

Thermodynamic Stability and Inversion Reaction of Tris[(-)cyclic-O,O'-1(R),2(R)dimethylethylenedithiophosphato]chromium(III), $\Lambda(-)\{\text{Cr}[(+)\text{bdtp}]_3\}$

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Abstract

The $\Lambda(-)\text{Cr} \rightleftharpoons \Delta(-)\text{Cr}$ equilibrium constant of the title complex, $\text{Cr}[(+)\text{C}_4\text{H}_9\text{O}_2\text{PS}_2]_2$, was measured in chloroform between 5 and 40 °C by CD spectroscopy giving values between 2.01 and 1.60 ± 0.03 . The thermodynamic parameters were: $\Delta G^\circ = -1.39 \pm 0.04 \text{ kJ mol}^{-1}$, $\Delta H^\circ = -4.8 \pm 0.3 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -11.4 \pm 1.0 \text{ J mol}^{-1} \text{ K}^{-1}$, indicating differences in the stability of the two diastereoisomers in chloroform solution, $\Delta(-)\text{Cr} > \Lambda(-)\text{Cr}$. The kinetic data at different temperatures in chloroform solution of the $\Lambda(-)\text{Cr} \rightleftharpoons \Delta(-)\text{Cr}$ inversion reaction indicate a first order intramolecular process with the following kinetic constants and activation parameters at 25 °C: $k_1 = 1.03 \times 10^{-3} \text{ s}^{-1}$, $k_2 = 5.82 \times 10^{-4} \text{ s}^{-1}$, $\Delta H^\ddagger = 106 \text{ kJ mol}^{-1}$, $\Delta G^\ddagger = 91.4 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = 49 \text{ J mol}^{-1} \text{ K}^{-1}$. A bond-rupture mechanism is favoured by the activation parameters.

Introduction

The characterization of the $\Lambda(-)\text{Cr}[(+)\text{bdtp}]_3$ complex, (I), has evidenced its optical lability in various solvents, showing the inversion to the $\Delta(+)\text{Cr}[(+)\text{bdtp}]_3$ diastereoisomer, (II), and developing a solvent dependent equilibrium mixture of the two $\Lambda(-)\text{Cr}$ and $\Delta(-)\text{Cr}$ diastereoisomers [1].

Theoretical calculations and experimental measurements of chiral discrimination energies of corresponding diastereoisomers could clarify the interactions between chiral molecules [2, 3]. The enantiomerization of tris(*o*-phenanthroline)nickel(II) ions in (-)-2,3-butanediol was studied by CD spectroscopy to define in energy terms the extent of the interactions between enantiomers and the chiral solvent [4]. Energy discriminations between the enantiomers of tris-chelate coordination compounds in chiral α -hydroxy ester solutions were measured to discuss the stereochemical and energetic aspects of the intermolecular associations [5]. Recently,

the chiral discrimination in the liquid state between the two chlorofluoroacetonitrile enantiomeric forms was calculated [6].

Moreover there has been a great deal of interest in the dynamic stereochemistry of tris(dithiocarbamate)metal(III) complexes, which have been studied by NMR solution spectra to establish the optical intramolecular metal-centred ($\Delta \rightleftharpoons \Lambda$) inversion mechanism [7, 8]. However the resulting chromium complex was not labile in CDCl_3 [8].

Optical resolution of cobalt(III) complexes afforded direct polarimetric measurement of loss of optical activity using a variety of organic solvents, without the requirement of a diastereotopic substituent in the compound [9, 10].

The aim of the present work was the determination of the equilibrium constant of the two (I) and (II) diastereoisomers in chloroform, and the kinetic study of their inversion reaction to obtain precise thermodynamic data about the intra- and intermolecular interactions in this system and inferences on the reaction mechanism.

We report here the results in chloroform solution obtained by a CD spectroscopic method for the measurements of the inversion process in $\text{M}^{\text{III}}\text{S}_6$ stereochemically-labile metal transition complexes.

Experimental

Preparation of the Compounds

The ligand and $\Lambda(-)\text{Cr}[(+)\text{bdtp}]_3$, (I), complex were prepared as previously reported [1].

Measurement of Inversion Process

Kinetic measurements of the inversion process were obtained by CD measurements at a fixed wavelength (665 nm) of solutions with concentrations of approximately $2 \times 10^{-3} \text{ mol/dm}^3$ in spectroscopic degree solvents, and were recorded in a time scale. The solutions were placed in a cell, $l = 1 \text{ cm}$, inserted

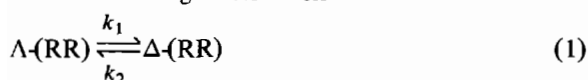
in a thermostated jacket by connections with a constant-temperature water bath. The temperature, accurate to ± 0.1 K, was controlled by a thermocouple directly in the cell. Inversion reactions were followed to the equilibrium conditions and controlled after completion (12–24 h). Starting time was considered the half volume addition point of solvent. All the measurements were done at least in duplicate.

The ΔOD value at zero time was obtained by graphical extrapolation of the plot of ΔOD against time, recorded directly. The OD value of the same solution was obtained from the UV-Vis. spectrum so that the maximum value of $g = \Delta OD/OD$ at zero time and at the fixed wavelength was derived.

Kinetic Relationship

A linear relationship of $\ln(\Delta OD_t - \Delta OD_e)$ against time verified the first-order nature of the inversion process.

The following reaction scheme



was assumed to calculate the kinetic constants for the inversion of the dissymmetric chromium centre.

The results were analysed by least-squares regression to determine the rate constants. Activation parameters were calculated from the Arrhenius plots of $\log k_i$ against T^{-1} and the entropy of activation (ΔS^\ddagger) was calculated from ΔH^\ddagger and ΔG^\ddagger . Maximum mean square errors in all derived parameters were calculated at the 95% confidence level by the total differential method.

If C_{Λ_0} and C_{Δ_0} are the initial concentrations of $\Lambda\text{-(R,R)}$ and $\Delta\text{-(R,R)}$ diastereoisomers respectively, the actual concentrations will be $C_\Lambda = C_{\Lambda_0} - x$ and $C_\Delta = C_{\Delta_0} + x$, with x representing the concentration variation of the two species.

In the CD spectrum of a solution in equilibrium conditions (1) the ΔOD is a function of the actual concentrations of the two diastereoisomers, and at a particular wavelength:

$$\Delta OD = \Delta \epsilon_\Lambda (C_{\Lambda_0} - x)l + \Delta \epsilon_\Delta (C_{\Delta_0} + x)l \quad (2)$$

If $C_{\Delta_0} = 0$, x will represent the concentration C_Δ of $\Delta\text{-(RR)}$ at any time.

A solution of the $\Lambda\text{-(RR)}$ diastereomer at zero time with $x = 0$ will give

$$\Delta OD_0 = \Delta \epsilon_\Lambda C_{\Lambda_0} l \quad (3)$$

at t time

$$\Delta OD_t = \Delta \epsilon_\Lambda C_{\Lambda_0} l + (\Delta \epsilon_\Delta - \Delta \epsilon_\Lambda)x l \quad (4)$$

at equilibrium, $x = x_e$,

$$\Delta OD_e = \Delta \epsilon_\Lambda C_{\Lambda_0} l + (\Delta \epsilon_\Delta - \Delta \epsilon_\Lambda)x_e l \quad (5)$$

Subtracting (5) from (4) and (3):

$$\Delta OD_t - \Delta OD_e = (\Delta \epsilon_\Delta - \Delta \epsilon_\Lambda)(x - x_e)l \quad (6)$$

$$\Delta OD_0 - \Delta OD_e = (\Delta \epsilon_\Delta - \Delta \epsilon_\Lambda)(-x_e)l \quad (7)$$

The ratio between (7) and (6),

$$(\Delta OD_0 - \Delta OD_e)/(\Delta OD_t - \Delta OD_e) = x_e/(x_e - x) \quad (8)$$

has been substituted in the equation for the reversible reactions [11]

$$\ln[x_e/(x_e - x)] = (k_1 + k_2)t \quad (9)$$

obtaining

$$\ln(\Delta OD_t - \Delta OD_e) = -(k_1 + k_2)t + \ln(\Delta OD_0 - \Delta OD_e) \quad (10)$$

A plot of $\ln(\Delta OD_t - \Delta OD_e)$ vs. time should be linear with a slope equal to $-(k_1 + k_2)$ and an intercept from which one could obtain ΔOD_0 , if ΔOD_e is known.

Since

$$K = k_1/k_2 \quad (11)$$

and the slope

$$k = -(k_1 + k_2) \quad (12)$$

knowing K we can obtain

$$k_1 = k_2 K \text{ and } k_2 = -k/(K + 1) \quad (13)$$

Thermodynamic Equilibrium Constant

The equilibrium (1) constant, K , can be determined independently as

$$K = C_{\Delta_e}/C_{\Lambda_e} = x_e/(C_{\Lambda_0} - x_e) \quad (14)$$

If the total concentration C is known by absorbance measurements, knowing $\Delta \epsilon$ and measuring ΔOD one can calculate the diastereomeric excess,

$$C_{\text{exc}} = \Delta OD/\Delta \epsilon \cdot l \quad (15)$$

and consequently the concentrations of the two diastereoisomeric forms at equilibrium would be:

$$C_{1e} = (\frac{1}{2})(C + C_{\text{exc}}), C_{2e} = (\frac{1}{2})(C - C_{\text{exc}}) \quad (16)$$

If $\Delta\text{-(RR)}$ will be the predominant form at equilibrium, $C_{1e} = C_{\Delta_e}$ and

$$K = (C + C_{\text{exc}})/(C - C_{\text{exc}}). \quad (17)$$

TABLE I. Constants and Thermodynamic Parameters of the Equilibrium: $\Lambda\text{-Cr}[(+)\text{bdtp}]_3 \rightleftharpoons \Delta\text{-Cr}[(+)\text{bdtp}]_3$ in Chloroform Solution.^a

$T^\circ\text{C}$	5	15	20	25	30	35	40
$K \pm 0.03$	2.01	1.89	1.84	1.76	1.71	1.65	1.60
$\Delta H^\circ \text{ kJ mol}^{-1}$				-4.8 \pm 0.3			
$\Delta G^\circ \text{ kJ mol}^{-1}$				-1.39 \pm 0.04			
$\Delta S^\circ \text{ J mol}^{-1} \text{ K}^{-1}$				-11.4 \pm 1.0			

^aAll errors are estimated at the 95% confidence level.

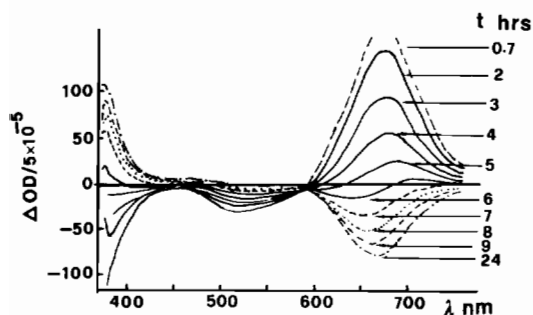


Fig. 1. The CD spectra of $\Lambda(-)_{589}\{\text{Cr}[(+)\text{bdtp}]_3\}$ in CHCl_3 solution (0.00247 M) at 5 °C and different times since the solubilization (0–24 h).

From the value of K the free energy variation for the two forms

$$\Delta G^\circ = -RT \ln K \quad (18)$$

is obtained.

Measurements of equilibrium concentrations at different temperatures will give different values of K . A plot of $\ln K$ against $1/T$ will give the enthalpy ΔH° , and consequently it is possible to calculate the entropy variation

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \quad (19)$$

Results and Discussion

The CD spectra of the $\Lambda(-)_{589}\{\text{Cr}[(+)\text{bdtp}]_3\}$ complex in many solvents show with time a change in the differential optical density, ΔOD , of many bands [1]. Particularly in chloroform solutions it is possible to follow the lowering of the intense positive CD band at 675 nm, in the region of the d–d ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transition which is replaced by another negative band shifted to 665 nm (Fig. 1). The sign of this band characterizes the absolute configuration Λ or Δ at the metal centre of the complex, and its

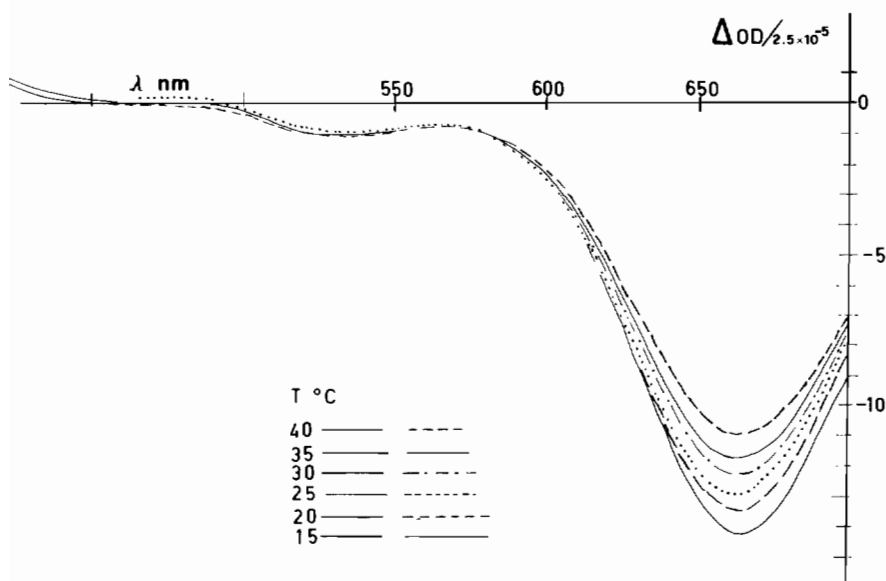


Fig. 2. The CD spectra of the $\Lambda(-)_{589}\{\text{Cr}[(+)\text{bdtp}]_3\} \rightleftharpoons \Delta(+)-_{589}\{\text{Cr}[(+)\text{bdtp}]_3\}$ equilibrium in CHCl_3 solution ($\sim 0.002 \text{ M}$) at different temperatures (5–40 °C).

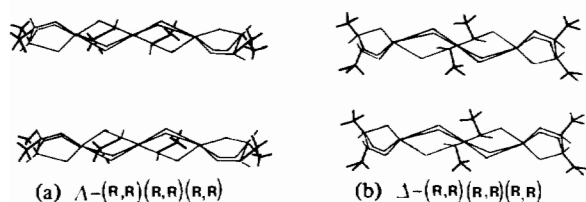


Fig. 3. A projection on the plane of C_3 rotation axis of, a) $\Lambda(-)\{Cr[(-)S_2PO_2C_4H_8]_3\}$ and b) $\Delta(+)\{Cr[(-)S_2PO_2C_4H_8]_3\}$ structural models viewed along a C_2 axis, illustrating the different disposition of CH_3 groups with respect to the plane containing the CrP_3 atoms.

actual intensity, ΔOD , is proportional to the relative concentrations of the two diastereoisomers. At the end of the inversion process the solution reaches an equilibrium state characterized by a positive or negative ΔOD_e value, depending on the solvent [1].

However, at different temperatures the CD spectra in chloroform show that the system attains different equilibrium conditions (see Fig. 2). The measurements of ΔOD_e of the equilibrium solutions between 5 and 40 °C allow us to determine the concentrations of the two diastereoisomers and the equilibrium constant K (eqns. 14–16). $\Delta \epsilon = -6.7$ in the negative band at 665 nm of the pure diastereoisomer, (II), has been assumed to be equal to that of the isolated diastereoisomer, (I), directly measured from the positive band at 675 nm [1].

The mean values of the equilibrium constant values, obtained from repeated measurements of different concentration solutions, and thermodynamic parameters of equilibrium (1) in chloroform, are given in Table I. Heats of inversion were obtained from $\ln K$ vs. $1/T$ plots. The data were treated by a least squares analysis including the mean values of K at each temperature. Standard free energy and entropy of inversion were calculated at 25 °C.

The negative value of the standard free energy change shows that $\Delta(+)\{Cr[(-)bdtp]_3\}$ is thermodynamically favoured in chloroform solutions, compared with $\Lambda(-)\{Cr[(-)bdtp]_3\}$ in spite of the negative value of the standard entropy change because the latter is compensated by a strong negative enthalpic contribution. The equilibrium constant is higher at low temperatures, so a shift to the left side of the equilibrium reaction may be foreseen at high temperatures. If ΔH° and ΔS° are temperature independent, the free energy variation should become zero and the diastereomeric equilibrium constant become unity at 135 °C.

However, the negative entropic change ($\Delta S^\circ = -11.4 \pm 1.0 \text{ J mol}^{-1} \text{ K}^{-1}$) indicates an order production when the $\Delta-(R,R)$ form predominates over the $\Lambda-(R,R)$ diastereoisomer. Thus the higher thermodynamic stability of complex (II) over complex (I) could be explained by supposing a stronger interaction of the solvent with the Δ than with the Λ

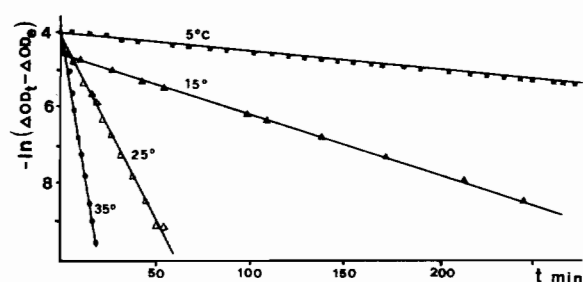


Fig. 4. The relationship between time and the logarithm of the differential ΔOD at time t and at equilibrium conditions.

configuration complex, and/or a differently high intramolecular interaction between the chiral Cr^{III} - S_6 group and the chiral tails of the ligands for the two diastereoisomers.

The structure of the isolated species was not resolved because of the difficulties in obtaining single crystals suitable for the determination. However, it could be interesting to observe the molecular models which show the coexistence of the two concentric propellers with opposite chirality, rotating around a C_3 axis. In the double helical model the first propeller consists of four-atom CrS_2P rings, connected with five-membered cycles PO_2C_2 in a plane at 90° with respect to that of the first cycle [1]. In the $\Delta-(RR)(RR)(RR)$ diastereoisomer (Fig. 3) the H atoms are arranged in the cylindrical solid formed by rotating the propellers, while the CH_3 groups are nearly parallel to the C_3 axis in axial position with respect to the plane containing the chromium and phosphorus atoms.

In the $\Lambda-(RR)(RR)(RR)$ diastereoisomer the situation is inverted and the CH_3 groups are all arranged in apparently equatorial positions with respect to the plane containing chromium and phosphorus atoms, covering the external cylindrical space of the rotating propeller and perpendicular to the C_3 axis.

In the Δ isomer minimum steric intramolecular interactions should occur, since the CH_3 groups are outside the plane containing all other atoms and at greater distances from each other than in the Λ isomer. Under these conditions the alkyl tails should have a greater freedom of movements than in the $\Lambda-(R,R)$ diastereoisomer. However, it is known that chloroform interacts strongly with tris-dithiocarbamate metal(III) complexes [12].

A similar interaction in the $\Delta(+)\{Cr[(-)bdtp]_3\}$ complex could be responsible for the diastereomeric stabilization observed. The solvent molecules inserting between the blades of the $\Delta-(R,R)$ propellers reduce the freedom of vibration and rotation of the alkylic tails.

In dichloromethane and ethanol solutions, complex (II) is similarly stabilized. In polar solvents, which are not capable of forming hydrogen bonds, the stability of the diastereoisomers is apparently invert-

TABLE II. Rate Constants and Activation Parameters for the Configurational Inversion Reaction at the Metal Centre of $\Lambda(-)_{589}\{\text{Cr}[(-)\text{bdtp}]_3\}$ in Chloroform Solution.^a

T °C	$C \times 10^3$ mol/dm ³	$-k$ s ⁻¹	k_1 s ⁻¹	k_2 s ⁻¹
5	2.47	$(7.6 \pm 0.2) \times 10^{-5}$	$(5.1 \pm 0.2) \times 10^{-5}$	$(2.53 \pm 0.08) \times 10^{-5}$
15	0.96	$(2.63 \pm 0.04) \times 10^{-4}$	$(1.72 \pm 0.06) \times 10^{-4}$	$(9.1 \pm 0.2) \times 10^{-5}$
25	1.98	$(1.609 \pm 0.004) \times 10^{-3}$	$(1.03 \pm 0.02) \times 10^{-3}$	$(5.820 \pm 0.006) \times 10^{-4}$
35	2.26	$(5.8 \pm 0.5) \times 10^{-3}$	$(3.6 \pm 1.0) \times 10^{-3}$	$(2.2 \pm 0.6) \times 10^{-3}$
E_a kJ mol ⁻¹			104 ± 12	109 ± 12
lnA			35 ± 6	36 ± 6
ΔH^\ddagger kJ mol ⁻¹			101 ± 12	106 ± 12
ΔG^\ddagger kJ mol ⁻¹			90.0 ± 0.2	91.4 ± 0.1
ΔS^\ddagger J mol ⁻¹ K ⁻¹			38 ± 42	49 ± 44

^aAll errors are estimated at the 95% confidence level.

ed [1]. Apolar solvents such as petroleum ether, n-pentane and ethyl ether, in diluting the solutions, could cause the solute-solvent interactions to be eliminated and favour the crystal packing of the more stable Λ -(R,R) complex form in those conditions.

Kinetic study of the $\Lambda(-)_{589}\{\text{Cr}[(-)\text{bdtp}]_3\} \rightleftharpoons \Delta(+)_589\{\text{Cr}[(-)\text{bdtp}]_3\}$ inversion process might contribute to the understanding of the mechanism and of the role of the solvent also in the activation path.

Table II reports the kinetic data and the thermodynamic activation parameters obtained from CD data for the inversion reaction in chloroform solution. The linear correlations between $\ln(\Delta\text{OD}_t - \Delta\text{OD}_e)$ vs t , $r = 0.99$, indicate a first-order intramolecular inversion process with a change of absolute configuration of the dissymmetric chromium centre (eqn. 1 and 10 and Fig. 4). The k_1 and k_2 values were obtained from eqns. 12 and 13 using the values of the equilibrium constant K given in Table I. The high values of the kinetic constants obtained (Table II) indicate the optical lability of the diastereomers (I) and (II). The half-life times of the two diastereoisomers at 25 °C prove to be 11.2 and 19.8 min respectively. The slower inversion reaction of the Δ -(RR) form could be the result of the relatively strong interaction of $\Delta(+)_589\{\text{Cr}[(-)\text{bdtp}]_3\}$ and CHCl_3 molecules. This should hinder one-ended dissociation of a dithiophosphate ligand (or force this to return to its original position), or prohibit a twisting motion through a stiffening of the Δ -(RR) form, these being some of the possible mechanisms of the inversion process.

The half-life time of racemisation of tris(oxalato)-chromium(III) ion, $[\text{Cr}(\text{ox})_3]^{3-}$ is reported to be 18.4 min in aqueous solution at 25 °C, and this complex ion proved particularly suitable for the study of the enantiomeric discrimination by a chiral

solvent [5, 12]. In this case the racemisation is thought to occur by interaction with the solvent. The effect of high pressure on the rates of acid-catalyzed racemisation of $[\text{Cr}(\text{ox})_3]^{3-}$ confirms a one-ended dissociative mechanism where the negative activation entropy values could indicate a solvent-water interaction in the transition state [14].

To date no data are reported for the inversion of a CrS_6 chromophoric group. The tris(diethyldithiocarbamate)chromium(III) complex, $\text{Cr}(\text{Et}_2\text{dtc})_3$ is optically stable up to +84 °C in chloroform in a NMR time scale [8]. Solvent effects on the racemisation of optically active tris(N-substituted carbamodithioato)cobalt(III) complexes, $\text{Co}(\text{RRcd})_3$, have been studied [10]. A uniform reaction mechanism is likely to operate with solvent-solute interactions in the transition state but it is not possible to identify the mechanism leading to inversion as either bond rupture or twisting, because of the high variation of activation parameters ΔH^\ddagger and ΔS^\ddagger in the different solvents used. However, the inversion reactions involving a breaking mechanism in tris(benzylacetate)cobalt(III), $\text{Co}(\text{bzac})_3$ and tris(5-methylhexane-2,4-dionato)cobalt(III), $\text{Co}(\text{mhd})_3$ are expected to have high positive entropies of activation and simultaneously high Arrhenius frequency factors [15, 16]. If a trigonal twist mechanism is postulated, the entropy variation should be close to zero or negative with low values of the frequency factor [7].

The high positive values of ΔH^\ddagger and ΔS^\ddagger for both k_1 and k_2 in the inversion processes of Λ and Δ , $\text{Cr}[(-)\text{bdtp}]_3$ complexes (see Table II) should be indicative of the absence of strong interactions with chloroform during the rate-determining step. The high values of the frequency factors exclude a twist mechanism, and a one-ended dissociative mechanism involving extension of a partially charged bdtp^-

arm into the solvent in the transition state could be envisaged.

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