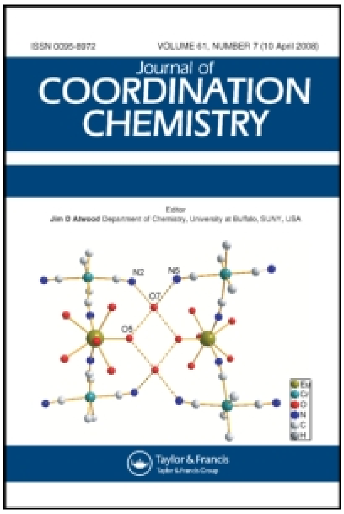

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Potential propelling and rotating functions of propeller-type complexes. III. Detection of the propelling motion in *fac*-tris(*S*-2,3-diaminopropionato)cobalt(III) in an aqueous solution upon IR irradiation

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Potential propelling and rotating functions of propeller-type complexes. III. Detection of the propelling motion in *fac*-tris(*S*-2,3-diaminopropionato)cobalt(III) in an aqueous solution upon IR irradiation

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Circular dichroism spectra of the *fac* and *mer* isomers of tris-cobalt(III) complexes of *S*-2,3-Hdap (Hdap = diaminopropionic acid); *fac* and *mer*-[Co(*S*-dap)$_3$] (Λ or Δ), and [Co(en)$_3$]$^{3+}$ (Λ or Δ, en = ethylenediamine) in an aqueous solution without and upon IR irradiation were measured. The detection of the propelling motion that corresponds to circular dichroism spectral changes of the propeller-type complex, *fac*-[Co(*S*-dap)$_3$] in an aqueous solution upon IR irradiation gave good agreement with the computer-simulation result, that is, the propelling (translation and rotation) motion occurs in propeller-type metal complexes in aqueous solution as a consequence of an appropriate energy supply, which had been obtained by theoretical study based on molecular dynamics (MD) simulations by the use of AMBER 6 program.

Keywords: Propeller-type complexes; Propelling function; Detection of propelling motion

1. Introduction

The pursuit of “bottom-up” nanoscopic solutions to problems of minimization and to the advancement of computing, engineering, and medicine is gathering great interest as classical electronics approaches its size limit and the public clamors for ever faster, cheaper, and more efficient devices [1–3]. A molecular-level machine can be defined as an assembly of a number of molecular components designed to perform mechanical-like movements (output) as a consequence of appropriate external stimuli (input). Extension of the concept of a machine to the molecular level is important not only for basic research but also for the growth of nanoscience and nanotechnology. The “bottom-up” approach towards functionalized nanostructure is a field of research

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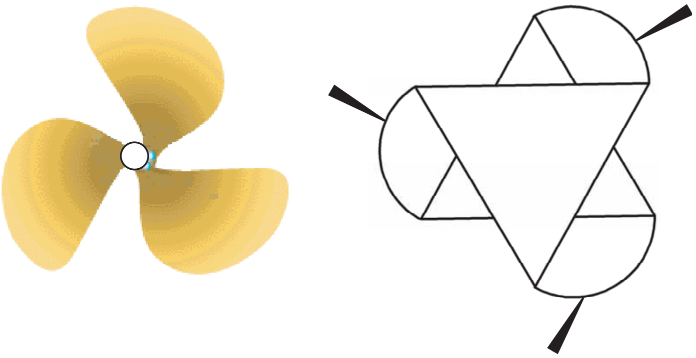

Λ-configuration

Figure 1. Propeller-type complex with a C_3 axis of symmetry perpendicular to the plane of the paper.

that has emerged only in the last few years. A number of groups have created functional systems based on molecules or molecular assemblies, but so far no new paradigm for "bottom-up" construction of molecular devices has emerged. The number and variety of molecular systems that are of potential use in nano-technological devices exploded over the last decade indicating that for "bottom-up" construction of artificial molecular devices, it has become very important to control molecular movement to fulfill a certain function [4–11]. Artificial machines powered by chemical energy ("fuels") produce waste products whose accumulation compromises the operation of the machine unless they are removed from the system. Photochemical and electrochemical energy inputs can be used to make a machine work without formation of waste products. Attention in our group has been paid to the construction of molecular devices and smart functional materials by the use of propeller-type metal complexes (figure 1), *fac*-[Co(*S*-dap)$_3$], in which propelling motion occurs as a consequence of a photochemical energy supply.

Preliminary information on the preparation and isolation of *fac*-[Co(dap)$_3$], has been published [12]. Four isomers of [Co(dap)$_3$] were prepared and effectively isolated by ion-exchange column chromatography on SP-Sephadex (C-25). Λ-*fac* and Λ-*mer*-[Co(dap)$_3$] are depicted in figure 2 (a and b). The C_3 axes of symmetry and propeller structures were confirmed by X-ray structural analysis of the *fac*-isomers. In the structure, three carboxyl groups were aligned on the same side with respect to cobalt on the C_3 axis of symmetry, whereas one of the carbonyl groups was aligned opposite to the other two in the *mer*-isomers (in this case, the axis is a pseudo C_3 axis). Theoretical investigation based on molecular dynamics simulations by the use of AMBER 6 revealed that distinct propelling behavior can be obtained in propeller-type metal complexes with a C_3 axis of symmetry such as *fac*-[Co(*S*-dap)$_3$] and *fac*-tris(5-carboxy-2,2′-bipyridine)cobalt(III) ions in the aqueous solution upon IR irradiation [12–14]. Figure 3 shows the model of Λ-*fac*-[Co(*S*-dap)$_3$] rotating about and moving along the C_3 axis of symmetry, in the direction opposite to the carboxyl groups. In this article we give experimental evidence for detection of the propelling motion that corresponds to circular dichroism spectral changes of the propeller-type complex, *fac*-[Co(*S*-dap)$_3$] in an aqueous solution upon IR irradiation.

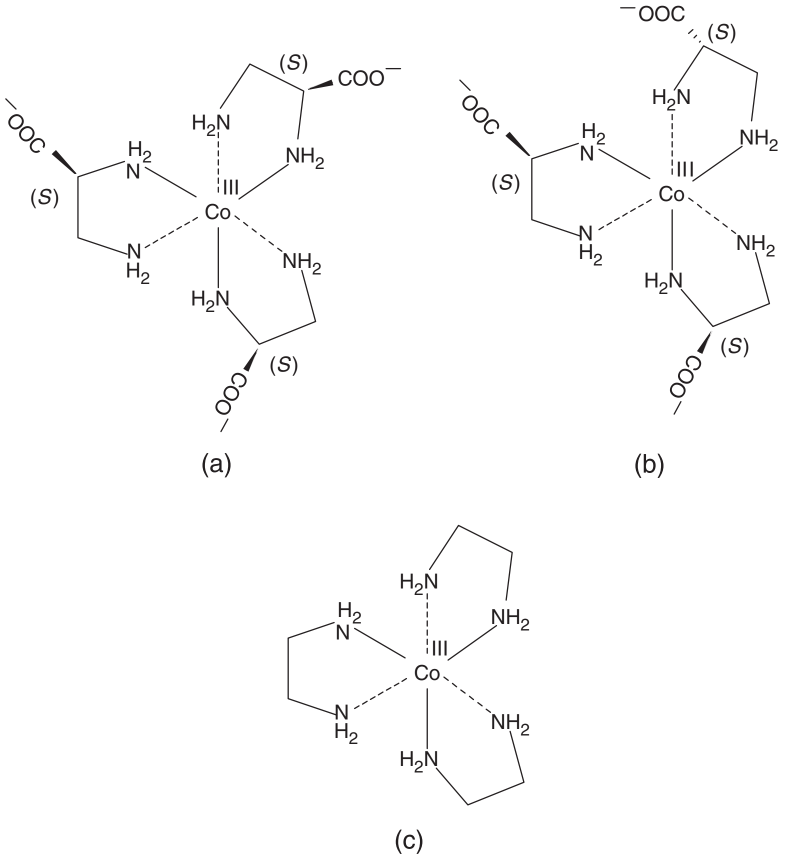

Figure 2. Schematic representation of Λ-*fac* (a), Λ-*mer*-[Co(*S*-dap)$_3$] (b), and Λ-[Co(en)$_3$]$^{3+}$ (c).

2. Experimental

The expected light-driven motion was monitored by detecting the CD (Circular Dichroism) spectral changes of the propeller-type complex, *fac*-[Co(*S*-dap)$_3$], which has three carboxyl groups on the same side with respect to cobalt on the C_3 axis of symmetry, in aqueous solution upon IR irradiation between 1626 and 1770 cm^{-1}. The same experiments were also conducted for the *mer*-[Co(*S*-dap)$_3$] isomer, in which one carboxyl group was aligned opposite to the other two, and the D_3 complex [Co(en)$_3$]$^{3+}$, which has no carboxyl groups as controls. The complexes *fac* and *mer*-[Co(*S*-dap)$_3$] were prepared and isolated according to literature procedures [12]. The preparation and resolution of [Co(en)$_3$]$^{3+}$ were performed according to literature procedures [15]. CD spectra were recorded at room temperature using a JASCO J-720 spectropolarimeter. Four milliliters of an aqueous solution containing Λ-*fac*, Λ-*mer*-[Co(*S*-dap)$_3$] or Λ-[Co(en)$_3$]$^{3+}$ (3.0×10^{-4} M) was aliquoted in a plastic cell with a CaF$_2$ window ($10 \times 10 \times 2$ mm^3, ANALYTICS NET, INC. JAPAN). The samples were subsequently irradiated with light from a 1.16 W IR emitter (SA7275-M3, CAL-SENSORS, INC. JAPAN) fitted with a 1626–1770 cm^{-1} bandpass filter (IR SYSTEM, INC. JAPAN).

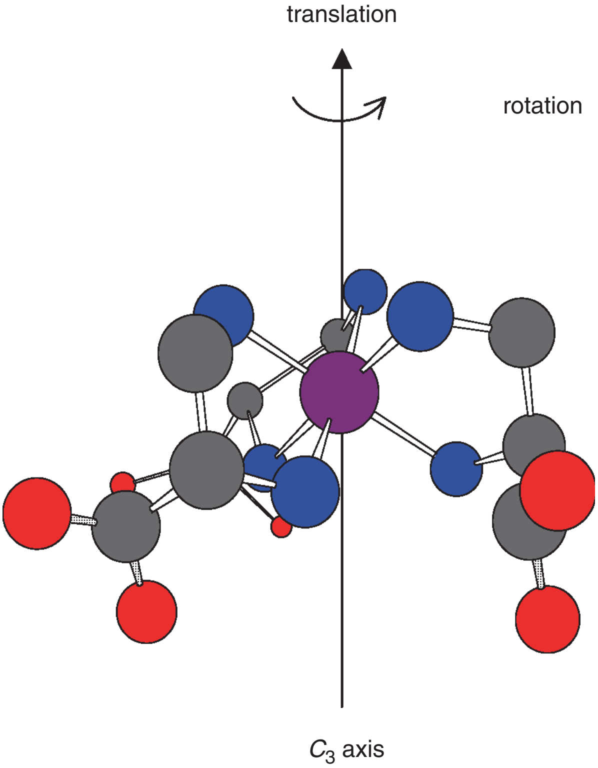

Figure 3. Model of the results of MD simulation of Λ-*fac*-[Co(*S*-dap)$_3$] in the aqueous solution upon IR irradiation.

3. Results and discussion

Figure 4 shows the CD spectra of Λ-*fac*-[Co(*S*-dap)$_3$] in an aqueous solution exposed and not exposed to irradiation, and the difference spectrum of them. The shape of the difference CD spectrum remained unaltered from the original one, however, a significant decrease in the intensity was observed upon irradiation. This decrease indicates that no deterioration in the structure occurred, rather, the concentration of the irradiated solution decreased. Some of the Λ-*fac*-[Co(*S*-dap)$_3$] complex was thought to be forced out of the path of light upon IR irradiation. The energy gained by the presence of a chemical functional group in the absorption of a photon generally does not remain in that molecule, but lost by any of a number of mechanisms. Some of the absorbed energy is degraded as heat activating the solvent near the functional group and thereby returning the molecule from its excited to its ground state. On the other hand, the activated solvent would be expected to exert actions on the functional group. In the case of Λ-*fac*-[Co(*S*-dap)$_3$] complex, the absorption band of the carbonyl stretching vibration appears at 1728 cm^{-1}. Upon IR irradiation in the region of 1626–1770 cm^{-1}, the solvent around the carboxyl functional groups was activated by energy gained from the carbonyl groups, and therefore would be expected to exert interactions with the carboxyl groups. The Λ-*fac*-[Co(*S*-dap)$_3$] complex with the propeller structure would thus rotate about and move along the C_3 axis of symmetry,

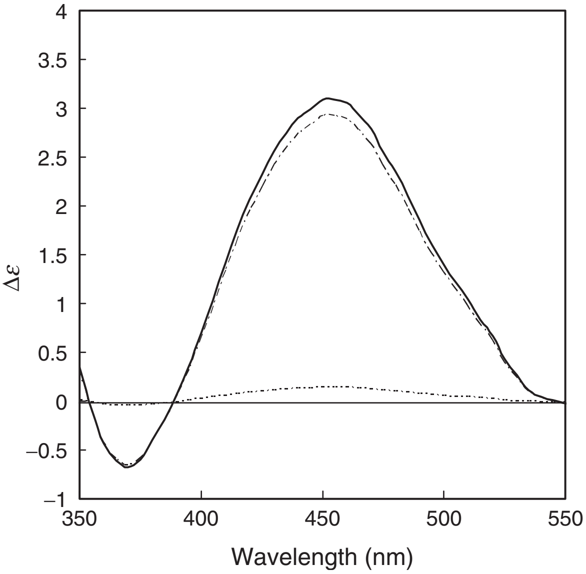

Figure 4. CD spectra of Λ-*fac*-[Co(*S*-dap)$_3$] in an aqueous solution upon IR irradiation (—— without irradiation, – · – · – upon irradiation, ······ difference spectra exposed and not exposed to irradiation).

in the direction opposite to the carboxyl groups. Besides Brownian motion, complexes in the path of irradiation can obtain additional light-driven motion. Thus more complexes escape from the path of irradiation than return in the path of irradiation just by thermodynamic motion. As detected by CD spectra, the concentration of the irradiated solution decreased. Perhaps the concentration of irradiated solution could be decreased to zero by using specific technologies such as a semipermeable membrane.

In addition, the light-driven motions in complexes in the path of IR irradiation were confirmed by the CD difference spectral strength at 460 nm with the maximum CD strength for Λ-*fac*-[Co(*S*-dap)$_3$] in an aqueous solution exposed and not exposed to irradiation versus the irradiation time, as shown in figure 5. Upon initial irradiation, the CD strength decreased constantly until reaching its minimum. After irradiation was terminated, the CD strength increased constantly until reaching its maximum (the original strength). These observations confirmed that the decrease of CD strength, that is, diluting of the complex ions in the light-path of irradiation indeed occurred in response to external photochemical stimuli. Modulation of the CD strength at 460 nm over three cycles is characteristic of repetitive unidirectional motion. This aspect is particularly important for future applications as photoactive materials, photo-controlling, and monitoring. These experiments were also conducted for the Λ-*mer*-[Co(*S*-dap)$_3$] complex, but a significant difference in the CD strength was not detected when exposed and not exposed to IR irradiation (figure 6). This is thought to be because in the Λ-*mer*-[Co(*S*-dap)$_3$] complex, one of the three carboxyl groups is aligned opposite to the other two. Therefore, the driving forces for either translating or rotating are considerably weaker than those of the *fac* isomer, indicating that a propeller structure, in which three carboxyl groups are oriented in the same side, is essential to obtain propelling behavior upon irradiation. This observation was in good agreement with the results obtained from molecular dynamics (MD) simulation

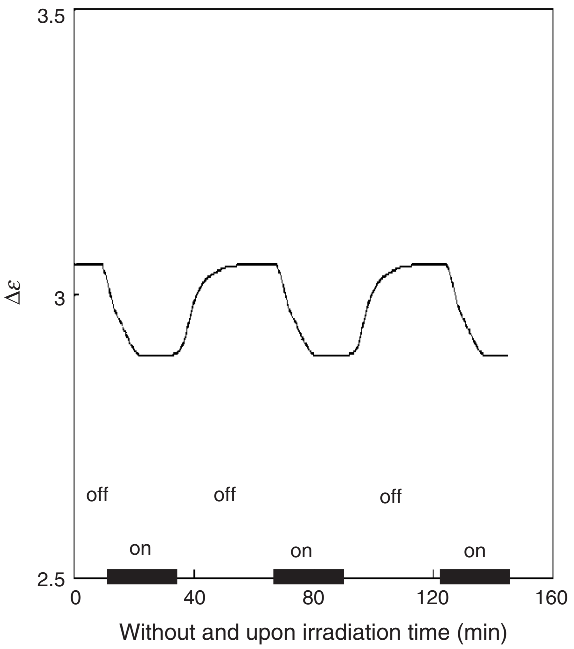

Figure 5. Changes in maximum CD strength at 460 nm for Λ-*fac*-[Co(*S*-dap)$_3$] in an aqueous solution exposed and not exposed to irradiation.

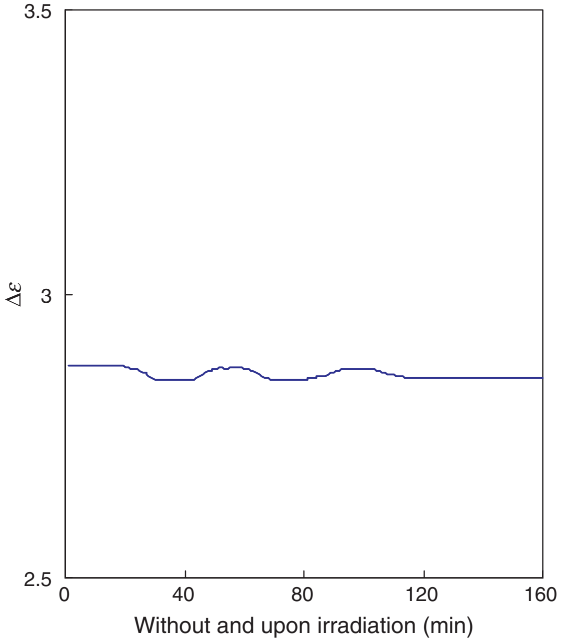

Figure 6. Changes in maximum CD strength at 460 nm for Λ-*mer*-[Co(*S*-dap)$_3$] in an aqueous solution exposed and not exposed to irradiation.

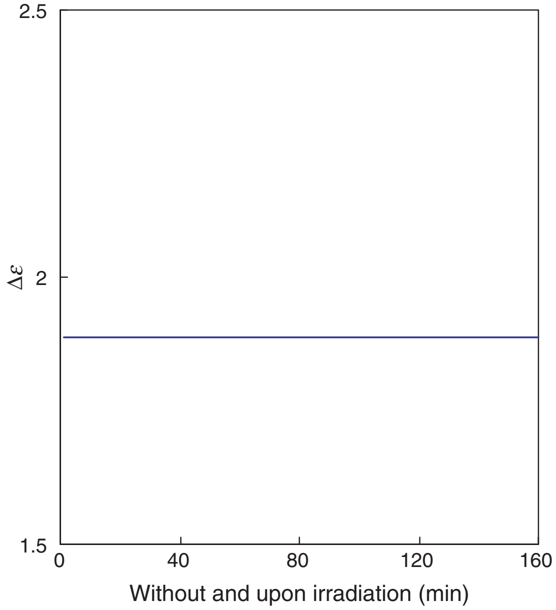

Figure 7. Changes in maximum CD strength at 498 nm for Λ-$[Co(en)_3]^{3+}$ in an aqueous solution exposed and not exposed to irradiation.

studies using the AMBER 6 program that propelling (translation and rotation) motion occurs in propeller-type metal complexes in an aqueous solution as a consequence of an appropriate energy supply.

In an effort to confirm the above conclusion, we also performed the same experiments for Λ-$[Co(en)_3]^{3+}$ ions. In this case, the same CD spectra were detected when exposed and not exposed to IR irradiation (figure 7). Compared to Λ-*fac*-$[Co(S\text{-dap})_3]$ complex, the Λ-$[Co(en)_3]^{3+}$ ion cannot obtain light-driven motion because there is no carboxyl group in the D_3 complex (figure 2c) that can obtain a sufficient amount of energy upon IR irradiation. These observations revealed that the functional groups at key positions are extremely important to obtaining light-driven motion for metal complexes. Propeller-type complexes with functional groups possessing the characteristic absorption bands in the visible or ultraviolet region are expected to obtain light-driven motion upon visible or ultraviolet irradiation.

4. Conclusions

The propelling motion that corresponds to circular dichroism spectral changes of the propeller-type complex, Λ-*fac*-$[Co(S\text{-dap})_3]$ in an aqueous solution upon IR irradiation was detected for the first time. For such complexes, three functional groups oriented on the same side, is absolutely essential to obtain propelling behavior upon irradiation.

The present investigation marks preliminary studies for the construction of molecular level devices using propeller-type metal complexes. The roles of functional groups, the size and rigidity of chelate rings, remain to be investigated in order to construct a better molecular engine. Investigations of *fac*-tris(5-carboxy-2,2′-bypyridine)cobalt(III), *fac*-tris(3-nitro-phenanthroline)cobalt(III), and *fac*-tris(*N*-phenyl-1,2-ethanediamine) cobalt(III) ions are currently underway. In parallel experiments we are also trying to demonstrate molecular machining using a technology for precise orientation of one molecule in a certain direction. Moreover, these light driven motions may also be expected on other compounds with high symmetry and structures whose right and left are different along the axis of symmetry, such as substituted propellanes and fullerenes. Although the present systems are fairly primitive, these studies may help to accomplish light-driven motion of objects and ultimately guide us to constructing molecular engines and other smart functional materials.

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