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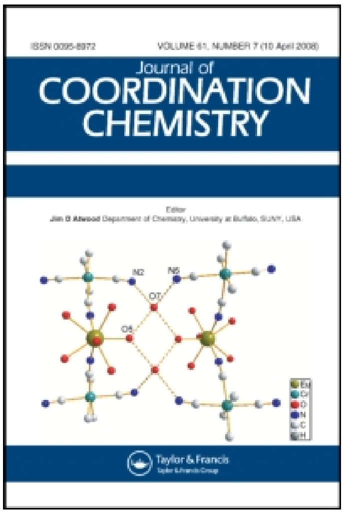

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Potential propelling and rotating functions of propeller-type complexes. II. Preparation and molecular dynamics simulation of tris(5-carboxy-2,2'-bipyridine)cobalt(III)

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Potential propelling and rotating functions of propeller-type complexes. II. Preparation and molecular dynamics simulation of tris(5-carboxy-2,2′-bipyridine)cobalt(III)

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Isolation of four optically active isomers of the 5-substituted 2,2′-bipyridine complexes $[Co(cbpy)_3]^{3+}$ (cbpy = 5-carboxy-2,2′-bipyridine) was achieved using cation-exchange column chromatography (SP-Sephadex C-25) eluting with either sodium (−)-*O*,*O*′-dibenzoyltartrate or sodium ((+)-tartrato)antimonate(III). Structure optimization and molecular dynamics (MD) simulations of the system consisting of the propeller-type complex *fac*-$[Co(cbpy\text{-}H)_3]$ (cbpy-H = 2,2′-bipyridine-5-carboxylate anion) and 80 water molecules were performed using the AMBER 6 program. Results of the MD simulation revealed that distinct translating and rotating behaviors can be obtained in this complex in aqueous solution upon IR irradiation.

Keywords: Propeller-type complexes; Propelling and rotating functions; Molecular dynamics simulation; Tris(5-carboxy-2,2′-bipyridine)cobalt(III) complex

1. Introduction

The bottom-up construction of motors and machines with nanosize dimensions offers an enormous challenge to science [1, 2]. Recently, much attention has been paid to the design of molecular and supermolecular systems in which their shapes change, switching processes work and/or certain motions occur as a consequence of an appropriate energy supply [3–9]. The results of molecular dynamics (MD) simulations using the AMBER 6 program revealed that distinct propelling behavior was obtained in propeller-type metal complexes with a C_3 axis of symmetry such as *fac*-tris(*S*-2,3-diaminopropionato)cobalt(III) in aqueous solution upon IR irradiation [10]. This encouraging finding prompted us to attempt to construct molecular engines from propeller-type metal complexes with a C_3 axis of symmetry. The properties of the propeller-type complexes have potential applications as models

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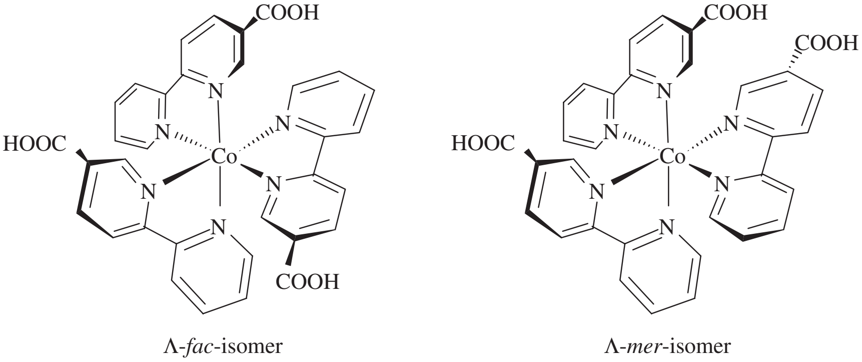


Figure 1. The Λ-*fac*- and Λ-*mer*-isomers of tris(5-carboxy-2,2′-bipyridine)cobalt(III).

for photochemically-induced drug delivery, molecular-level transportation, guidance systems and concentration changes of solution. Moreover, the propeller-type complexes may be used in the future to construct molecular-level devices with applications in agriculture (biology), pharmacology, medicine and engineering (optics). Despite the wealth of literature examining the polypyridine complexes of ruthenium(II), rhodium(II) and osmium(II) [11, 12], the preparation and stereochemistry of the tris(5-functionalized-2,2′-bipyridine) complexes of cobalt(III) has not been studied. Tris-chelate complexes containing monofunctionalized 2,2′-bipyridine ligands can adopt both the meridional (*mer*-) and facial (*fac*-) isomers in both Λ- and Δ-optical isomers. The *fac*-isomer has the three functional groups placed towards one face of the pseudo-octahedral geometry, while the *mer*-isomer places its carboxyl groups separately in two opposite faces. MD simulations indicate that the behavior of tris(5-carboxy-2,2′-bipyridine) complexes in solution is very dependent on the ligand orientation. Consequently, isolation of geometrical and optical isomers is important in the preparation of new functional materials. To realize isomerically pure *fac*-functionalized species for the construction of molecular devices, we discuss here the isolation and characterization of four isomers, geometrical and optical, the Λ-*fac*, Δ-*fac*, Λ-*mer* and Δ-*mer*-isomers of the tris(5-carboxy-2,2′-bipyridine)cobalt(III) complexes (figure 1).

2. Experimental

2.1. *Instrumentation*

Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O 2400 instrument. UV–Vis absorption (AB) spectra were recorded on a Jasco V-550 spectrophotometer. IR spectra of KBr pellets were recorded on a Jasco FT/IR spectrometer. Circular dichroism (CD) spectra were recorded at room temperature using a Jasco J-720 spectropolarimeter. ^{1}H NMR spectra were recorded on a Varian VXR500 spectrometer using the solvent as internal reference.

2.2. *Materials*

All starting materials were used as received from the supplier. Laboratory grade solvents were used unless specified otherwise. Water was deionized and distilled on an ion-exchange column. SP-Sephadex (C-25) (Aldrich Chemical Company, Inc.), which has sulfopropyl groups as the cation-exchange group, was used for chromatographic purification of the metal complexes. $[CoCl(NH_3)_5]Cl_2$ was prepared according to a literature method [13].

2.3. *Ligand synthesis*

2,2′-Bipyridine-5-carboxylic acid was prepared by modified literature procedures [14].

2.3.1. (((2-Pyridyl)carbonyl)methyl)pyridinium iodide. Some 2.42 g (0.02 mmol) of 2-acetylpyridine were dissolved in 20 mL of pyridine, heated for 3 h at 70 °C with stirring, stored overnight at room temperature and then filtered. The residue was washed with pyridine and ethanol, and recrystallized from 18 parts EtOH to give 4.73 g of cream-colored powder (0.015 mol, 72.8%). Characterization was consistent with published results.

2.3.2. 5-Methyl-2,2′-bipyridine. A mixture of 6.5 g (0.02 mol) of (((2-pyridyl)carbonyl)methyl)pyridinium iodide, 40 mL of formamide and 40 g of ammonium acetate were stirred at 60 °C. After the compounds had dissolved completely, 2.25 mL (0.038 mol) of methacrolein was added. Stirring was continued for 4 h at 60 °C and subsequently overnight at room temperature. The product was isolated from the reaction mixture by extraction with hexane (3 × 100 mL). The hexane layers were combined and washed with 100 mL of 1 wt% aqueous sodium sulfate solution and concentrated under vacuum to yield 2.73 g of a brown oil (0.017 mol, 84.6%).

2.3.3. 2,2′-Bipyridine-5-carboxylic acid. A solution of 3.0 g (0.0187 mol) of 5-methyl-2,2′-bipyridine and 12 g of potassium permanganate in 150 mL of water was heated for 5 h at 70 °C with stirring. After being cooled to room temperature the reaction mixture was filtered. The filtrate was acidified to pH 1 by adding concentrated HCl and subsequently concentrated under vacuum to approximately 50 mL. After standing overnight in a refrigerator the precipitate was collected on a filter, washed with ethanol and air dried to give 2.10 g of a white powder (0.011 mol, 59%).

2.4. *Complex synthesis*

Tris(5-carboxy-2,2′-bipyridine)cobalt(III) complexes were synthesized following a modified literature method [15, 16]. $[CoCl(NH_3)_5]Cl_2$ (0.5 g, 2 mmol), 2,2′-bipyridine-5-carboxylic acid (1.4 g, 7 mmol) and 0.5 g activated charcoal were refluxed in 30% methanol (60 mL) until ammonia was no longer evolved. The resulting orange reaction mixture was filtered, and sodium perchlorate monohydrate (0.84 g, 6 mmol) was added. After standing overnight in a refrigerator the product that precipitated as a yellow powder was collected on a filter, washed with ethanol, and air dried. Further purification was achieved by passage down an SP-Sephadex (C-25) column eluting with 2 L of water, precipitation with sodium perchlorate monohydrate, and recrystallization from water: yield 1.3 g of a yellow powder (1.36 mmol, 67.9%).

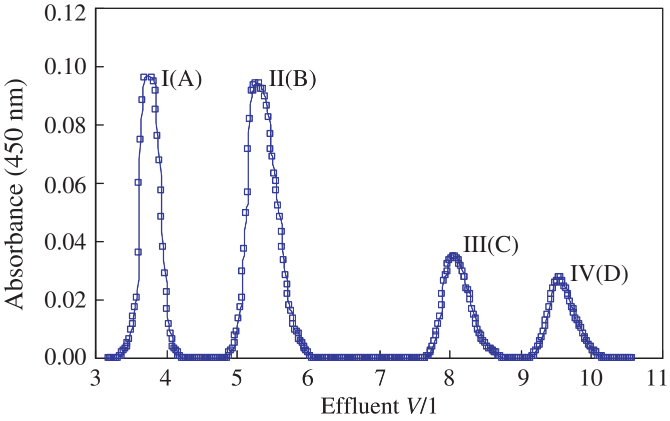


Figure 2. Elution curve. Eluent: 0.1 M $Na_2[Sb_2\{(+)\text{-tart}\}_2]$ aqueous solution.

2.5. *Chromatographic separation of the isomers*

A chromatographic method on an SP-Sephadex column was used to separate the isomers [17, 18]. The prepared complexes dissolved in water were deposited onto an SP-Sephadex (C-25) column (φ 2.4 × 140 cm). Elution with 0.1 M aqueous sodium ((+)-tartrato)antimonite(III), $Na_2[Sb_2\{(+)\text{-tart}\}_2]$, as the eluent proceeded at a rate of 0.5 mL min^{-1}. Under these conditions, about 10 days was required for complete elution of the complex, which produced four separate yellow bands, I, II, III and IV (figure 2). The effluent was separated into fractions of 20 mL each, and the absorbance of each fraction at 450 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 III being plus, II and IV being minus for the Na-D line; their band-area ratios were about 3 : 3 : 1 : 1; no further separation was possible, even by repeated chromatography.

2.6. *Purification of the isomers*

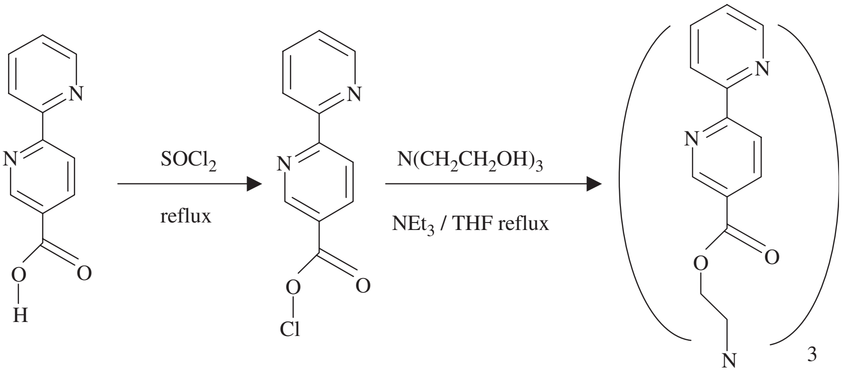
The fractions corresponding to I, II, III and IV were diluted 10 times with water, respectively; then they were again adsorbed onto an SP-Sephadex (C-25) column (φ 1 × 10 cm), washed with 1 L of water, followed by elution with 1 M sodium chloride solution. The perchlorate crystals were obtained by addition of sodium perchlorate monohydrate to these solutions and recrystallization from water. The chemical composition of the four isomers thus prepared are given in table 1.

2.7. *Isolation of* fac-*$[Co(cbpy)_3]^{3+}$*

In an alternative strategy, the *fac*-$[Co(cbpy)_3]^{3+}$ isomer was prepared by forming a tripodal podand ligand L (scheme 1) by a modified literature method [19]. Subsequent loss of the three arms gave the *fac*-isomer. First, 2,2′-bipyridine-5-carboxylic acid (1.26 g, 6 mmol) was refluxed in thionyl chloride (50 mL) for 3 h. The thionyl chloride

Table 1. Chemical composition of the isomers.

	Elemental analysis (%) (Calcd value)		
Complex	C	H	N
A. Λ-*mer*-$[Co(cbpy)_3](ClO_4)_3$	41.34 (41.38)	2.52 (2.53)	8.73 (8.77)
B. Δ-*mer*-$[Co(cbpy)_3](ClO_4)_3$	41.39	2.58	8.79
C. Λ-*fac*-$[Co(cbpy)_3](ClO_4)_3$	41.44	2.46	8.69
D. Δ-*fac*-$[Co(cbpy)_3](ClO_4)_3$	41.36	2.56	8.63



Scheme 1. Synthesis of the tripodal tris-bipyridine ligand L.

was removed under reduced pressure and the pale yellow solid was dried *in vacuo* for 2.5 h. The resulting solid was dissolved in dry THF (150 mL) and triethylamine (6 mL) to which triethanolamine (0.30 g, 2 mmol) was added. This mixture was refluxed for 8 h and stirred for a further 36 h at room temperature. The solvent was then removed *in vacuo*, and the resulting solid was dissolved in $CHCl_3$. After washing with water (100 mL), drying over anhydrous magnesium sulfate and removing the solvent, the crude cream-colored product was recrystallized from acetone/water. Yield 0.9 g (1.18 mmol, 58%). Characterization was consistent with published results. The cage-like cobalt(III) complex of the ligand L was prepared by a similar method to the synthesis of $[Co(cbpy)_3]^{3+}$ complexes. Δ-*fac*- and Λ-*fac*-$[Co(cbpy)_3]^{3+}$ isomers were obtained by stirring the cage-like cobalt(III) complex of the ligand L in 0.1 M aqueous NaOH solution and resolved by cation-exchange chromatography on SP-Sephadex C-25 eluting with 0.1 M aqueous solution of $Na_2[Sb_2\{(+)\text{-tart}\}_2]$.

3. Results and discussion

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

In figure 3 the AB and CD spectra of the C isomer are shown, while table 2 lists data for all the isomers. The electronic AB spectra of the separated isomers did not show any significant differences, with ligand-centered absorptions at 310 and 321 nm and the characteristic metal-to-ligand band at 454 nm. Both these absorptions are red shifted

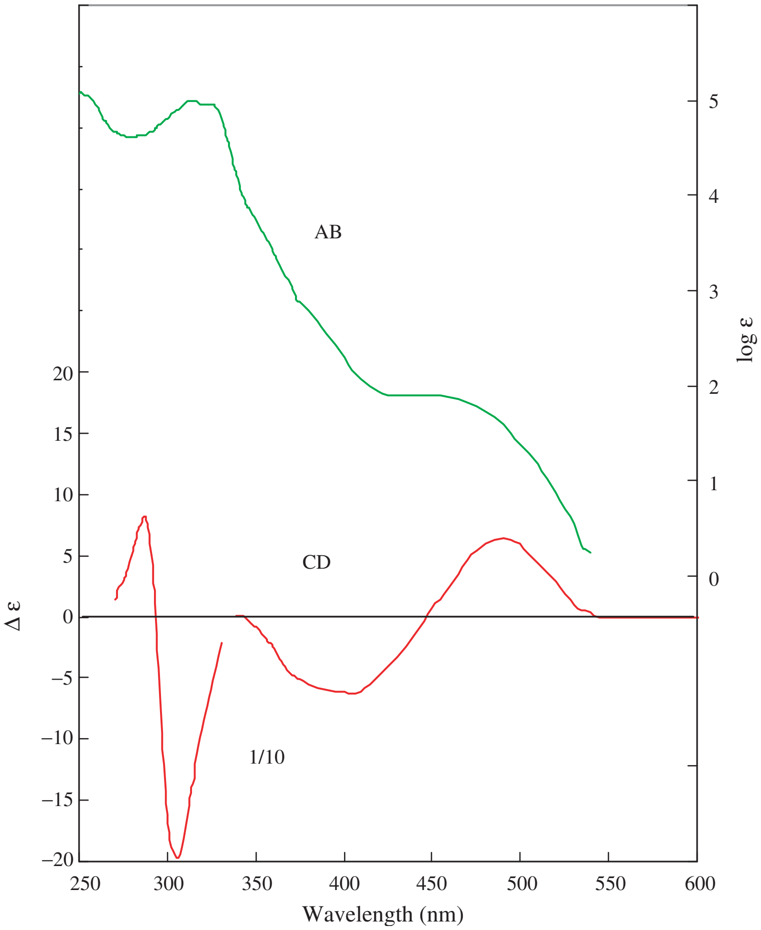


Figure 3. AB and CD spectra of Λ-*fac*-$[Co(cbpy)_3]^{3+}$ in methanol/water (1 : 1).

with respect to $[Co(2,2'\text{-}bpy)_3]^{3+}$ as a consequence of the electron-withdrawing nature of the carboxyl groups. Correspondingly, the CD bands in the d–d region of the separated cbpy complex are at longer wavelength, and their intensities are greater than those of the bpy complex. The rotatory strength in the d–d transition region of the cbpy complex is greater than that of bpy [20, 21], presumably because of the electron-withdrawing carboxyl groups. The CD spectrum of the A isomer is almost the same to that of C. B and D show symmetric CD spectra compared to those of the A and C isomers. Comparison of the CD spectra of A and B, and those of C and D, reveals that the isomers have been separated into A and B, and C and D coupled enantiomers.

3.2. *Infrared (IR) spectra*

The IR spectra of the four isomers are slightly different in shape and position. It is difficult to assign their configuration on the basis of the IR spectra alone. The carbonyl stretching vibration of *fac*-$[Co(cbpy)_3](ClO_4)_3$ appears at 1720 cm^{-1}.

Table 2. Absorption and circular dichroism spectra.

		Absorption		CD	
Complex		$\nu_{max}/10^{-4}\,cm^{-1}$ (λ_{max} nm)	$\log \varepsilon$	$\nu_{max}/10^{-4}\,cm^{-1}$ (λ_{max} nm)	$\Delta\varepsilon_{max}$
A. Λ-*mer*-[Co(cbpy)$_3$](ClO$_4$)$_3$	First band	2.20 (454)	1.90	2.05 (486)	+6.2
				2.55 (392)	−6.0
	$^1A_1 \rightarrow {}^1A_2$	3.11 (321)	4.96	3.29 (304)	−194.5
	$^1A_1 \rightarrow {}^1E$	3.22 (310)	4.97	3.50 (286)	+78.3
B. Δ-*mer*-[Co(cbpy)$_3$](ClO$_4$)$_3$	First band	2.20 (454)	1.90	2.05 (486)	−6.2
				2.55 (392)	+6.1
	$^1A_1 \rightarrow {}^1A_2$	3.11 (321)	4.96	3.29 (304)	+194.0
	$^1A_1 \rightarrow {}^1E$	3.22 (310)	4.97	3.50 (286)	−78.3
C. Λ-*fac*-[Co(cbpy)$_3$](ClO$_4$)$_3$	First band	2.20 (454)	1.90	2.04 (491)	+6.4
				2.50 (400)	−6.15
	$^1A_1 \rightarrow {}^1A_2$	3.11 (322)	4.96	3.29 (304)	−194.5
	$^1A_1 \rightarrow {}^1E$	3.22 (310)	4.97	3.50 (286)	+78.3
D. Δ-*fac*-[Co(cbpy)$_3$](ClO$_4$)$_3$	First band	2.20 (454)	1.90	2.04 (491)	−6.4
				2.50 (400)	+6.2
	$^1A_1 \rightarrow {}^1A_2$	3.11 (321)	4.96	3.29 (304)	+194.4
	$^1A_1 \rightarrow {}^1E$	3.22 (310)	4.97	3.50 (286)	−78.3

3.3. ^{1}H NMR spectra

The ^{1}H NMR spectra of the C and D isomers were observed with seven aromatic signals of the three equivalent ligands expected for the *fac* isomer. However, the ^{1}H NMR spectra for the A and B isomers were complicated because of the *mer*-isomer with three inequivalent ligands.

3.4. Assignment of the structures

The configurations of the separated isomers were assigned by means of the formation ratio, the CD and NMR spectra. In a typical synthesis, using three identical ligands, a statistical distribution of three parts of the *mer*-isomer will be produced to one *fac*-isomer. The assignment of the absolute configuration can be made from CD spectra [22–24]. According to the cotton effects of optical activity, it can be predicted that tris(cbpy) complexes show two intense CD bands of opposite sign in the d–d region; that is, for Λ configuration strongly positive at lower energies and strongly negative at higher energies, and the reverse for Δ configuration. Thus, the formation ratio of 3 : 1 found for the A and B, and D and C isomers (figure 2) and the fact that both A and C show two CD signals of opposite sign (about 450 nm, figure 3), strongly positive at lower energies and strongly negative at higher energies, indicate that the A and B isomers are Λ-*mer* and Δ-*mer*, and the C and D isomers are Λ-*fac* and Δ-*fac* isomers.

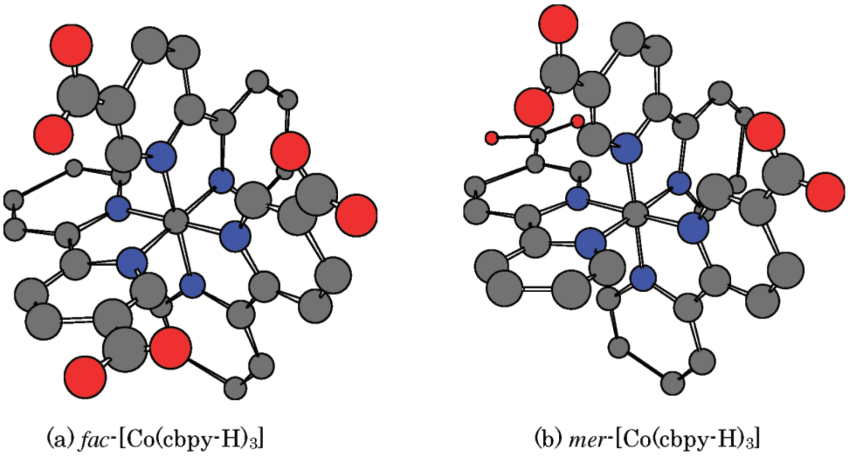
The assignment was also supported by the X-ray structural analysis. Crystals suitable for X-ray structure analysis of tris(5-carboxy-2,2′-bipyridine)cobalt(III) complexes were obtained as the *mer*-isomer.

3.5. Molecular dynamics simulation of fac-[Co(cbpy-H)$_3$]

To explore whether distinct propelling and rotating behaviors can be obtained in *fac*-[Co(cbpy-H)$_3$] in aqueous solution upon IR irradiation, geometry optimization

Table 3. The partial charges distributed on the atoms.

Atom	Partial charge
Co	+0.960
H (bonded to N)	+0.100
Lp (bonded to O of COO$^-$)	−0.170
O (water)	−0.048
H (bonded to O of water)	+0.274
Lp (bonded to O of water)	−0.25
Others	0


(a) *fac*-[Co(cbpy-H)$_3$]

(b) *mer*-[Co(cbpy-H)$_3$]

Figure 4. The AMBER 6 optimized structures of (a) *fac*-[Co(cbpy-H)$_3$] and (b) *mer*-[Co(cbpy-H)$_3$].

and MD calculations were performed using the AMBER 6 program, as described previously [10], on the systems consisting of the complex *mer*- or *fac*-[Co(cbpy-H)$_3$] and 80 water molecules. Table 3 shows the partial charges that were required for calculation of electrostatic interactions.

The optimized structures (figure 4) were similar to those found by the X-ray crystallographic study of *mer*-[Co(cbpy)$_3$](ClO$_4$)$_3$. The crystals of *mer*-[Co(cbpy)$_3$](ClO$_4$)$_3$ suitable for X-ray structural analysis were obtained from a methanol solution. The X-ray structure determination shows that the asymmetric unit contains one [Co(cbpy)$_3$] cation with the metal coordinated to the six pyridyl nitrogens of the three ligands in a distorted octahedral arrangement, three ClO$_4$ anions and two water molecules.

The details of the protocol used for the MD simulations of *mer*- and *fac*-[Co(cbpy-H)$_3$] are as follows:

(1) The potential energy of *mer*- or *fac*-[Co(cbpy-H)$_3$] 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 water (a total of 80 water molecules were used to solvate *mer*- or *fac*-[Co(cbpy-H)$_3$]). Then with the complex frozen, only the energy of solvating water was minimized to avoid water molecules 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 to a temperature of 300 K during 10 sequential (1 ps) runs. The stepwise manner was selected to avoid disruption of the complex that might result from a large increase in the temperature.

(4) The entire production of MD with constant volume conditions was performed up to 300 ps with constant pressure conditions. The size of the simulation box was $30 \times 30 \times 30\,\text{Å}^3$.

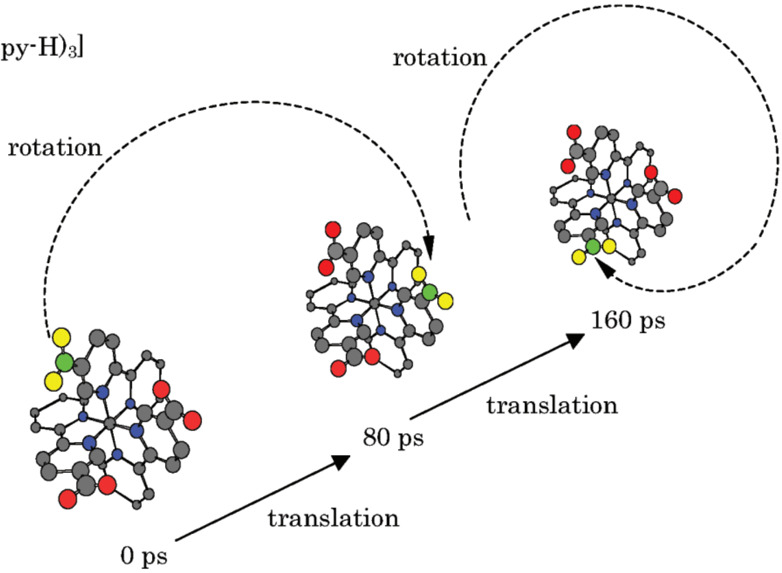
(5) The value of ε used for the van der Waals parameter of O belonging to the carboxyl group was increased to 25 times, estimated according to the particular absorption of carboxyl at $1720\,\text{cm}^{-1}$, to fulfill the purpose of obtaining enough propelling and rotating functions.

The expected propelling and rotating 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 was stabilized around 100 ps and remained stable afterwards. Potential energy reached a stable equilibrated level after nearly 100 ps. It was assumed that the MD period before 100 ps should be considered as an equilibrium-searching period. The snapshots of [Co(cbpy-H)$_3$] showed that the propeller structure with the C_3 symmetry axis for the *fac*-isomer and the structure with the pseudo-C_3 symmetry axis for the *mer*-isomer were well kept through all the simulations. Some of the results from 100 to 300 ps are shown in figure 5. For *fac*-[Co(cbpy–H)$_3$], the center of the complex moved almost straightforwardly along the C_3 symmetry axis in the opposite direction of the carboxyl functional groups, while rotated clockwise 120° about the C_3 symmetry axis for about 80 ps of MD simulations (figure 5a), and for *mer*-[Co(cbpy-H)$_3$], the center of the complex only zigzagged along in the same direction, rotating clockwise about 120° about the pseudo-C_3 symmetry axis for about 90 ps of MD simulations (figure 5b). The results suggest that in aqueous solution on IR irradiation, distinct propelling and rotating functions can be obtained in *fac*-[Co(cbpy-H)$_3$] with three functional groups placed towards one face of the pseudo-octahedral geometry. Both propelling and rotating functions were revealed in *mer*-[Co(cbpy-H)$_3$], with three carboxyl groups in two opposite faces. Compared with the MD calculations for *fac*-[Co(*S*-dap)$_3$] [10], stronger propelling and rotating functions were obtained in *fac*-[Co(cbpy-H)$_3$] in aqueous solution on IR irradiation. The observed stronger propelling and rotating functions seem to be related to the π-conjugation of the bpy rings.

4. Conclusions

We have succeeded for the first time in the preparation and separation of all four optically active isomers of tris(5-carboxy-2,2′-bipyridine)cobalt(III) complex. We have also developed a method of selectively isolating *fac*-tris(substituted bipyridine) complexes of cobalt(III). The three carboxyl groups offer new opportunities to allow the introduction of a great variety of new functionalities with a unique orientation. The preparation of the propeller-type complexes [Co(L)$_3$]$^{3+}$ containing 5-functionalized 2,2′-bipyridine ligands (where L = 2,2′-bipyridine-5-carboxylic

(a) *fac*-[Co(cbpy-H)$_3$]



(b) *mer*-[Co(cbpy-H)$_3$]

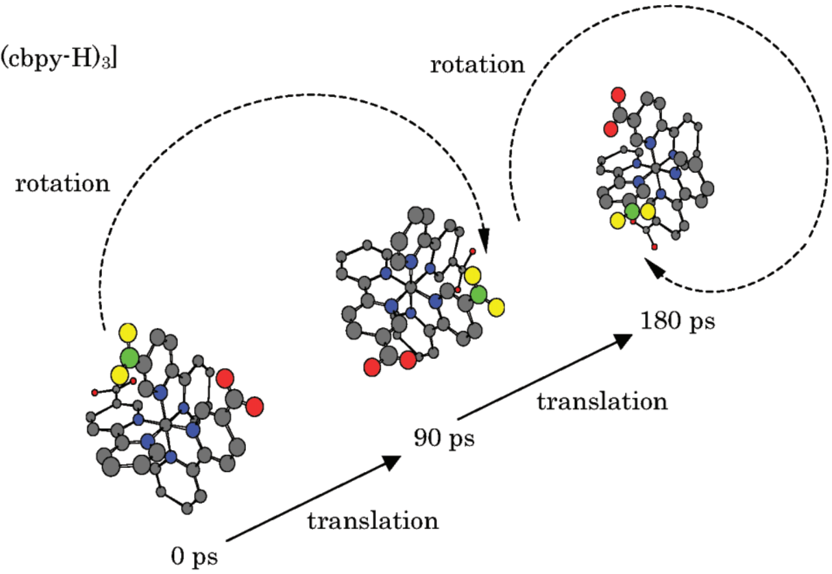


Figure 5. Model of the results of MD simulation of (a) *fac*-[Co(cbpy-H)$_3$] and (b) *mer*-[Co(cbpy-H)$_3$] in aqueous solution.

acid phenyl ester, 2,2′-bipyridine-5-carboxylic acid *para*-nitrophenyl ester) is in progress. The results of MD simulations suggest that observable propelling and rotating functions can be obtained in the propeller-type complex *fac*-[Co(cbpy-H)$_3$] on IR irradiation in aqueous solution. Further study is planned to confirm these suggestions by detecting the changes in UV and CD spectra of *fac*-[Co(cbpy)$_3$]$^{3+}$ in aqueous solution on IR excitation and other similar propeller-type complexes will be designed and prepared.

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