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Unusual Enlargment of Magnetic Interactions in the Lowest Excited States of Nitroxide Radical Chromium(III) Complexes as Revealed by Magnetic Circular Dichroism and Luminescence

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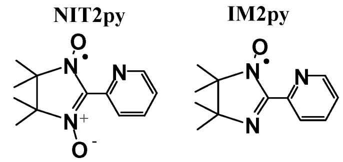
Magnetic circular dichroism and NIR luminescence of nitroxide radical complexes, $[Cr^{III}(\beta\text{-diketonato})_2(\text{NIT2py or IM2py})]PF_6$, demonstrate that the energy gaps between the singlet (^1L_D) and triplet (^3L_D) spin coupled levels in the lowest excited ^2E_g,$^2T_{1g}$ states are much larger than those in the ground state. This is the first observation of magnetic interactions in the excited states of radical complexes, which could be elucidated in terms of the exchange mechanism.

Introduction

Among many investigations[1−5] of magnetic properties of 3d metal complexes with nitroxide radicals, most of them were focused on the ground electronic states. Recently we have been exploring the magnetic and spectroscopic properties of the paramagnetic or diamagnetic metal complexes with nitroxide radicals NIT2py (2-(2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxyl) and IM2py (2-(2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxy) (Scheme 1).[6−13] In the course of these investigations, we claimed that the luminescence of $[Cr(acac)_2(NIT2py)]PF_6$ is due to the lowest $^1L(^2E,^2T_1)$ levels which originate from the coupling between the NIT2py radical and the metal $^2\Gamma(^2E,^2T_1)$ levels.[6] However, the definitive interpretation of the luminescence had to await the comparable examination of the analogous $[Cr(acac)_2(IM2py)]PF_6$, the luminescence of which could not be measured owing to the instrumental limitations at that time. It is indispensable to evaluate the magnetic interaction in the lowest excited state for both nitroxide radical complexes in connection with the influence of the radical coordination on their magneto-optical and photochemical properties. In this paper, the magnetic circular dichrosim (MCD) and luminescence for the NIT2py and IM2py complexes will be presented and interpreted in terms of an exchange mechanism.

Scheme 1



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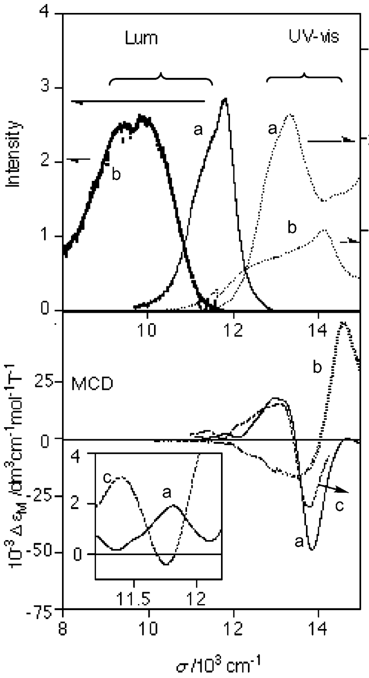

Figure 1. Top: UV−vis absorption spectra in CH_3CN at 300 K and luminescence spectra in the solid state at 15 K of $[Cr(acac)_2(NIT2py)]PF_6$ (a) and $[Cr(acac)_2(IM2py)]PF_6$ (b). Bottom: MCD spectra of $[Cr(acac)_2(NIT2py)]PF_6$ (a), $[Cr(acac)_2(IM2py)]PF_6$ (b), and $[Cr(bzac)_2(NIT2py)]PF_6$ (c) in CH_3CN at 300 K.

Experimental Section

Preparation of the Complexes. The NIT2py and IM2py bis(β-diketonato) Cr(III) complexes were prepared by the already reported methods.[6,7] The Lu(III) complex was prepared by the modified method of the literature.[14]

Physical Measurements. UV−visible absorption spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer at room temperature. Low-temperature UV−vis measurements were carried out on the same spectrophotometer with an Oxford Cryostat DN1704 (static). Magnetic circular dichroism (MCD) spectra were measured on a JASCO J-720W spectropolarimeter. NIR luminescence spectra were obtained on a SPEX 1269 spectrometer with a Ge-pin photodiode (North Coast EO-817L) detector cooled by liquid nitrogen.

Results and Discussion

The absorption and MCD bands near 13.00−14.50 × 10^3 cm^{-1} for the NIT2py and IM2py Cr(III) complexes (Figure 1) are due to the formally spin forbidden $^3L_0(^4A_2) \rightarrow {}^3L_D(^2\Gamma)$ transitions between the spin-coupled states originating from the $^4A \rightarrow {}^2\Gamma(^2E,{}^2T_1)$ d−d transitions (Figure 2), which was confirmed by the intensification on lowering the temperature,[6,7] and further supported by the fact that the MCD bandwidths are as large as those of $[Cr(acac)_2(en)]^+$.[9a]

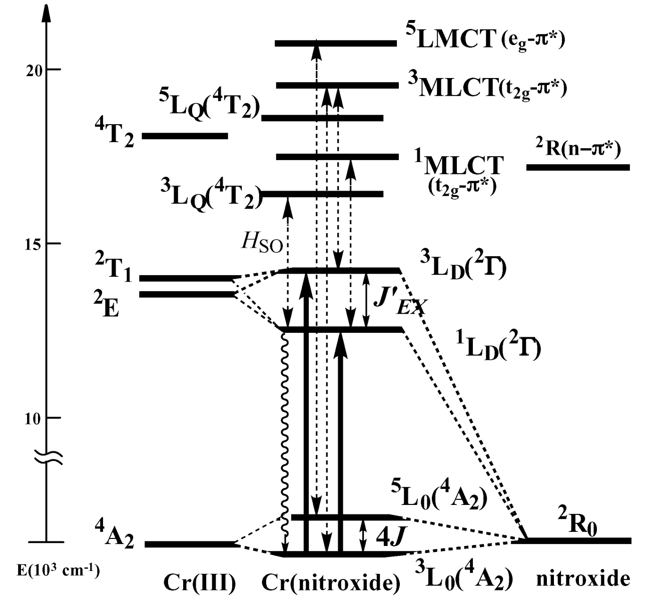

Figure 2. Energy levels of nitroxide radical Cr(III) complexes (center) together with nonradical Cr(III) complexes (left) and nitroxide itself (right). Thick solid vertical lines and a wavy vertical line indicate MCD and luminescence, respectively. Dotted vertical lines show the configurational interactions (CI) between the ground and the excited states and/or MLCT states with the same spin multiplicity.

For the NIT2py complex, the fairly sharp luminescence band with a longer wavelength shoulder appears at about 12000 cm^{-1}.[6] The IM2py complex gives the luminescence band around 9500 cm^{-1} with the whole emission profile, whereas the previous measurement[6] showed only the shorter wavelength envelope. These luminescence bands are displaced to lower energy from the lowest energy absorption bands by 1500 cm^{-1} and 4340 cm^{-1} for the NIT2py and IM2py complexes, respectively. The emission features may arise from three possible causes. (i) Intraligand (ligand centered) luminescence from the SOMO π* to the n(HOMO) orbital in the NIT2py or IM2py radical; (ii) $^3L_D(^2\Gamma) \rightarrow {}^3L_0(^4A_2)$ d−d fluorescence; (iii) $^1L_D(^2\Gamma) \rightarrow {}^3L_0(^4A_2)$ d−d phosphorescence. In order to examine case i, the luminescence of the NIT2py Cr(III) complex is compared with the intraligand luminescence observed for the 4f−4f nonemittive radical lanthanide complex, $[Lu^{III}(hfac)_3(NIT2py)]$. The absorption spectra in CH_2Cl_2 at 180 K and the luminescence in the solid state at 5 K are very similar in vibronic structure to each other as well as to the reported spectra[15] and exhibit a mirror image as shown in Figure 3. This spectral behavior indicates that the luminescence at 9.00−15.00 × 10^3 cm^{-1} must be assigned to the intraligand SOMO $\pi^* \rightarrow$ n(HOMO) luminescence. This is in line with recent reports[15a,b] on the luminescence in Ln(III) complexes with two chelating NITBzImH radicals and in NITBzImH radical itself, which arises from ligand-centered transitions. As compared with this radical intraligand luminescence, the shape and the peak position of the luminescence for the NIT2py complex are qualitatively different (Figure 3). Thus, the luminescence of the NIT2py complex does not originate from a radical intraligand transition. The band envelopes and each vibronic component of the absorption and the corresponding luminescence spectra of the NIT2py and IM2py Cr(III) complexes

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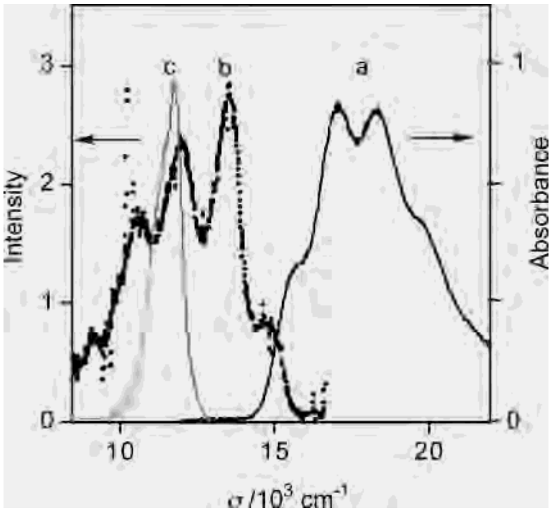

Figure 3. UV−vis absorption spectra (a) in CH_2Cl_2 at 180 K and luminescence spectra (b) in the solid state at 15 K of [Lu(hfac)$_3$(NIT2py)]. Luminescence spectrum (c) in the solid state at 15 K of [Cr(acac)$_2$(NIT2py)]-PF_6.

appear to be correlated to each other with mirror images (Figure 1: top). This suggests that case ii applies with a large Stokes shift. However, the displacements (1500−4340 cm^{-1}) are found to be as large as the Stokes shifts[16] for the inter-subshell (e_g−t_{2g}) fluorescence from $^4T_{2g}$ to $^4A_{2g}$ of $[CrF_6]^{3-}$ and $[CrF_3(H_2O)_3]$. Thus, these "shifts" are too large for the $^3L_D(^2\Gamma) \rightarrow {}^3L_0(^4A_2)$ d−d luminescence involving spin-flip intra-subshell (t_{2g}−t_{2g}) transitions at the metal centers, even in view of a possible mixing with the MLCT. Therefore, the origin of the luminescence is not due to the case ii. Thus, case iii must apply. In order to obtain further information on the lowest excited states, MCD spectroscopy was applied. Our previous MCD measurement on the NIT2py and IM2py complexes demonstrated the presence of bands around 13.00−14.50 × 10^3 cm^{-1}, but not in the region of the luminescence peak. However, as a result of the MCD remeasurement where an attempt to extend was made in the range of 11.50−12.00 × 10^3 cm^{-1} in more concentrated solution, a weak positive MCD band of the NIT2py complex could be observed at 11.80 × 10^3 cm^{-1}. This MCD feature may be due to the intrinsic spin-forbidden transition, $^3L_0(^4A_2) \rightarrow {}^1L_D(^2\Gamma)$, the intensity of which is borrowed from the spin-allowed $^3L_0(^4A_2) \rightarrow {}^3L_Q(^4T_2)$ d−d transition through the spin−orbit coupling (H_{so}) between the $^1L_D(^2\Gamma)$ and $^3L_Q(^4T_2)$ as shown in Figure 2. Moreover, the MCD intensity $\Delta\epsilon_M$ = ca. 3 × 10^{-3} M^{-1} cm^{-1} T^{-1} and the MCD bandwidth $\nu_{1/2}$ = ca. 300 cm^{-1} are much smaller than those of the higher energy transitions. Importantly, the MCD peak positions correspond to the luminescence bands (Table 1) and the half bandwidth of this lowest energy MCD peak is similar to those of the deconvoluted components of the main luminescence band. Therefore, the luminescence is in fact due to the $^1L_D(^2\Gamma) \rightarrow {}^3L_0(^4A_2)$ transition. For the IM2py Cr(III) complex, the luminescence is also quite different from that of the IM2py Lu(III) complex, though the corresponding MCD could not be observed owing to the instrumental limitations. Two series of the β-diketonate complexes give similar results; i.e., absorption and/or MCD and luminescence patterns corresponds to each other (Figure 1 and Table 1).

Table 1[a]

compounds	E_{lum} ($10^3\sigma$/cm^{-1})	E_{SF} ($10^3\sigma$/cm^{-1})	$\lvert 4J_{obs}\rvert$ (cm^{-1})	J'_{EX} (cm^{-1})
[Cr(acac)$_2$(NIT2py)]PF_6	11.80	13.30	246	1500
[Cr(dbm)$_2$(NIT2py)]PF_6	11.30	13.25	280	1950
[Cr(bzac)$_2$(NIT2py)]PF_6	11.50	13.30	121	1800
[Cr(acaMe)$_2$(NIT2py)]PF_6	11.30	13.10	36	1800
[Cr(acaPh)$_2$(NIT2py)]PF_6	11.40	13.17	78	1770
[Cr(dpm)$_2$(NIT2py)]PF_6	11.80	13.33	394	1530
[Cr(acac)$_2$(IM2py)]PF_6	9.80	14.14	752	4340
[Cr(acaMe)$_2$(IM2py)]PF_6	10.20	13.80	408	3600
[Cr(acaPh)$_2$(IM2py)]PF_6	9.90	14.00	476	4100

[a] E_{lum} and E_{SF} refer to the positions of the luminecensce ($^1L(^2\Gamma)$) and the formally spin-forbidden $^3L(^2\Gamma)$ MCD bands, respectively. $4J_{obs}$ is the exchange coupled energy gap in the ground state derived by applying the spin Hamiltonian $H = -2J(S_1 \cdot S_2)$.[6,7] $J'_{EX} = E_{SF} - E_{lum}$ for the energy gap in the lowest excited state.

It is therefore concluded that the luminescence of the NIT2py and IM2py complexes originate from the $^1L_D(^2\Gamma) \rightarrow {}^3L_0(^4A_2)$ transition. For these complexes, an efficient energy transfer from the SOMO π^* to the $^1L_D(^2\Gamma)$ levels occurs. This is in contrast to the case of the IMBzimH or the NITBzimH Eu(III) complex where intraligand and 4f−4f luminescence was simultaneously observed.[15a,b] The energy gaps between the singlet and triplet levels in the lowest excited state are estimated to be much larger than those in the ground state (Table 1). This is in accordance with the generally observed enlargement of the magnetic interactions for the excited states as compared with the ground state in exchange coupled systems of metal−metal dimers.[17−20] The difference between the ground and excited states originates from an increase of electron-transfer character in the excited states.[17−19] The increase of magnetic interactions in the excited state as compared with those in the ground state is much larger than that found for the metal−metal dimers.[17,19] This large increase results from the fact that the ^{3}MLCT and ^{1}MLCT energy levels of the NIT2py and IM2py complexes are much lower in energy than the LMCT or MMCT in the Cr^{III}−Cr^{III} or other metal−metal dinuclear complexes.[17−20] The energy lowering leads to larger configurational interaction (CI) among the excited states (Figure 2), which increases the energy gap in the first lowest excited state.[6,7,13]

For the NIT2py and IM2py complexes, the magnetic interactions in the excited states are found to vary from 1500 to 2000 cm^{-1} and from 3600 to 4400 cm^{-1}, respectively. Notably, these variations are much smaller than those[6,7,13] in the ground state for the β-diketonato complexes (Table 1). In contrast, the peak positions of the luminenscence ($^1L_D(^2\Gamma)$) and the absorption ($^3L_D(^2\Gamma)$) with variation of

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β-diketonates are not much different from one another. It follows through the VBCI model that the configurational interaction between $^1L_D(^2\Gamma)$ and ^{1}MLCT[21] or $^3L_D(^2\Gamma)$ and ^{3}MLCT depends upon the integral $\langle t_{2g}|h|\pi^*\rangle$ or the orbital overlap, $\langle t_{2g}||\pi^*\rangle$, between the t_{2g} and π^* orbitals which exert no coligand effect,[6,7,13] whereas CI between the ^{5}LMCT and $^5L_Q(^4A_2)$ depends upon $\langle e_g||\pi\rangle$, which is why the ferromagnetic interaction is affected by the coligand effect.[6,7,13]

Further studies on the lifetime and the quantum yield for the luminescence are in progress in our laboratory.

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(21) The real singlet (doublet) wave function is given by $\Psi(^1L_D(^2\Gamma)) = \Psi_0(^1L_D(^2\Gamma)) + b\Psi(^1\mathrm{MLCT})$. $\Psi_0(^1L_D(^2\Gamma))$ and $\Psi(^1\mathrm{MLCT})$ are approximated to denote $|t_{2g}{}^+t_{2g}{}^+t_{2g}{}^-\pi^{*-}|$ and $|t_{2g}{}^+t_{2g}{}^-\pi^{*+}\pi^{*-}|$, respectively, and b is represented as $b = \langle|\Psi_0(^1L_D(^2\Gamma))|h|\Psi(^1\mathrm{MLCT})|\rangle/\Delta E_{CT} = \langle|t_{2g}{}^+t_{2g}{}^+t_{2g}{}^-\pi^{*+}|h|t_{2g}{}^+t_{2g}{}^-\pi^{*+}\pi^{*-}|\rangle/\Delta E_{CT} = \langle|t_{2g}{}^+|h|\pi^{*+}|\rangle/\Delta E_{CT} = h(\mathrm{CT})/\Delta E_{CT}$ where $h(\mathrm{CT})$ is the electron-transfer integral and ΔE_{CT} is the energy difference between E_{CT} and E_{SF} (Table 1).