituents) dual luminescence has been reported under some experimental conditions, indicating that a ^{3}MC level lies at higher energy than the ^{3}LC level, which is responsible for the stronger (or unique) luminescence band at 77 K. For Rh(bpy)$_3^{3+}$, Rh(phen)$_3^{3+}$, and Rh(4,7-dmphen)$_3^{3+}$ a temperature dependence study has also been performed, leading to the following activation parameters: Rh(bpy)$_3^{3+}$, $A_2 \simeq 10^{12}$ s^{-1}, $\Delta E_2 = 2200$ cm^{-1} (in MeOH/EtOH, 1:4);[23] Rh(phen)$_3^{3+}$, $A_2 \simeq 10^{11}$ s^{-1}, $\Delta E_2 = 2100$ cm^{-1} (in acetonitrile);[25] Rh(4,7-dmphen)$_3^{3+}$, $A_2 \simeq 10^{11}$ s^{-1}, $\Delta E_2 = 2400$ cm^{-1} (in acetonitrile).[25] The behavior observed for Rh(phpy)$_2$(bpy)$^+$ and Rh(thpy)$_2$(bpy)$^+$ (Table I, Figure 6) is consistent with that exhibited by the Rh(III)–polypyridine complexes. More specifically, the E_2 values obtained (Figure 6) suggest that the ligand field strength decreases in the order phpy$^-$ > bpy > thpy$^-$. While the higher ligand field strength of phpy$^-$ compared to that of bpy is clearly due to the higher σ-donor ability of C$^-$ compared to that of N, the lower ligand field strength of thpy$^-$ compared to that of bpy could be due to either σ or π factors.

Agreement between experimental results and ligand field expectations is also shown by the Pd and Pt complexes (Figure 7). The stronger ligand field of Pt(II) compared to that of Pd(II) is reflected in the relative energy position of the E_2 levels of Pt(thpy)$_2$ and Pd(thpy)$_2$. The much higher ligand field strength of Pt(IV) compared to those of Pd(II) and Pt(II) is reflected in the absence of accessible MC levels in Pt(thpy)$_2$(CHCl$_2$)Cl. On the basis of the experimental results, it can be estimated that, at room temperature (298 K), ΔE_2 for a process having $A_2 = 10^{13}$ s^{-1} should have been lower than 4600 cm^{-1} to make k_2 experimentally detectable for Pt(thpy)$_2$(CHCl$_2$)Cl (Figure 7).

Conclusion

From the study of the temperature dependence of the luminescence lifetimes of Pd(thpy)$_2$, Rh(thpy)$_2$(bpy)$^+$, Rh(phpy)$_2$(bpy)$^+$, Pt(thpy)$_2$, and Pt(thpy)$_2$(CHCl$_2$)Cl between 77 and 310 K, it has been possible to obtain information on the factors that govern the decay of the luminescent ^{3}LC or ^{3}MLCT state via upper lying levels. We have also shown that for structurally similar complexes it is possible to infer the relative positions in the spectrochemical series of different cyclometalated ligands or of different metals in cyclometalated complexes.

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Registry No. *cis*-Pd(thpy)$_2$, 115756-71-3; Rh(thpy)$_2$bpy$^+$, 107053-32-7; Rh(phpy)$_2$bpy$^+$, 106266-44-8; *cis*-Pt(thpy)$_2$, 100012-12-2; C,C,C-*fac*-Pt(thpy)$_2$(CHCl$_2$)Cl, 111822-52-7.

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Use of the Pfeiffer Effect To Probe the Optical Activity of Europium(III) Complexes with 2,6-Pyridinedicarboxylate

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Circularly polarized luminescence (CPL) and circular dichroism (CD) results are presented for aqueous Eu(dipicolinate)$_3^{3-}$ upon addition of (+)-dimethyl-L-tartrate. The added chiral species has been shown to cause a shift in the racemic equilibrium of the approximately D_3 lanthanide complexes. Similar data for Dy(dipicolinate)$_3^{3-}$ are reported, and in combination with CPL measured from the racemic solution, these data yield quantitative information concerning the equilibrium shift and the chiroptical properties of the pure enantiomers. Comparison is made with published CD and CPL from crystalline Eu(oxydiacetate)$_3^{3-}$, and it is concluded that the addition of (+)-dimethyl-L-tartrate results in an excess of the Λ isomer.

Introduction

Aqueous lanthanide complexes with 2,6-pyridinedicarboxylate [dipicolinate = DPA] are known to be tris-terdendate complexes and possess D_3 symmetry over a wide range of pH.[1,2] These relatively high-symmetry species have been studied fairly extensively, since they are easy to prepare in aqueous solution, are, in

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(1) Grenthe, I.; Toblasson, I. *Acta Chem. Scand.* **1963**, *17*, 2101.

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