Structural Deformation of a Ring-shaped Re(I) Diimine Dinuclear Complex in the Excited State

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Abstract

We investigated the excited state of a ring-shaped dinuclear Re(I) diimine bis-carbonyl complex that shows promise with regard to efficient photosensitized reactions and multi-electron storage, using time-resolved infrared (TR-IR) vibrational spectroscopy and quantum chemical calculations. Anomalous peaks in the CO stretching region of the TR-IR spectrum were well reproduced by the calculations. It was found that metal-to-ligand charge transfer occurs only in one of the Re complex units, and that the excited state geometry is deformed relative to the ground state in order to relax the associated steric tension. This structural deformation generates the unique photophysical properties of the complex.

1. Introduction

Assembling photofunctional molecules into ring structures is one means of improving their performance, although only a few examples have been reported thus far. The best-known compounds of this type are the ring-shaped chlorophyll compounds employed during photosynthesis by purple bacteria [1], along with the ring-shaped porphyrin oligomers [2,3]. However, compared to these compounds, ring-shaped Re(I) diimine complexes have many advantages [4-6], since mono-nuclear Re(I) diimine complexes absorb and emit visible light efficiently [7,8] and their excited states exhibit long lifetimes and can function as photo-redox agents or photocatalysts [9-16]. Subsequent to forming a ring-shape, these complexes are more efficient redox photosensitizers [4] and can store a greater quantity of electrons [5]. In addition, it is easy to control the size of these ring structures and to generate hetero-membered rings.

The photophysical properties of such systems, including absorption wavelength, emission wavelength and phosphorescence lifetime, have already been systematically investigated [4,6]. It has been determined that these properties depend greatly on the size of the ring, since decreasing the size of the internal ring cavity can significantly affect the photophysical properties of the rings themselves. In particular, the dinuclear ring (**R2b²⁺**) shown in Fig. 1 exhibits an emission quantum yield ($\Phi_{em} = 0.081$) 4.5 times greater and an emission wavelength ($\lambda_{em}^{max} = 611$ nm) 24 nm shorter than those of the corresponding mononuclear Re(I) complex (**M⁺**: $\Phi_{em} = 0.018$ and $\lambda_{em}^{max} = 635$ nm), even though the absorption maxima of both complexes are very similar (**R2b²⁺**: $\lambda_{abs}^{max} = 415$ nm, **M⁺**: $\lambda_{abs}^{max} = 414$ nm) [4]. In order to elucidate the manner in which the characteristic properties of this compound are affected by forming a ring, the present work explored the electronic and molecular structures of a ring-shaped Re(I) dinuclear complex in the excited state, using a combination of time-resolved infrared spectroscopy (TR-IR) and quantum chemical calculations.

TR-IR is one of the most useful methods of studying the excited state characteristics of transition metal complexes. The CO ligands of metal complexes are an especially good probe for the investigation of electronic and molecular structures in the excited state, owing to the $d\pi-\pi^*$ back donation between the central metal and these ligands [17]. In the case of the Re(I) diimine carbonyl complexes, many excited state characteristics have been clarified by observing the vibrations of CO ligands by TR-IR [16-33]. Quantum chemical calculations, using a program package such as Gaussian, are another important tool for the study of transition complexes in the excited state. Although the results of such calculations for the excited states of organic compounds are not especially reliable,

it has recently been shown that the results obtained for the lowest triplet state (T_1) are in good agreement with the TR-IR spectra generated by the meta-stable triplet states of transition metal complexes [22, 25, 26, 28, 34-36]. Considering that the energies and intensities of sharp vibrational bands are very sensitive to electronic and molecular structures, the reliability of the quantum calculations is sufficiently high so as to allow a discussion of the properties of such metal complexes in the excited state.

2. Experimental

2.1. Acquisition of TR-IR spectra

TR-IR spectra were obtained via the pump-probe method using a femtosecond Ti:sapphire chirped pulse amplifier (CPA, wavelength: 800 nm, pulse duration: 120 fs, repetition rate: 1 kHz). The details of the procedure have been previously reported [34-36]. A tunable mid-infrared pulse ($1000 - 4000\text{ cm}^{-1}$) was obtained by difference frequency generation (DFG) between the signal and idler beams of an optical parametric amplifier (OPA) pumped by a part of the output of the CPA. The ultraviolet pump pulse (400 nm) was obtained by second harmonic generation (SHG) of the other part of the output of the CPA. The pump and probe pulses were focused on an infrared flow cell equipped with BaF_2 windows (optical path length: 0.1 mm). The fluence of the pump pulse was approximately 10 mJ/cm^2 . The probe pulse passed through the flow cell and was subsequently dispersed by a 19 cm polychromator and detected with a 64 channel linear array IR detector.

The sample complexes were synthesized following a previously reported procedure [4]. Following the preparation of 1 mM acetonitrile solutions of each complex using this procedure, the air dissolved in the solutions was purged by sparging with Ar gas for more than one hour.

2.2. Quantum chemical calculations

The quantum chemical calculations were performed with the Gaussian 09 program [37]. The optimized structures were obtained using the mPW1PW91 functional and the LanL2DZ basis set with polarization functions. The calculated lowest singlet (S_0) and lowest triplet (T_1) states correspond to the observed ground and excited states, respectively. The IR spectra of the S_0 and T_1 states were obtained from the optimized geometries with a scaling factor of 1.005. Time-dependent density functional theory (TD-DFT) calculations were also performed to allow study of the vertical excitation from the S_0 to S_1 states.

3. Results and discussion

The target ring-shaped complex **R2b²⁺** contains two $\text{Re(I)(bpy)(CO)}_2(\text{PPh}_2)_2$ units connected to one another via two $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ bridge ligands. The detailed structure of this complex, as determined by X-ray diffraction, has been reported in Ref. [4]. Figure 2(a) shows the TR-IR spectra acquired 800 ps after photoexcitation, over the range of $1825 - 2050 \text{ cm}^{-1}$ in which the CO stretching vibrations are located. Three transient absorption bands are evident at 1860 , 1900 and 1994 cm^{-1} as well as two bleach bands at 1876 and 1932 cm^{-1} . At this delay time, the complex has already relaxed to the bottom of the lowest triplet state; thus, these transient absorption bands are assigned to vibrational transitions from the vibrational ground state of the triplet excited state. In contrast, the bleach bands are attributed to the reduction of IR absorption in the ground state.

The IR absorption spectra of the CO stretching vibrations of mononuclear Re(I) diimine bis-carbonyl complexes with *acis,trans*- $[\text{Re}(\text{diimine})(\text{CO})_2(\text{PR}_3)]^+$ structure have been comprehensively investigated [38] and the TR-IR spectra of some mononuclear Re(I) diimine bis-carbonyl complexes have also been studied [17, 18]. According to these reports, the higher and lower wavenumber bands are generally assigned to the symmetric and anti-symmetric vibrations of the two CO bonds, respectively. As an example, we show the TR-IR spectrum of **M⁺** obtained by the same procedure as employed for the **R2b²⁺** complex in Fig. 2(b). Upon photoexcitation with $<500 \text{ nm}$ light, the meta-stable triplet metal-to-ligand charge transfer state ($^3\text{MLCT}$) is generated, in which the excited electron is localized on the diimine ligand. As a result of this charge transfer, the CO stretching bands in the TR-IR spectrum exhibit a significant blue shift of $35\text{-}60 \text{ cm}^{-1}$. This occurs because there is an electron-pair donation from the $d\pi$ orbital of the central metal to the π^* orbitals of the CO ligands (representing $d\pi\text{-}\pi^*$ back donation) in the ground state. The associated reduction of the negative charge on the central metal by photoexcitation weakens this effect and strengthens the bonds inside the CO ligands. Table I summarizes the wavenumbers of the CO stretching vibrational modes of the mononuclear Re(I) diimine bis-carbonyl complexes and of **R2b²⁺**.

In the TR-IR spectrum of **R2b²⁺**, the bands at 1900 and 1994 cm^{-1} can be assigned to the vibrational modes associated with the MLCT excitation of one of the two Re complex units. However, the band at 1860 cm^{-1} cannot be explained by this simple theory, indicating that some other process occurs only in the excited state of the ring dinuclear complex. In order to investigate this spectral anomaly, we carried out quantum chemical calculations. Figs. 2(c) and (d) show the calculated difference spectrum between the T_1 and S_0 states and the calculated spectra for the T_1 (red line) and S_0 (blue line) states,

respectively. The calculated difference spectrum well reproduces the characteristics of the TR-IR spectral pattern, including the anomalous 1860-cm^{-1} band. According to Fig. 2(d), this characteristic spectral pattern results from the four vibrational bands of the T_1 state. This result indicates that the symmetry of the excited state is different from that of the ground state. It is worth noting that the anomalous positive scaling factor of 1.005 is presumably caused by the residual steric tension induced upon forming the ring, as discussed further on.

The arrows in Fig. 3 indicate the vibrational phasing between the CO stretching vibrations as estimated from the calculated normal vibrational modes. In the S_0 state, the observed bands at 1876 and 1932 cm^{-1} are assigned to the anti-symmetric and symmetric vibrations of both Re complex units, respectively. In contrast, in the case of the T_1 state, the wavenumbers of the bands differ between the Re complex units: the bands at 1860 and 1994 cm^{-1} (indicated by the blue circle in Fig. 2a) are assigned to the anti-symmetric and symmetric vibrations of one Re complex unit (blue arrows on the right side), respectively, whereas the bands at 1932 and 1900 cm^{-1} (indicated by the red circle in Fig. 2a) are assigned to the anti-symmetric and symmetric vibrations of the other (red arrows on the left side). Thus, it is concluded that this loss of symmetry between the two Re complex units causes the anomalous vibrational pattern in the TR-IR spectrum.

The electronic characteristics of the ground and excited states were estimated from the frontier molecular orbitals of the S_0 and T_1 states obtained from calculations. Fig. 4 shows the highest occupied molecular orbitals (HOMOs) of the S_0 state and the lower and higher singly occupied molecular orbitals (SOMO1 and SOMO2) of the T_1 state. Because of symmetry, the HOMOs in the S_0 state are degenerate, whereas this degeneracy is resolved due to the loss of symmetry in the T_1 state, as shown in the upper panel in Fig. 4. We note that the total charge of each Re complex unit is neutral in both the S_0 and T_1 states; thus, no charge transfer occurs between the two Re complex units. In the S_0 state, the HOMOs are evenly delocalized on both Re atoms. In the T_1 state, the SOMO1 is still localized on the Re atom but only on one Re complex unit (the right side), and the orbital distribution is very similar to that of the HOMO on one side of the Re complex in the S_0 state. Considering that the difference in the frontier orbitals determines the variation in charge distribution between the two states, there is almost no change in charge distribution on the right side Re complex unit. Conversely, the SOMO2 is localized on the bpy ligand on the other Re complex unit (the left side). This difference in the frontier molecular orbitals indicates that the MLCT from the Re atom to the bpy ligand occurs on the left side Re complex unit. These molecular orbitals

are only minimally distributed to sites other than the Re, CO and bpy, such as the phenyl groups and alkyl bridges. Thus, it can be said that all the structural deformation in the excited state originates from this MLCT on the one Re complex unit.

At this point, we discuss the details of the structural changes on going from the ground to excited state on the basis of the calculated optimized geometries shown in Fig. 5. Fig. 6 summarizes the differences in the bond lengths and angles in the geometries of the S_0 and T_1 states. The most noticeable difference is that the plane defined by the two CO ligands and Re atom of the right side Re complex unit is tilted by 7° relative to that of the left side Re complex unit, as can be seen in Fig. 5. Strictly speaking, the planes are slightly deviated from the Re-Re axis. Another remarkable feature is that the P-Re-P angle of the left side Re complex unit (P2-Re1-P5) is decreased by 5° . In addition, some angles and bond lengths of both the left and right side Re complex units are slightly changed, $\sim 1^\circ$ or $\sim 0.01 \text{ \AA}$.

Based on these results, we propose a mechanism for the structural deformations in the excited state. In this mechanism, the MLCT induced by photoexcitation reduces the negative charge of the Re atom in one Re complex unit (the left side in this case) and reduces the $d\pi-\pi^*$ back donation associated with both the Re-CO and Re-P bonds in this unit. As a result, the P-Re-P angle in the photoexcited Re complex unit is changed significantly (by 5°). To confirm this, we examined the corresponding structural changes in the mononuclear complex, $\mathbf{M}^+$, as shown in Fig. 7, because the photoexcitation occurs on only one Re complex unit in this case. As expected, the P-Re-P angle in $\mathbf{M}^+$ is decreased by 10° on going from the S_0 to T_1 state. Because there is no change in the distribution of the frontier molecular orbitals in the other parts of the complex, we conclude that this bond bending is the origin of the structural changes in all the other parts.

This being the case, it is of interest to determine the driving force for the structural changes in the remainder of the complex. Upon forming the ring, the structure of $\mathbf{R2b}^{2+}$ becomes congested, and so the bending of the P-Re-P angle in one Re complex unit induced by photoexcitation would be expected to generate significant structural tension as the result of steric hindrance. To reduce this tension, the structural deformation occurs in regions other than the P-Re-P angle. In particular, a change occurs in the plane consisting of the two CO ligands and Re atom of the other Re complex unit. This structural deformation mechanism explains the unique photophysical properties of $\mathbf{R2b}^{2+}$. It is known that a large structural deformation in the excited state generates a phosphorescence red shift owing to the large difference in equilibrium position between the ground and excited potentials. However, this simple theory is not applicable to our

case because the two complexes, $\mathbf{M}^+$ and $\mathbf{R2b}^{2+}$, have quite different potentials each other. Thus, we consider the relationship between the structural deformation and the energy of the excited state. The tension created by the bending of the P-Re-P angle in one Re complex unit is presumably not fully relaxed, because of the congested structure. In fact, the change in the P-Re-P angle in $\mathbf{R2b}^{2+}$ is 5° , a value that is much smaller than that in $\mathbf{M}^+$ (10°). The residual tension renders the excited state somewhat unstable and this destabilization causes the 24 nm phosphorescence blue shift relative to the mononuclear complex, even though the absorption maxima of both complexes are very similar.

This destabilization is supported by the calculations. Figure 8 summarizes the observed and calculated relative energies of the various states of both $\mathbf{R2b}^{2+}$ and $\mathbf{M}^+$. The experimental energy values given here were estimated from the absorption and emission spectra reported in Ref. [4]. The calculated energies of the S_1 states were obtained from TD-DFT calculations while those for the T_1 states were derived from the optimized geometry of the lowest triplet state. Although the absolute values are different, the relative energy positions obtained from the calculations are in good agreement with the experimental data. This is consistent with that the specific photophysical properties of $\mathbf{R2b}^{2+}$ originate from destabilization of the excited state due to residual tension.

In general, when a transition metal complex undergoes a phosphorescence blue shift, its lifetime becomes shorter because the energy gap to the triplet metal-centered state (3MC), via which non-radiative decay or a ligand substitution reaction occurs. In fact, it is known that some Re(I) diimine *tris*-carbonyl complexes undergo a ligand substitution reaction via 3MC [21]. In contrast, Re(I) diimine *bis*-carbonyl complexes hardly undergo a ligand substitution reaction [39,40]; thus, the non-radiative decay in $\mathbf{R2b}^{2+}$ would occur by the direct coupling to the ground state. In this case, the destabilization and structural deformation reduce the coupling to the ground state and increase the quantum yield of the phosphorescence by a factor of approximately five. These proposed mechanisms on the photophysical properties do not agree with the simple theory assuming one-dimensional potentials and no change in normal modes; however, if a complex undergoes a large structural deformation so as to change the normal modes in the excited state, this assumption is no longer valid [41].

4. Conclusion

This study successfully acquired transient IR vibrational spectra of the ring-shaped dinuclear Re(I) diimine bis-carbonyl complex $\mathbf{R2b}^{2+}$ in the meta-stable triplet excited state. Anomalous CO stretching vibrational bands were identified in these spectra

compared to the spectra of mononuclear Re(I) diimine bis-carbonyl complexes. Simulated spectra of the ground (S_0) and the lowest triplet (T_1) states obtained from quantum chemical calculations closely matched these anomalous spectral patterns. Based on these calculations, it was determined that MLCT occurs in only one of the Re complex units and the P-Re-P angle in this unit is significantly modified. To reduce the tension created by this bending, the structure in other parts of the complex is deformed and this structural deformation breaks the symmetry and results in the anomalous CO stretching vibrations. Furthermore, the destabilization generated by residual tension in the complex results in the observed phosphorescence blue shift and high quantum yield. It is expected that this same phenomenon will also be exhibited by other ring-shaped Re(I) diimine carbonyl complexes as well as other types of ring-shaped metal complexes, and should be helpful with regard to understanding and designing new photofunctional materials using ring-shaped compounds.

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Figure Captions

Figure 1. Molecular structures of the ring-shaped Re(I) dinuclear complex and the corresponding mono-nuclear Re(I) complex.

Figure 2. TR-IR spectra acquired 800 ps after photoexcitation with a 400 nm pulse from acetonitrile solutions of (a) **R2b⁺** and (b) **M⁺**, (c) calculated difference IR spectra between the T₁ and S₀ states of **R2b⁺**, and (d) calculated IR spectra for the T₁ (red line) and S₀ (blue line) states of **R2b⁺**. The colored circles indicate the Re(I) complex unit associated with each vibrational mode when the Re(I) complex is in the excited state (for details, see the text).

Figure 3. Vibrational phases of CO bonds (indicated by arrows) as estimated from the calculated normal vibrational modes. The wavenumbers represent the corresponding observed and calculated vibrational bands.

Figure 4. Molecular orbitals associated with the S₀ and T₁ states of **R2b⁺**.

Figure 5. Optimized geometries of the S₀ and T₁ states of **R2b⁺**.

Figure 6. Selected bond lengths and angles of the S₀ and T₁ states of **R2b⁺**.

Figure 7. Optimized geometries of the T₁ states of **M⁺** and **R2b⁺**.

Figure 8. Energy diagram of the S₀, S₁ and T₁ states of **M⁺** and **R2b⁺**. The experimental energy values were estimated from the absorption and emission maxima in Ref. [4].

Fig. 1. S. Tanaka et al.

Fig. 2. S. Tanaka et al.

Table I. Wavenumbers of the CO stretching vibrational modes in $\text{Re(I)(bpy)(CO)}_2\text{L}_2$ (L = monodentate ligand) complexes. Here ν_{GS} and ν_{ES} designate ground and excited states and $\Delta\nu$ is $\nu_{\text{ES}} - \nu_{\text{GS}}$.

Complex	$\nu_{\text{GS}}(\text{cm}^{-1})$	$\nu_{\text{ES}}(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$
$[\text{Re}(\text{bpy})(\text{CO})_2(\text{Ph}_2\text{P-C}\equiv\text{C-PPh}_2)_2]^+$ (in acetonitrile) ^a	1870	1905	+35
	1940	1990	+50
$[\text{Re}(\text{bpy})(\text{CO})_2\{\text{P}(\text{OEt})_3\}_2]^+$ (in dichloromethane) ^b	1882	1927	+45
	1956	2012	+56
M ⁺ (in acetonitrile)	1863	1900	+37
	1934	1983	+49
R2b ²⁺ (in acetonitrile)	1876	1860	-16
		1900	+24
	1932	1994	+62

^aRef. [8]

^bRef. [18]

Fig. 3. S. Tanaka et al.

Fig. 4. S. Tanaka et al.

Fig. 5. S. Tanaka et al.

Structure parameter		S_0	T_1
bond length	Re1— P2	2.52 Å	2.57 Å
	Re1— P5	2.52 Å	2.57 Å
	Re10— P11	2.52 Å	2.52 Å
	Re10— P14	2.52 Å	2.52 Å
	Re1— C6	1.90 Å	1.92 Å
	Re1— C8	1.89 Å	1.94 Å
	Re10— C15	1.90 Å	1.89 Å
	Re10— C17	1.89 Å	1.88 Å
	C6— O7	1.19 Å	1.18 Å
	C8— O9	1.19 Å	1.18 Å
	C15— O16	1.19 Å	1.19 Å
	C17— O18	1.19 Å	1.20 Å
bond angle	P2—Re1—P5	175°	170°
	P11—Re10—P14	175°	176°
	C6—Re1—C8	90°	86°
	C15—Re10—C17	90°	91°
dihedral angle			
Re(CO) ₂ plane — Re(CO) ₂ plane		0.00°	7°

Fig. 6. S. Tanaka et al.

Fig. 7. S. Tanaka et al.

Fig. 8. S. Tanaka et al.

Graphical Abstract