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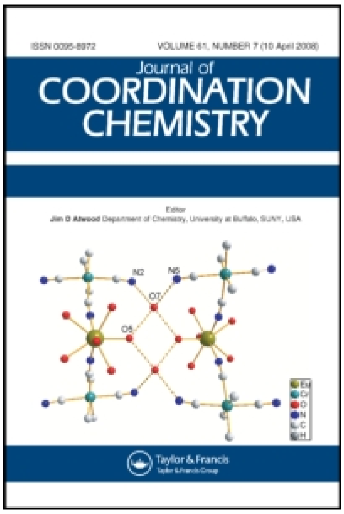

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Potential propelling and rotating functions of propeller-type complexes. I. Preparation and molecular dynamics simulation of tris(*S*-2,3-diaminopropionato)cobalt(III)

Hong-Ling Liu[a]; Hiroyuki Ishida[a]; Yuzo Yoshikawa[a]
[a] Department of Fundamental Science, Division of Molecular and Material Science, Graduate School of Natural Science and Technology, Okayama University, Tsushima, Okayama 700-8530, Japan

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Potential propelling and rotating functions of propeller-type complexes. I. Preparation and molecular dynamics simulation of tris(*S*-2,3-diaminopropionato)cobalt(III)

HONG-LING LIU[†], HIROYUKI ISHIDA[‡] and YUZO YOSHIKAWA*[†]

[†]Department of Fundamental Science, Division of Molecular and Material Science,
Graduate School of Natural Science and Technology, Okayama University,
Tsushima, Okayama 700-8530, Japan
[‡]Department of Chemistry, Faculty of Science, Okayama University, Tsushima,
Okayama 700-8530, Japan

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Four optically active geometric isomers of tris(*S*-2,3-diaminopropionato)cobalt(III) were prepared and separated by ion-exchange column chromatography on SP-Sephadex (C-25). The identification of the four diastereomers is based on the elution order of the complexes, elemental analysis, electronic spectra, circular dichroism spectra, ^{13}C NMR spectra, X-ray structure analysis and comparison of these properties with those of analogous series consisting of three isomers of the bis(*S*-2,3-diaminopropionato)cobalt(III) ion. Structure optimization and molecular dynamics (MD) simulation of the system, consisting of the propeller-type complex *fac*-tris(*S*-2,3-diaminopropionato)cobalt(III) and 240 water molecules, were performed using AMBER 6. The results of the MD simulation suggest that distinct propelling and rotating behavior can be obtained in this complex in aqueous solution.

Keywords: Propeller-type complexes; Propelling and rotating functions; Molecular dynamics simulation; Cobalt(III)

1. Introduction

The concept of "machine" can be extended to the molecular level by designing transition metal complexes capable of performing mechanical movements when energy is supplied. 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 input, however, can be used to make a machine work without formation of waste products [1–5]. The C_3 symmetrical cobalt(III) complexes of multidentate ligands described in this article have been prepared in our laboratory and proposed as "machines" that

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*Corresponding author. E-mail: yyoshi@cc.okayama-u.ac.jp

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are set in motion by sending a photochemical signal. The potential applications of these photochemically powered molecular-level machines are related to molecular-level transportation, changing concentration of solution and promoting permeability, which can be exploited for the construction of molecular-level devices applied to agriculture (biology), pharmacy, medicine and engineering (optics).

Usually, the energy gained by a chemical functional group on absorption of a photon does not remain in that molecule but is lost by any of several mechanisms. Of considerable importance in solution chemistry is the case in which a part of the energy absorbed is degraded as heat, which activates the solvent around the functional group, returning the molecule from its excited state to the ground state. Conversely, activated solvent would be expected to react with the functional group and the vector sum would be along the bond between the functional group and the body of the molecule. In the case that the functional groups are planted to make a complex possess a C_3 symmetry axis, like a propeller, the complex would be propelled to move along the C_3 symmetry axis toward the opposite direction of the functional groups on forces supplied by the components parallel to the C_3 axis, while the components perpendicular to the C_3 axis present torques causing rotation about the C_3 axis.

Photochemically powered motions would also be expected in complexes with high symmetry and distinct difference based on attached functional groups looking out from opposite directions along the symmetry axis, such as substituted propellane and fullerene compounds. In this study we designed and prepared a propeller-type complex with a C_3 symmetry axis, *fac*-tris(*S*-2,3-diaminopropionato)cobalt(III) (figure 1), using an unsymmetrical didentate ligand *S*-Hdap (*S*-2,3-diaminopropionic acid) (scheme 1).

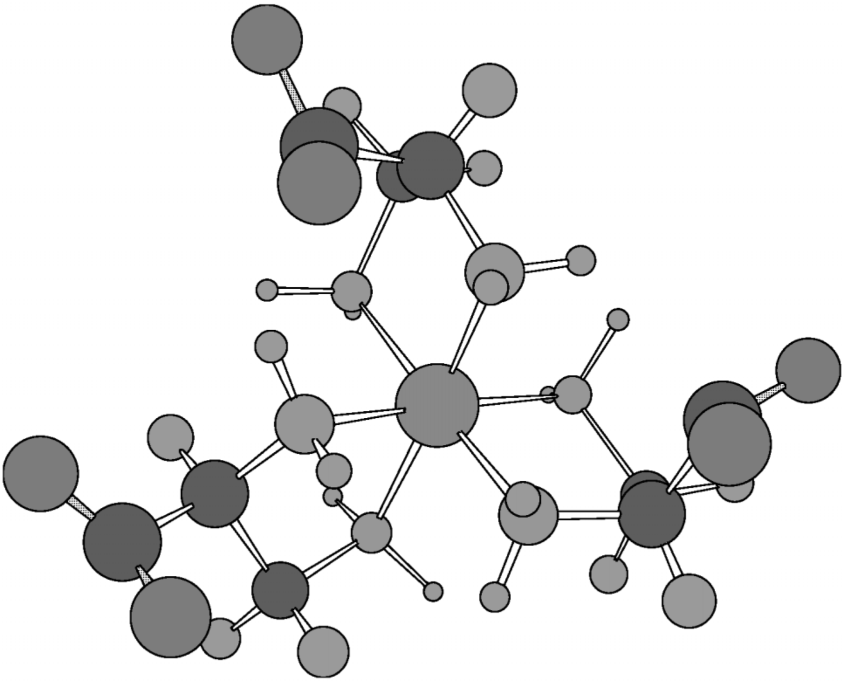
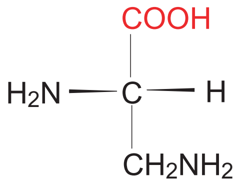


Figure 1. The structure of Λ-*fac*-[Co(*S*-dap)$_3$].



Scheme 1. Hdap = *S*-2,3-diaminopropionic acid.

For tris(*S*-2,3-diaminopropionato)cobalt(III), four isomers (figure 2) would be expected. The separation was performed successfully by ion-exchange chromatography on an SP-Sephadex (C-25) column. Bis(*S*-2,3-diaminopropionato)cobalt(III) complexes have been known for more than 30 years [6,7], but to our knowledge no studies on tris(*S*-2,3-diaminopropionato)cobalt(III) complexes have been reported. The synthesis and isolation of tris(*S*-2,3-diaminopropionato)cobalt(III) in this study have led to new discoveries about the stereochemistry of cobalt(III) complexes.

Molecular dynamics (MD) calculations provide a valuable tool for the theoretical investigation of static and dynamic properties of systems. In the present study, MD simulations were performed for metal complexes using the AMBER 6 program with the force field parameters selected based on those frequently used for analyses of metal coordination compounds. As predicted, the MD calculations revealed that the propeller-type complex with a C_3 symmetry axis, *fac*-tris(*S*-2,3-diaminopropionato)cobalt(III), can produce observable propelling and rotating functions on IR irradiation in aqueous solution.

2. Experimental

2.1. *Materials and general methods*

All reagents used were of reagent grade. The water was distilled and deionized on an ion-exchange column. *S*-2,3-Diaminopropionic acid hydrochloride was purchased from Tokyo Kasei (Tokyo, Japan). $[CoCl(NH_3)_5]Cl_2$ was prepared according to a literature method [8]. SP-Sephadex (C-25), which has sulfopropyl groups as the cation-exchange group, was purchased from Aldrich Chemical Company, Inc. Elemental analyses were performed on a Perkin Elmer Series II CHNS/O 2400 instrument. Electronic absorption spectra were recorded on a Jasco V-550 UV/VIS spectrophotometer. IR spectra were recorded on a Jasco FT/IR spectrometer with KBr pellets. Circular dichroism (CD) spectra were recorded at room temperature using a JASCO J-720 spectropolarimeter. ^{13}C NMR spectra were recorded on a Varian VXR500 spectrometer.

2.2. *Preparation of complexes*

$[CoCl(NH_3)_5]Cl_2$ (0.55 g, 2.2 mmol) dissolved in 100 mL of water was added slowly to a stirred 25 mL water slurry of Hdap (*S*-2,3-diaminopropionic acid hydrochloride, 1 g, 7.11 mmol) at ambient temperature. The pH of the solution was adjusted to 2 with hydrochloric acid. After addition of 0.125 g of activated charcoal, the water slurry

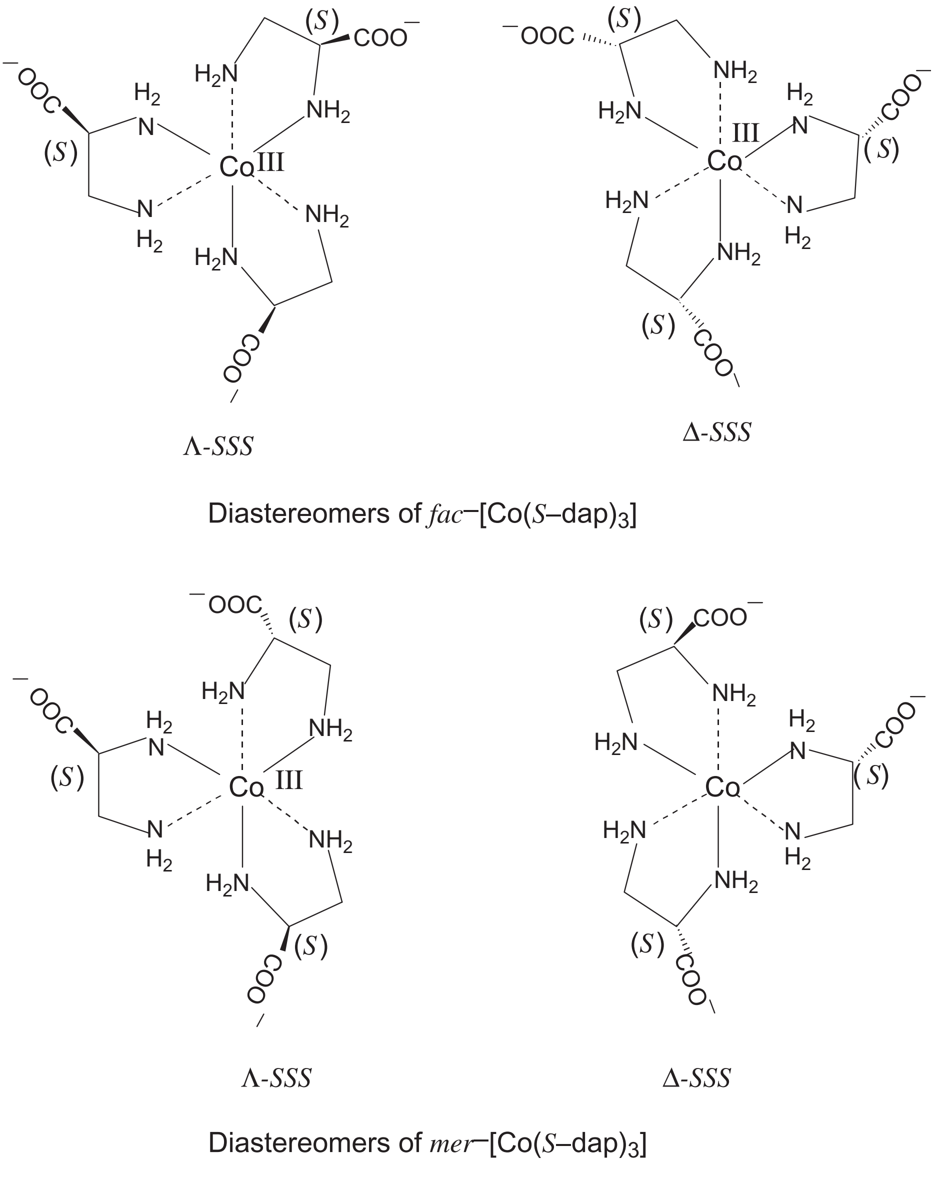


Figure 2. Isomers of tris(*S*-2,3-diaminopropionato)cobalt(III).

was stirred 1 week at ambient temperature. The resulting orange reaction mixture was filtered and the activated charcoal was carefully extracted with warm water to recover any trace of the least soluble isomer, which crystallized on it.

2.3. *Chromatographic separation of the isomers*

Chromatography on an ion-exchange Sephadex column was used to separate the isomers. The prepared solution was deposited on a preparatory SP-Sephadex (C-25) column (2.7 × 50 cm), washed with 2 L of 0.01 M HCl; elution was allowed to proceed

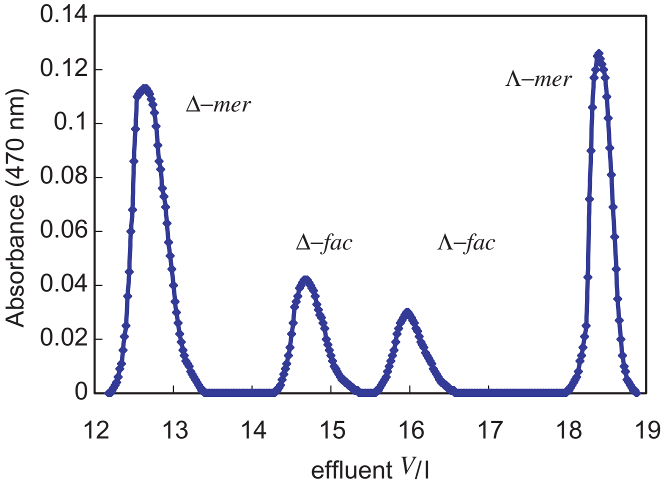


Figure 3. Elution curve; eluent was 0.20 M $NaHSO_4$ aqueous solution.

slowly (about 1 drop every 15 s). A minor pink band that developed initially was thought to contain bis-cobalt(III) complexes of *S*-2,3-diaminopropionato, but no further investigation of these complexes was carried out. The main orange band was collected and loaded on an SP-Sephadex (C-25) column (4.5 × 240 cm) with 0.20 M $NaHSO_4$ as eluent, elution proceeding at 0.5 mL min^{-1}. Under these conditions, about 1 month was required for complete elution of the complex, producing four separate orange bands, I–IV (figure 3). The effluent was separated into fractions of 20 mL each, and the absorbance of each fraction at 471 nm (cell thickness 1 cm) was plotted against the effluent volume. The isomers corresponding to the fastest, second, third and the slowest bands (I, II, III, and IV) were named A, B, C, and D, respectively. All these fractions were optically active, the signs of I and II being minus, and III and IV being plus for the Na-D line; their band to area ratio was about 3:1:1:3; no further separation was possible, even by repeated chromatography.

2.4. *Purification of the isomers*

The fractions corresponding to I, II, III, and IV were diluted 10 times with 0.01 M HCl; then they were again each adsorbed onto an SP-Sephadex (C-25) column (1 × 10 cm), washed with 1 L of 0.01 M HCl, eluted with 1 M HCl rapidly, and the effluents were evaporated to dryness *in vacuo*. The chemical compositions of the four isomers thus prepared are given in table 1.

2.5. *X-ray crystallography*

Orange crystals of Δ-*fac*-[Co(*S*-dap)(*S*-Hdap)$_2$]Cl$_2$ · 2H$_2$O suitable for X-ray structure determination were grown by MeOH diffusion into an aqueous solution of B (Δ-*fac*-tris-cobalt(III) complexes of *S*-2,3-diaminopropionic acid) in the pH range 5–6. X-ray diffraction data were recorded on a Rigaku AFC-5R diffractometer at the X-ray Laboratory of Okayama University. The structure was solved by SIR92 [9] and refined by SHELXL97 [10]. H atoms attached to O atoms were refined isotropically,

Table 1. Chemical composition of the isomers.

Complex		Elemental analysis (calcd value)		
		C (%)	H (%)	N (%)
A	$[Co(S\text{-dap})_3]\cdot H_2O$	27.84 (27.98)	6.09 (5.48)	21.36 (21.75)
B	$[Co(S\text{-dap})_3]\cdot H_2O$	27.77	5.89	21.43
C	$[Co(S\text{-dap})_3]\cdot H_2O$	27.68	5.71	21.63
D	$[Co(S\text{-dap})_3]\cdot H_2O$	27.83	5.56	21.74

Table 2. Selected crystallographic data for Δ-*fac*-$[Co(dap)(Hdap)_2]Cl_2\cdot 2H_2O$.

Formula	$C_9H_{27}CoN_6O_8Cl_2$
M_r	477.20
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a, b, c [Å]	7.949(5), 14.619(16), 15.503(5)
V [Å^3]	1802(2)
Z	4
D_x [g cm^{-3}]	1.759
μ(Mo Kα) [mm^{-1}]	1.302
F(000)	992
Crystal size [mm]	$0.25\times 0.30\times 0.38$
Temperature [K]	296
Radiation [Å]	Mo Kα, 0.71073
θ_{min}, θ_{max} [°]	2.6, 27.5
h, k, l	−1:10; −2:18; −1:20
Total, unique data, R_{int}	3287, 3005, 0.013
Absorption correction	ψ scans [19]
T_{min}, T_{max}	0.588, 0.722
Observed data [$I > 2\sigma(I)$]	2700
Refinement on	F^2
N_{ref}, N_{par}	3005, 259
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0247, 0.0587, 1.00
$(\Delta/\sigma)_{max}$	0.001
Flack parameter [20]	0.025(16)
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ [Å^3]	−0.25, 0.22

$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.75P]$, where $P = (F_o^2 + 2F_c^2)/3$.

while the other H atoms attached to C and N atoms were treated as riding atoms with $U_{iso}(H) = 1.2U_{eq}$ (C or N). Crystallographic results and other details are listed in table 2.

3. Results and discussion

3.1. *Absorption (AB) and circular dichroism (CD) spectra*

In figure 4 the AB and CD spectra of the C isomer are shown, while table 3 lists the data for all the isomers. The maxima of the octahedral $^1T_{1_g} \leftarrow ^1A_{1_g}$ absorption (470 or 471 nm) are at significantly shorter wavelengths than for the $[Co(S\text{-dap})_2]^+$ ion (at more than 495 nm for all three isomers), coordinating two oxygen and four nitrogen atoms [6], but are similar to tris(diaminosuccinato)cobaltates(III) (*ca.* 473 nm), $[Co(en)_3]^{3+}$ (467 nm), $[Co(l\text{-pn})_3]^{3+}$ (467 nm), and tris(2-methyl-1,2-propanediamine)cobalt(III)

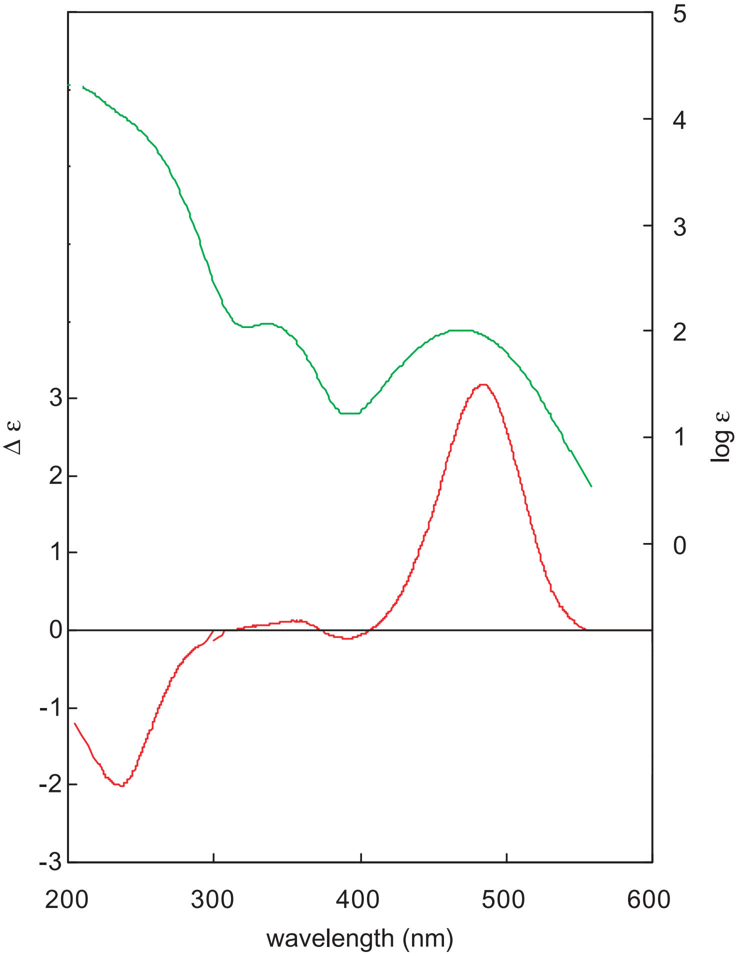


Figure 4. AB and CD spectra of Λ-*fac*-[Co(*S*-dap)$_3$] in water.

Table 3. Absorption and circular dichroism spectra.

Complex		Absorption		CD	
		$\nu_{max}/10^{-4}\,cm^{-1}$ (λ_{max})	ε_{max}	$\nu_{max}/10^{-4}\,cm^{-1}$ (λ_{max})	$\Delta\varepsilon_{max}$
A	Δ-*mer*-[Co(*S*-dap)$_3$] · H_2O	First band 2.12 (471 nm)	106	2.03 (491 nm)	−2.8
		Second band 2.95 (338 nm)	117	2.34 (425 nm)	+0.07
				2.78 (360 nm)	−0.15
B	Δ-*fac*-[Co(*S*-dap)$_3$] · H_2O	First band 2.12 (471 nm)	106	2.04 (489 nm)	–3.1
		Second band 2.95 (339 nm)	117	2.36 (424 nm)	+0.02
				2.78 (360 nm)	−0.14
C	Λ-*fac*-[Co(*S*-dap)$_3$] · H_2O	First band 2.13 (470 nm)	108	2.06 (485 nm)	+3.2
		Second band 2.95 (338 nm)	119	2.51 (399 nm)	−0.10
				2.78 (360 nm)	+0.12
D	Λ-*mer*-[Co(*S*-dap)$_3$] · H_2O	First band 2.13 (470 nm)	106	2.06 (486 nm)	+2.9
		Second band 2.95 (340 nm)	117	2.53 (395 nm)	−0.14
				2.78 (360 nm)	+0.16

(480 nm), all coordinating six nitrogen atoms [11,12]. The CD of the first absorption band is at 485 nm ($\Delta\varepsilon = +3.2$). The CD spectrum of the D isomer is almost the same as that of C. A and B show almost identical CD spectra, with the sign opposite to those of the C and D isomers. The CD spectra due to A and D, and B and C, are not symmetric because they are not pairs of enantiomers, respectively, but diastereomers caused by optically active didentate ligands.

3.2. *Infrared spectra*

The infrared spectra of the four isomers are slightly different in shape and position. It is difficult to assign their configuration on the basis of infrared spectra alone. The carbonyl stretch of *fac*-[Co(*S*-dap)$_3$] appears at 1728 cm^{-1}.

3.3. *^{13}C NMR spectra*

^{13}C NMR spectra were recorded to confirm observations described previously. ^{13}C NMR spectra of the B and C isomers were observed with three signals at 46 (CH_2), 58 (CH) and 172 (COO^-) ppm, but the spectra for the A and D isomers were complicated and broader (CH_2: 46.1 ppm, CH: 57.9 ppm, COO^-: 172, 173 ppm). The ^{13}C NMR data indicate that the A and D isomers are *mer*, and the B and C isomers are *fac* isomers.

3.4. *Assignment of the structures*

The configurations of the isomers separated were assigned by means of the formation ratio, and the CD and NMR spectra. The statistical formation ratio of the *mer* to the *fac* isomer should be 3:1 under equilibrium conditions. The relationship between the absolute configuration and the CD spectrum of the tris(diamine)cobalt(III) complexes has been well established [13]. For tris(diamine)cobalt(III) complexes, those which show a major positive CD band for the octahedral $^1T_{1_g} \leftarrow {}^1A_{1_g}$ absorption have Λ configuration (IUPAC nomenclature). Thus, the formation ratio, 3:1, found for the A and B, and D and C isomers (figure 4), combined with A and B showing a major negative CD band and C and D showing a major positive CD band in the first absorption region, indicate that the A and B isomers are Δ-*mer* and Δ-*fac*, and the C and D isomers are Λ-*fac* and Λ-*mer* isomers. The assignment is supported by the X-ray structural analysis.

3.5. *X-ray structural analysis*

The molecular structure of Δ-*fac*-[Co(*S*-dap)(*S*-Hdap)$_2$]$Cl_2 \cdot 2H_2O$ with the atom-numbering scheme is shown in figure 5. It is expected from the structure that Δ-*fac*-tris-cobalt(III) complexes of *S*-2,3-diaminopropionic acid exhibit a propeller structure in aqueous solution, that is the three carboxyl groups are aligned with the C_3 axis of symmetry. The bond angles of N1–Co–N2, N3–Co–N4 and N5–Co–N6 of the chelate rings [85.33(9), 85.47(9), 85.74(9)°] are similar to those of [Co(en)$_3$]$^{3+}$ [85.4(3)°] [14]. The six Co–N bond distances range from 1.958(3) to 1.995(3) Å [average 1.973(3) Å], comparable to those of [Co(en)$_3$]$^{3+}$ [1.964(8) Å] [14]. The compound contains two water molecules, one of which forms a hydrogen bond with the dap ligand (O8–H8(O3), and the other forms hydrogen bonds with the dap ligand and

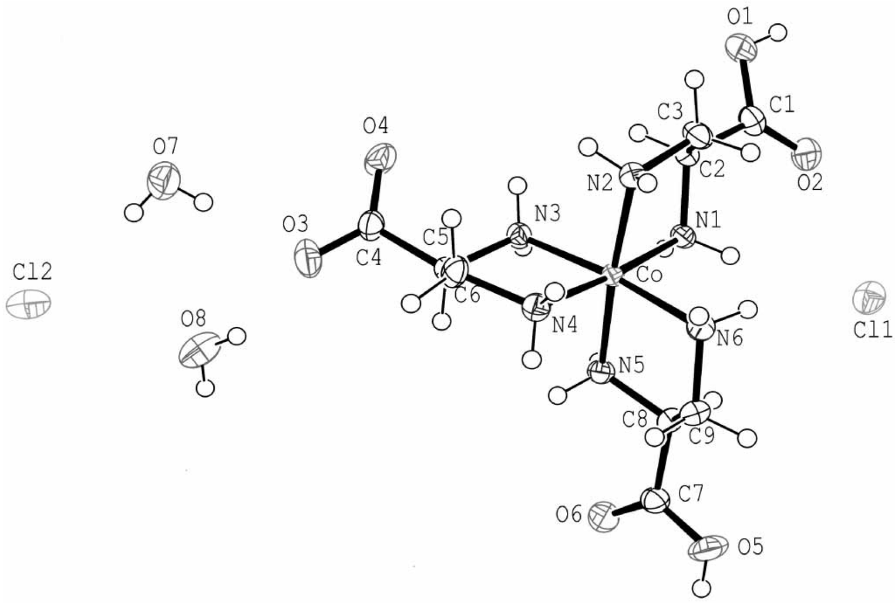


Figure 5. Molecular structure of Δ-*fac*-$[Co(dap)(Hdap)_2]Cl_2 \cdot 2H_2O$ showing 50% probability displacement ellipsoids. H-atoms are drawn as circles of arbitrary size.

the counterion Cl^- (O7–H7(O3 and O7–H7(Cl2). The carboxyl groups of the complex ion form O–H(O hydrogen bonds with the carboxylate groups of the neighboring complexes to give a three-dimensional, hydrogen-bonded network.

3.6. *Molecular dynamics simulation of* Λ-*fac-[Co(S-dap)*$_3$*]*

3.6.1. Strategy. Molecular dynamics is a simulation technique that yields dynamic properties of a molecular system by solving Newton's equations of motion for each atom. Solving these equations produces new atomic coordinates that can be used to calculate new energies. Static and dynamic properties of the system are then determined as time averages by analyzing the trajectory of the MD simulation [15–17]. Metal complexes have not been studied extensively in this field because experimental parameters for them are difficult to determine compared with those of organic compounds. The current simulation was performed using the MD software package AMBER 6. As for the force field parameters, each set closer to that of the AMBER 6 and MM2 was selected from those that had been used frequently for analyses in metal coordination compounds [18]. All torsional parameters containing a metal atom inside are assumed to be zero because their interaction energies are expected to cancel one another in octahedral complexes. The dielectric constant used for electrostatic interactions in the present force field is 1.0, a default value used for AMBER 6. For all other parameters in the force field potential functions, the default values included in AMBER 6 were derived especially for solvated systems. To ensure neutral conditions of the systems, which were required for calculation of electrostatic interactions, the electric charge was distributed on each atom as the partial atomic charge (table 4). This was mainly estimated from the value of the bond dipole moment between the two bonded atoms.

Table 4. The partial atomic charges distributed on the atoms.

Atom	Partial atomic charge
Co	+1.0000
H (bonded to N)	+0.1667
Lp (bonded to O of COO^-)	−0.1667
O (water)	−0.048
H (bonded to O of water)	+0.274
Lp (bonded to O of water)	−0.25
Others	0

The MD simulation of Λ-*fac*-[Co(*S*-dap)$_3$] was performed for 200 ps, and details of the MD protocol follow.

1. The potential energy of Λ-*fac*-[Co(*S*-dap)$_3$] was minimized and the metal complex was placed in the center of the simulation cell.
2. After the potential energy of the complex reaches its minimum, it was solvated in the water (240 water molecules were used to solvate Λ-*fac*-[Co(*S*-dap)$_3$]). With the complex frozen, the energy of solvating water was minimized to avoid water molecules being too close to the complex or to the walls of the box. Then the complete minimization including all atoms in the system was performed prior to the MD.
3. All the atoms of the system were heated up to a temperature of 300 K during 10 sequential (1 ps) runs. The stepwise manner was selected to avoid disruption of the complex, which might result from a large increase in the temperature.
4. The entire MD with constant volume conditions was performed up to 200 ps under constant pressure conditions. The density of the system was stabilized at 0.97 g cm^{-3}. The size of the simulation box was 30 × 30 × 30 Å.
5. The value of ε used for the van der Waals parameter of O of the carboxyl group was increased to 25 times, estimated according to the carboxyl absorption at 1728 cm^{-1}, to obtain enough propelling and rotating functions.

4. Results and discussion

We expected that distinct propelling and rotating functions could be obtained in Λ-*fac*-[Co(*S*-dap)$_3$] on IR irradiation in aqueous solution. These functions can be determined by analyzing the trajectory of the MD simulation of the system consisting of the complex and water molecules. Calculation of the kinetic energy showed that the system stabilized around 100 ps and remained stable afterwards. The potential energy reached a stable level after nearly 100 ps. We assumed that the MD period before 100 ps would be considered as an equilibrium-searching period. The snapshots of this propeller-type complex showed that the propeller structure with a C_3 symmetry axis remained through all the simulations. Simulations from 100 to 200 ps are shown in figure 6. The center of the complex moved about 14 Å along the C_3 symmetry axis opposite to the functional groups, $-COO^-$, while rotating clockwise 120° about the C_3 symmetry axis in the above-mentioned period. The results clearly suggest that distinct propelling and rotating functions can be obtained in Λ-*fac*-[Co(*S*-dap)$_3$] in aqueous solution on IR irradiation.

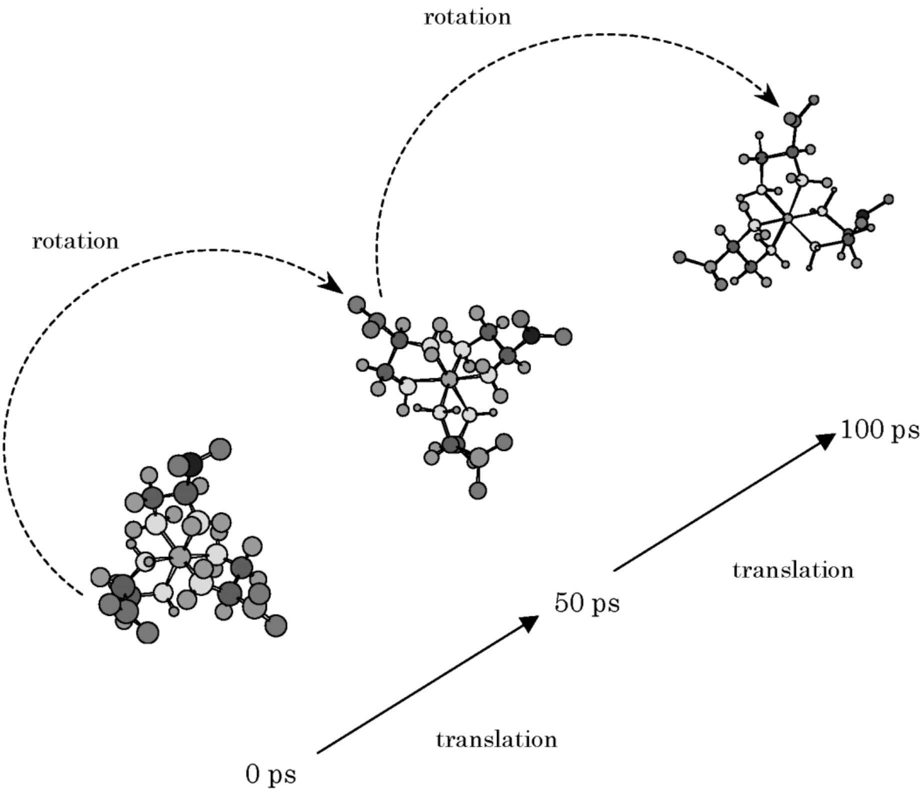


Figure 6. Model of the results of MD simulation of Λ-*fac*-[Co(*S*-dap)$_3$] in aqueous solution.

5. Conclusions

We have succeeded for the first time in the preparation and separation of all four optically active diastereomers of the tris-cobalt(III) complex of *S*-2,3-diamonopropionic acid. The MD simulation suggests that observable propelling and rotating functions can be obtained in the propeller-type complex, Λ-*fac*-[Co(*S*-dap)$_3$], on IR irradiation in aqueous solution. Further study is intended to confirm these suggestions by detecting changes in UV and CD spectra of Λ-*fac*-[Co(*S*-dap)$_3$] in an aqueous solution on IR excitation. Other similar propeller-type complexes will be designed and prepared soon. The detailed description of the MD calculations with related measurements will be reported in another paper.

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