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Luminescence and Circularly Polarized Luminescence of Optically Active $[Rh^{III}(diamine)_3]^{3+}$ Complexes: Conformation in the Luminescent Excited States

Taro Tsubomura,* Sonoko Morishita, Hiroshi Andoh, and Makoto Morita

Department of Industrial Chemistry, Faculty of Engineering,
Seikei University Kichijoji-kitamachi, Musashino,
Tokyo 180, Japan

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Introduction

Molecular structure in electronic excited states is generally different from that in the ground state. Circularly polarized luminescence (CPL) spectroscopy is one of the most valuable methods to obtain information on excited states.[1] Although CPL spectra of d–d metal complexes have been reported,[2,3] there is no paper studying the structure of metal complexes in spin-allowed d–d excited states by CPL spectroscopy.

We are interested in the conformation of the ligand in the excited states of metal complexes. Generally, irradiation upon ligand field bands of metal complexes leads to an occupation of the antibonding orbital, so that it should cause the metal–ligand bonds to be weaker and the bond length to be longer than that in their ground state. We thought that useful information could be obtained from comparative study on the CPL of ethylenediamine (en) complex and 1,2-diaminocyclohexane (dach) complexes. An en ligand is known to adopt a *gauche* conformation in the chelate ring. The conformation is expected to be more planer in excited states. For the tris(dach) complexes, both ob_3 and lel_3 conformers can be obtained when optically active dach isomers were used, and the conformations of the ligands should be rigid in a chelate. In order to investigate the conformations, we studied the luminescence and CPL spectroscopy of the Rh^{III} complexes.

Experimental Section

Synthesis of Complexes. Analytical data (CHN) of all the complexes prepared coincide with the calculated value within 0.5%.

Δ- and Λ-$[Rh(en)_3]Cl_3{\cdot}3H_2O$. The complexes were prepared and optically resolved according to the literature methods.[4]

Δ- and Λ-$[Rh(RR\text{- and }SS\text{-dach})_3]Cl_3{\cdot}H_2O$. *RR*- and *SS*-dach were optically resolved by a literature method.[5] The four isomers of the rhodium complexes were prepared by the method of Galsbøl *et al.*[6]

Spectroscopic Meaurements. Absorption spectra were obtained on a HITACHI U-3200 spectrophotometer. CD spectra were recorded by a JASCO J-40 spectropolarimeter.

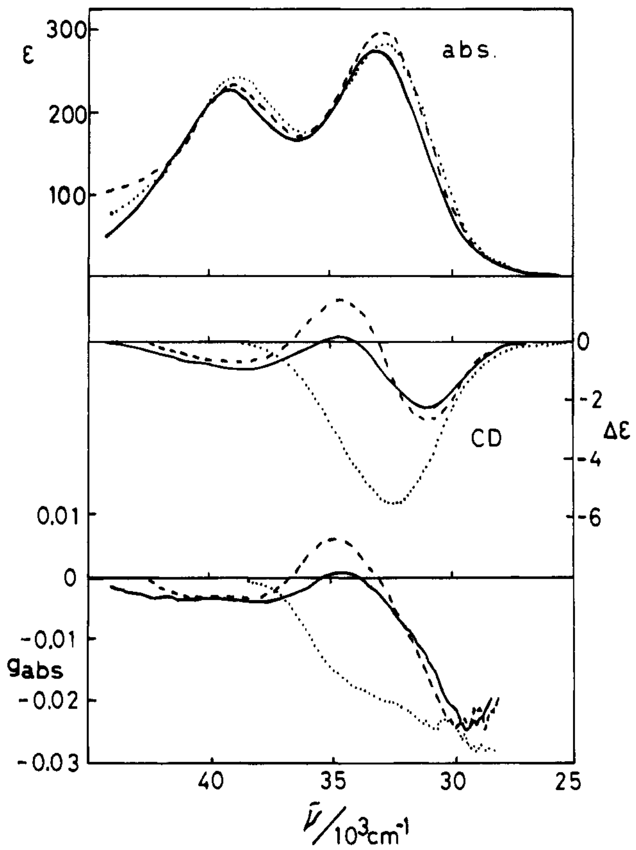

Figure 1. Absorption (top), CD (middle), and g_{abs} (bottom) spectra of the complexes. Key: (—) Δ-$[Rh(en)_3]^{3+}$; (- -) Δ-lel_3-$[Rh(RR\text{-dach})_3]^{3+}$; (···) Δ-ob_3-$[Rh(SS\text{-dach})_3]^{3+}$.

The system used for the CPL measurements in this study is nearly the same as reported earlier,[3,7] but sensitivity was improved using a smaller, but brighter monochromator. The solution of the rhodium complexes (5×10^{-3} M in water and ethylene glycol 1:1 mixed solvent) was degassed by freeze–pump–thaw cycles in a quartz cell. The cell was loaded in an optical cryostat and cooled with liquid nitrogen. To avoid the problems associated with the measurement of the rigid samples, some precautions to minimize the strain in the cell must be taken.[8] The sample was excited with a superhigh-pressure mercury lamp (500 W) equipped with a glass filter and a $CuSO_4$ solution filter (365 nm). The excitation light was chopped by an optical chopper at 10 Hz. The emission, which was detected at 180° angle with the direction of the unpolarized excitation light, was passed through a quartz photoelastic modulator (Morvue PEM-1) operated at 50 kHz and a polarizer sheet and analyzed by a Jovin-Yvon HR-320 monochromator. Output from a photomultiplier-tube (Hamamatsu R955) was fed to a PAR 181 current sensitive preamplifier; the doubly modulated ac signals (10 Hz for total luminescence and 50 kHz for CPL) were processed simultaneously by two lock-in amplifiers in parallel. The spectral intensities were corrected using a standard tungsten lamp.

Results and Discussion

Electronic Absorption and CD Spectra. Absorption spectra of the rhodium(III) complexes are shown in Figure 1. At 77 K in rigid glass solution, almost identical spectra were observed

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with that measured at room temperature. These two lower and higher-energy bands are assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively, in the O_h notation.

Figure 1 includes the CD spectra of the complexes having Δ-configuration. Galsbøl *et al.* reported the UV and the CD spectra of the complexes, but no discussion about the spectra was made.[6] The locations of CD bands shown in Figure 1 coincide with the Galsbøl data with the maximum error of 2 nm. The errors in the CD intensity between the Galsbøl data and ours presented in Figure 1 are within 10%. The transitions between the ground $^1A_1$ state and both the two trigonally split components of $^1T_{1g}$ ($^1A_2$ and ^1E) are magnetically allowed so that the transitions can be optically active.[9] It is well established for d^6 complexes containing five-membered chelates that the observed CD spectral bands in the first absorption region is created by a large cancellation due to overlapping of the two CD components closely located with opposite signs. Generally, the $^1A_1 \rightarrow {}^1E$ transition is negative and larger than that of the $^1A_1 \rightarrow {}^1A_2$ transition for Δ-configuration.[9] The observed CD spectra of *lel*$_3$-Δ-[Rh(*RR*-dach)$_3$]$^{3+}$ and Δ-[Rh(en)$_3$]$^{3+}$ are well explained by the rule.

On the other hand, the CD spectrum of Δ-*ob*$_3$-[Rh(*SS*-dach)$_3$]$^{3+}$shows a single band in the first absorption region. The CD spectrum resembles that of Δ-*ob*$_3$-[Co(dach)$_3$]$^{3+}$, which is reported by Piper *et al.*[10] They concluded that the trigonal splitting of the Co complex is very small.

Ground State Structure of the Complexes. The conformations of the ethylenediamine chelates have been extensively studied.[11] The most stable conformation of the tris(ethylenediamine)rhodium(III) complex present in D_2O solution at room temperature was reported to be *lel*$_2$*ob*$_1$.[12] The difference in Gibbs energy between the conformer and the *lel*$_3$ conformer is reported to be $\Delta G = 1.4 \pm 0.5$ kcal/mol at 298 K. Considering the contribution of the entropy term, the difference should be reduced at 77 K. As a whole, the *lel*-conformation is generally preferred to the *ob*-conformation for an ethylenediamine chelate. On the other hand, the conformations of diaminocyclohexane chelates should be fixed. Δ-[Rh(*SS*-dach)$_3$]$^{3+}$ and Δ-[Rh(*RR*-dach)$_3$]$^{3+}$ complex must have *ob*$_3$ and *lel*$_3$ conformations, respectively. It may be reasonably accepted that the conformation of the diaminocyclohexane chelate is held even in d−d excited states.

In this report we want to discuss the chiroptical properties with the dissymmetry factors, g_{abs} and g_{em}.[13] Both the shapes and values in the g_{abs} of *lel*$_3$-[Rh(dach)$_3$]$^{3+}$ complex are close to those in [Rh(en)$_3$]$^{3+}$, but *ob*$_3$-[Rh(dach)$_3$]$^{3+}$ appears different. The result indicates that the ground-state structure of [Rh(en)$_3$]$^{3+}$ has very close similarity to that of *lel*$_3$-[Rh(dach)$_3$]$^{3+}$ from a chiroptical point of view of d-d states.

Luminescence and CPL Spectra. Figure 2 shows the luminescence and CPL spectra of the three Rh(III) complexes measured at 77 K together with the emission dissymmetry factors. They have a single band with band width of 3000 cm^{-1}. Some shifts of the band maxima of the two [Rh(dach)$_3$]$^{3+}$ complexes compared with that of the en complex are observed. [Rh(NH$_3$)$_6$]$^{3+}$ is reported to show similar broad triplet d−d luminescence (λ_{max}, 17 × 10^3 cm^{-1}; band width, 3000 cm^{-1}).[14,15] The luminescence bands studied in this study are assigned to the phosphorescence originated from the energetically lower component of the trigonally-split $^3T_{1g}$ state. All the complexes show a broad CPL band. The signs of the CPL bands agree with the signs of the CD bands at the low-energy side.

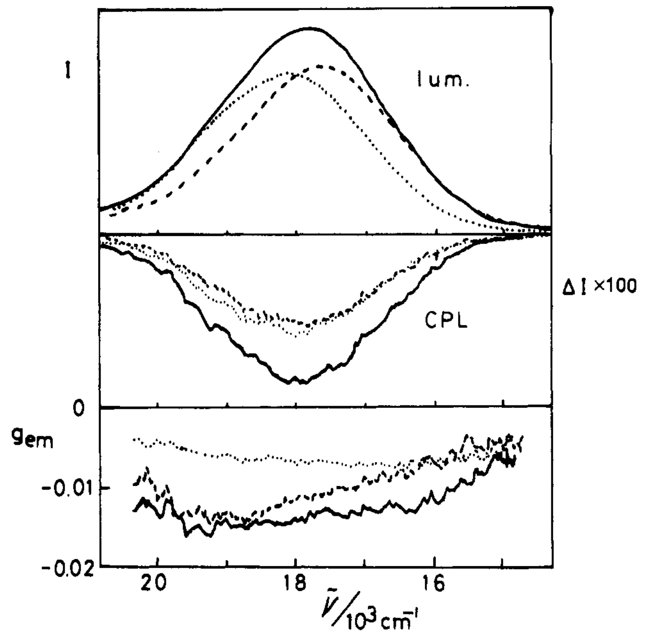

Figure 2. Luminescence (top), CPL (middle) and g_{em} (bottom) spectra of the complexes. Key: (—) Δ-[Rh(en)$_3$]$^{3+}$; (- -) Δ-*lel*$_3$-[Rh(*RR*-dach)$_3$]$^{3+}$; (• • •) Δ-*ob*$_3$-[Rh(*SS*-dach)$_3$]$^{3+}$.

Emission Dissymmetry Factor and Excited State Structures. The signs of g_{em} value agree with that of g_{abs} in the lowest-energy CD band, but the magnitudes are somewhat different. All the g_{abs} values for [Rh(en)$_3$]$^{3+}$, *lel*$_3$-[Rh(dach)$_3$]$^{3+}$, and *ob*$_3$-[Rh(dach)$_3$]$^{3+}$ at the lower-energy side of the $^1T_{1g}$ band are about −0.025. The g_{em} values are smaller than the g_{abs} values. Two factors can be pointed out for the relatively small g_{em} values. One is the difference in the multiplicity of the excited states. The absorption bands observed are due to the transitions between singlet states; however, the emissions are assigned to phosphorescence. Difference in the g values between fluorescence and phosphorescence have already been discussed.[8] Another factor is the dynamic Jahn−Teller effect. Urushiyama *et al.* reported[14] the structural distortion of [Rh(NH$_3$)$_6$]$^{3+}$ in its $^3T_{1g}$ excited state caused by the effect. If the luminescent state of our complexes is a degenerated E state, similar distortion can be possible and a noticeable change of g_{em} can occur.

The g_{em} values are not constant over the luminescence bands. The value at the higher-energy end is relatively large, and decreases with decreasing the wavenumber for both the en complex and the *lel*$_3$-dach complex. The decrease of g_{em} values should be caused by the contribution of vibration. Dissymmetry factors of vibronic transitions often become smaller than its pure electronic transition.[16] Thus, the chiroptical properties in the electronic excited state are to be characterized by the g_{em} values in the high-energy region of the bands around the electronic origin. The g_{em} value of the en complex in the region is close to that of the *lel*$_3$-dach complex. On the other hand, the g_{em}

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(13) The absorption- and emission-dissymmetry factor, g_{abs} and g_{em}, are defined as follows: $g_{abs} = \Delta\epsilon/\epsilon$, $g_{em} = 2\Delta I/I$.

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(16) See ref 3 and: Geiser, U.; Güdel, H. U. *Inorg. Chem.* **1981**, *20*, 3013.

values of the ob_3-dach complex are about half those of the other two complexes at the region. The g_{em} values at 19×10^3 cm^{-1} are −0.015, −0.013, and −0.0056, respectively. Further, g_{em} of the ob_3-dach complex shows almost constant values over the entire band, which is different from the other two complexes. If the trigonal splitting of the ob_3-complex is very small as reported for the ob_3-[Co(dach)$_3$] complex, the small g_{em} value is reasonable due to cancellation of the two transitions originated from both the E and A components. To confirm the validity of the data, the spectra of the three enantiomers were also measured, and mirror images of the g_{em} values are obtained for the Λ-complexes. The g_{em} values at 19×10^3 cm^{-1} for the en, lel_3-dach, and ob_3-dach complexes of Λ-configuration are +0.015, +0.010, and +0.0065, respectively. Although the absolute value for the Λ-lel_3-dach complex is somewhat smaller than that of the Δ-lel_3-dach complex, this is due to the low optical yield (88% of the Δ complex) of the complex.

As shown in the g_{em} spectra, the chiroptical property in the luminescent excited state of the en complex shows a considerable similarity with that of the lel_3-dach complex rather than the ob_3-dach complex. This means that the structures in the excited states—including electronic and vibrational states—of the two complexes are similar and the structure of the ob_3-dach complex is different. The conformation of the chiral dach chelates of the rhodium(III) complexes should be unchanged in the d−d excited states, so that the ethylenediamine chelates are concluded to have essentially *lel* character even in the d−d excited states.

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Additions and Corrections

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Ramon Vicente,* Albert Escuer, Joan Ribas, M. Salah El Fallah, Xavier Solans, and Mercé Font-Bardía: X-ray Structure Determination and Magnetic Behavior of the New Uniform $S = 1$ Chain [{Ni(Me$_2$[14]-1,3-dieneN$_4$)(μ-N$_3$)}$_n$]-(ClO$_4$)$_n$. Magneto−Structural Correlations.

Pages 1278−1281. In the original paper, the structure of the title compound was incorrectly refined in space group *I*4. According to a suggestion from W. B. Connick and L. M. Henling, California Institute of Technology, we have subsequently verified that the space group $I\bar{4}2d$ is consistent with the diffraction data. The structural parameters for both determinations are essentially the same. Results deviating from those of the original resolution are given here in Tables 1 and 2.

Table 1

space group	$I\bar{4}2d$	R	0.033
d_{calc}, g cm^{-3}	1.327	R_w	0.084
μ(Mo Kα), cm^{-1}	11.37		

Table 2

atom	x	y	z	U(eq), Å^2 × 10^3
Ni	0.2500	0.4023(1)	0.8750	37(1)
Cl(1)	0	0	0.2025(1)	63(1)
N(1)	0.2448(3)	0.5471(2)	0.9121(1)	54(1)
N(2)	0.2677(2)	0.2613(3)	0.9147(1)	50(1)
N(5)	0.0491(2)	0.4036(2)	0.8797(1)	54(1)
N(6)	0	0.5000	0.8789(1)	44(1)
C(1)	0.2147(4)	0.5293(4)	0.9540(1)	71(1)
C(2)	0.2665(5)	0.4116(5)	0.9698(1)	80(1)
C(3)	0.2119(4)	0.2898(5)	0.9531(1)	71(1)
C(4)	0.2231(3)	0.1498(3)	0.8953(1)	61(1)
C(9)	0.2637(3)	0.6527(3)	0.8534(1)	64(1)
O(1)	−0.0087(5)	0.1109(4)	0.2250(1)	97(1)
O(2)	0.1324(13)	0.0076(21)	0.1887(5)	107(5)
O(2′)	0.0899(11)	0.0109(18)	0.1749(4)	89(3)

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