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Stereoselective Synthesis and Characterization of the Optically Labile Chiral Cr(III) Complex Δ-(+)$_{589}${Cr[(–)bdtp]$_3$}

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Abstract

The diastereoisomeric complex Δ-(+)-tris(cyclic *O,O′*,1(*R*),2(*R*)(–)dimethylethylene dithiophosphato)chromium(III), was synthesized stereoselectively in tetrahydrofuran (THF) solution. The complex proves optically labile, $[\alpha]_D = +106$, in $CHCl_3$, changing quickly to $[\alpha]_D = +211$. The CD spectra in THF enable us to characterize the complex and show a configuration inversion which gives the diastereoisomeric equilibrium $\Lambda \rightleftharpoons \Delta$ with an excess of the Λ-(*R,R*)(*R,R*)(*R,R*) diastereoisomeric form. The equilibrium constant $K = 0.86$ at 25 °C is indicative of a different thermodynamic stability between the two diastereoisomers in THF solution, Λ-(*R,R*) > Δ-(*R,R*), $\delta\Delta H° = 1.5$ kJ mol^{-1}, $\delta\Delta G° = 0.3$ kJ mol^{-1}, $\delta\Delta S° = 4$ J mol^{-1} K^{-1}. The kinetic diastereoisomer Δ-(*R,R*)(*R,R*)(*R,R*) is stabilized in $CHCl_3$, CH_2Cl_2, EtOH solvents where it is highly soluble and optically stable with a maximum negative chirality factor, $g = -5 \times 10^{-3}$, in $CHCl_3$.

Introduction

Λ-(–)$_{589}$Cr[(–)bdtp]$_3$ (I) was obtained through a kinetically controlled synthesis in ethanol as solvent [1]. The thermodynamic stability of the diastereoisomer, Λ-(*R,R*) (I), changes with the solvent in the order THF > CH_3CN > $(CH_3)_2CO$ > C_6H_6 > EtOH > CH_2Cl_2 > $CHCl_3$. The Λ-(*R,R*) form seems strongly preferred in the solid and THF, CH_3CN, $(CH_3)_2CO$ solution states, but the Δ-(*R,R*) diastereoisomer, Δ-(+)$_{589}$Cr[(–)bdtp]$_3$ (II), seems favoured in a solution of polar hydrogen bonding solvents such as $CHCl_3$, CH_2Cl_2 and EtOH. In the latter cases a molecule–solvent interaction, fitting the solvent into the blades of this complex, favours the stabilization of the Δ-(*R,R*) diastereoisomer. The thermodynamic stability together with the kinetic study of the inversion reaction Λ-(*R,R*) ⇌ Δ-(*R,R*) in $CHCl_3$, led us to assume some contribution by the solvent to stabilizing Δ-(*R,R*) with respect to Λ-(*R,R*) [2].

Interest has been shown in the synthesis, resolution and energy discriminations between the enantiomers of tris(chelate)metal(III) complexes, ML_3, as well as in the dynamic stereochemistry of this type of transition metal complex [3, 4].

Chiral energy discrimination between Λ and Δ-tris(chelate)metal(III) complexes has been the subject of CD studies [5].

Theoretical calculations and experimental measurements of chiral discrimination energies of corresponding diastereoisomers could clarify the interactions between chiral molecules [3, 6].

The chiral butandithiophosphate ligand, (*R*)(*R*)-(–)bdtp$^-$ [7], is expected to yield a single diastereoisomer stereoselectively forming the corresponding tris-chelate complex, Cr[(–)bdtp]$_3$, while the Λ or Δ configuration on the metal could depend on the solvent used.

Λ-(*R,R*)(*R,R*)(*R,R*) (I) seems thermodynamically more favoured in THF than the Δ-(*R,R*) diastereoisomer (II). It could be interesting to discover if a preferential formation reaction also follows and what reasons there may be for any stereoselective synthesis. The aim of this work is to test this hypothesis by trying to synthesize the chiral Λ- or Δ-Cr[(–)-bdtp]$_3$ in tetrahydrofuran.

Experimental

Spectroscopic Measurements

Infrared (IR) spectra were obtained on a Perkin-Elmer spectrometer in CsI pellets between 4000 and 200 cm^{-1}.

Visible and ultraviolet (UV–Vis) spectra were measured with a Jasco UVIDEC 650 spectrophotometer in various solvents, between 750 and 200 nm.

Circular dichorism (CD) spectra were obtained in freshly prepared solutions, in nujol mull or in the filtered reaction solutions, between 750 and 200 nm on a Jasco J-500 A spectrophotometer.

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Preparation of the Compounds

The ligand (–)bdtpK was prepared as previously reported [7].

Tris(–)(cyclic O,O′-1(R)2(R)dimethylethylene dithiophosphate)chromium(III), Δ-(+)$_{589}${Cr[(–)-bdtp]$_3$} (II)

The reaction was achieved as described [1] by dissolving 0.53 g (2 mmol) of chromium trichloride hexahydrate in 150 cm^3 of anhydrous THF, adding a suspension of 1.35 g (6 mmol) of (–)bdtpK and stirring for 20 h at room temperature. The solution turned from gray–green to mauve and separated white solid potassium chloride.

(The CD spectrum of the reaction solution shows at the same time a growing negative Cotton effect at 660 nm indicating a formation of the Δ-(*R*,*R*) diastereoisomer in excess of Λ-(*R*,*R*).)

The reaction solution was filtered and the solvent evaporated under vacuum at a low temperature. The violet product separated as a residual, 0.4 g, melting point >340 °C, violet, $[\alpha]_D = +106$ ($c = 0.5$ in $CHCl_3$). This changed quickly to $[\alpha]_D = +211$.

The CD spectrum in nujol mull shows a negative Cotton effect below 650 nm. In $CHCl_3$ and CH_3Cl_2 the CD spectra show a negative Cotton effect at 665 nm, $g = -1.5 \times 10^{-3}$, which grows with time to higher negative values. In CH_3CN and THF the CD spectra are similar but the negative Cotton effect at 665 nm inverts to positive values in the course of time.

The product of the reaction is a mixture of the two diastereoisomers which is richer in the compound Δ-(+)-Cr[(–)bdtp]$_3$ (**II**). The fractionated crystallization of the mixture by chloroform and petroleum ether 60–80, first gives a small fraction that is richer in Λ-(–)-Cr[(–)bdtp]$_3$ (**I**) and thereafter various fractions, 0.37 g in all of the complex **II**: CD in $CHCl_3$, 665 nm, $g_{665} = -2.3 \times 10^{-3}$. *Anal.* Found: C, 24.0; H, 4.35. Calc. for $C_{12}H_{24}O_6P_3S_6Cr$: C, 23.95; H, 4.0%.

The IR spectrum (CsI pellets) shows strong bands at 1040 (P–O$_{asym}$), 935 (P–O$_{sym}$), 867, 814, 664, 635 (P–S$_{asym}$), 565 (P–S$_{sym}$), 410, 370, 326, 316 (Cr–S) cm^{-1}.

Measurement of Inversion Process and Thermodynamic Equilibrium Constant

Kinetic measurements of the inversion process were obtained by CD measurements at a fixed wavelength (665 nm) of solutions with concentrations of approximately 2×10^{-3} mol/dm^3 in spectroscopic degree solvents, and were recorded in a time scale [2].

Equilibrium constants were measured at various temperatures as described [2].

The solutions were placed in a thermostated cell, $l = 1$ cm, connected 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 up to a state of equilibrium and checked after completion (24–48 h). Starting time was considered to be the half volume addition point of solvent.

The following reaction scheme

$$\Lambda\text{-}(R,R) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \Delta\text{-}(R,R)$$

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

The linear relationship

$$\ln(\Delta OD_t - \Delta OD_e) = -(k_1 + k_2)t + \ln(\Delta OD_o - \Delta OD_e)$$

verified the first-order nature of the inversion process [2].

The results were analysed by least-squares regression to determine the rate constants, $k = -(k_1 + k_2)$.

The equilibrium constant $K = k_1/k_2 = C_\Delta/C_\Lambda$ can be determined independently as

$$K = (C + C_{d.e})/(C - C_{d.e})$$

where C is the total concentration and $C_{d.e}$ is the diastereoisomeric excess concentration.

If Λ-(*R*,*R*) proves to be the predominant form at equilibrium

$$K = (C - C_{d.e})/(C + C_{d.e})$$

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

$$\delta\Delta G^\circ = -RT \ln K$$

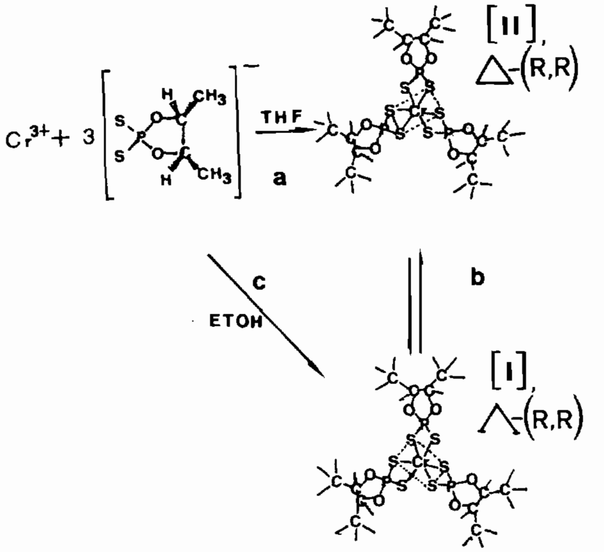
is obtained.

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

$$\delta\Delta S^\circ = (\delta\Delta H^\circ - \delta\Delta G^\circ)/T.$$

Results and Discussion

The chiral ion (–)bdtp$^-$ reacts in THF solution with $CrCl_3 \cdot 6H_3O$ at room temperature to give predominantly the complex (+)$_{689}$Cr[(–)bdtp]$_3$ (**II**) in the Δ-(*R*,*R*) configuration (see Scheme 1). The complex formed is highly soluble in the solvent used and can be characterized by CD spectroscopy. The circular dichroism spectra of the reaction in THF solution at room temperature show the formation of the Δ-(*R*,*R*) diastereoisomer during the period immediately after the start, reaching a maximum concentration of this by 20 h (Fig. 1a). Simultaneously a Δ → Λ inversion reaction takes place



Scheme 1. Formation reaction in THF (a) and in ethanol (c); inversion reaction in THF (b).

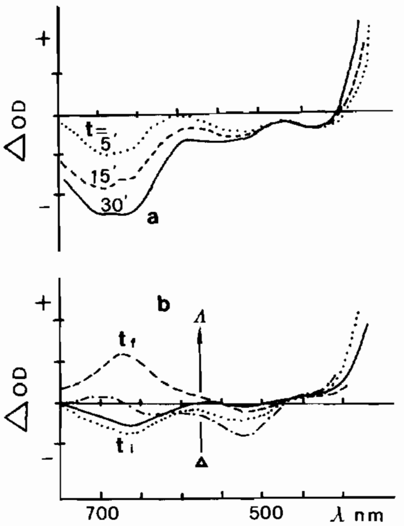


Fig. 1. Formation of the Δ-(*R*,*R*) diastereoisomer (a) and inversion reaction Δ-(*R*,*R*) → Λ-(*R*,*R*) (b) (t_i, initial time; t_f, final time) followed by CD spectroscopy in the cold tetrahydrofuran reaction solution.

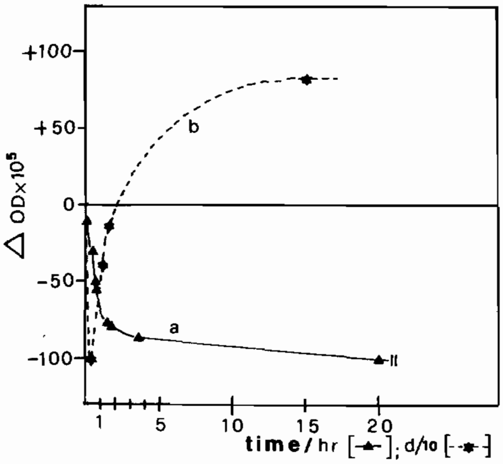


Fig. 2. Variation of the differential optical density ΔOD of the formed complex at 665 nm during the formation reaction of Cr[(–)bdtp]$_3$ in the THF solution in 0–20 h (a) and 3–150 days (b).

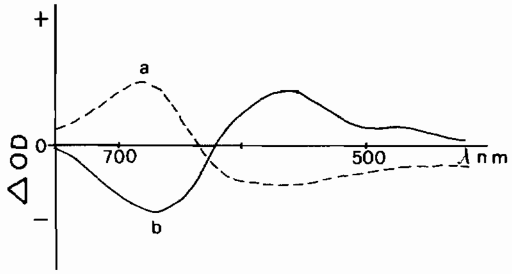


Fig. 3. CD spectra registered in nujol mulls immediately after the synthesis of the solid samples: (a) Λ-(–)$_{589}$Cr[(–)-bdtp]$_3$ (I), (- - - -); (b) Δ-(+)$_{589}$Cr[(–)bdtp]$_3$ (II), (——).

(Scheme 1b) and after 70–80 h an equilibrium state is reached with an excess of the Λ-(*R*,*R*) form. After 20 h the optical yield lowers, as is shown by the CD Cotton effect at 665 nm which progressively lowers its intensity and inverts the sign from negative to positive (Fig. 1b). The variation of the differential optical density and in the chirality factor g shows the optical purity change of the complex formed over the course of time (Fig. 2). The stoichiometric yield grows meanwhile as is shown by the absorbance growth and reaches the maximum after 20 h. The addition of an apolar solvent such as petroleum ether precipitates the product stopping the inversion process and the formation reaction each time. Thus the optical purity of the isolated compound depends on the time of reaction and the solvent used.

The Δ-(*R*,*R*) diastereoisomer is optically labile even in the solid state and after a long time inverts to the Λ-(*R*,*R*) form, (Fig. 3). The complex isolated shows a strong negative CD signal at 665 nm in nujol mull, characterizing the Δ-(*R*,*R*) form (**II**) (Fig. 3a). After a long time the same complex shows a positive Cotton effect at 685 nm, typical of Λ-(+)$_{589}$Cr[(–)-bdtp]$_3$ (**I**), (Fig. 3b).

Fractionated crystallization by CHCl$_3$ and petroleum ether separates the two, Λ-(*R*,*R*) (**I**), $g = +1.5 \times 10^{-2}$ in nujol, which in chloroform inverts to $g = -5 \times 10^{-3}$, and Δ-(*R*,*R*) (**II**), $g = -1.7 \times 10^{-2}$ in nujol, which in chloroform decreases to $g = -5 \times 10^{-3}$.

The formation reaction of the Cr[(–)bdtp]$_3$ complex in THF can be considered as happening in three steps

$$(1)\ [\mathrm{Cr(THF)_6}]^{3+} + (-)\mathrm{bdtp}^- \longrightarrow \{\mathrm{Cr}[(-)\mathrm{bdtp}]\cdot 4\mathrm{THF}\}^{2+} + 2\mathrm{THF}$$

$$(2)\ \{\mathrm{Cr}[(-)\mathrm{bdtp}]\cdot 4\mathrm{THF}\}^{2+} + (-)\mathrm{bdtp}^- \longrightarrow \{\mathrm{Cr}[(-)\mathrm{bdtp}]_2\cdot 2\mathrm{THF}\}^{+} + 2\mathrm{THF}$$

$$(3)\ \{\mathrm{Cr}[(-)\mathrm{bdtp}]_2\cdot 2\mathrm{THF}\}^{+} + (-)\mathrm{bdtp}^- \longrightarrow \{\mathrm{Cr}[(-)\mathrm{bdtp}]_3\} + 2\mathrm{THF}$$

In a six-coordinated complex one pair of chelate rings forms a segment of a left-handed (Λ) or a right-handed (Δ) helix, if the two rings do not share an octahedral vertex, nor possess a common mean plane. Moreover three chelate rings form a left- or a right-handed helix. Statistically Λ and Δ configurations on the metal atom should be formed in equal amounts in the second and third step of the formation process. The last formation step, giving the prevailing formation of the Δ-(*R*,*R*)(*R*,*R*)(*R*,*R*) diastereoisomer (**II**) evidently depends on the third ligand hindrance or the different intramolecular electrostatic repulsions between the alkyl chains of the ligands in the two forms or even on molecule–solvent interaction. We exclude the last hypothesis because in THF the molecule–solvent interactions are greatly reduced as was shown recently [1, 2].

The kinetic formation of the Δ-(*R*,*R*)(*R*,*R*)(*R*,*R*) diastereoisomer ought to be sterically favoured, because the ligands are differently oriented in the two pro-chiral forms obtained after the second formation step.

The formation of this diastereoisomer is favoured in THF on account of the lower hindrance and interactions between the alkyl groups of the three ligands coordinating on the metal. The chiral ligand (*R*,*R*)-(–)butandithiophosphato, (–)bdtp$^-$, can interact with the metal ion building better a right- than a left-handed propeller. In the Δ propeller evidently the three chelating blades are coordinated so as to minimize the interligand steric hindrances of the alkylic tails.

The crystal structures of the two diastereoisomers are not known but the models of the two diastereoisomers show different dispositions of the alkyl groups in respect to the plane of the Cr..P..P..P atoms. Equatorial and axial CH_3 are observable in the Λ-(*R*,*R*) and Δ-(*R*,*R*) forms respectively. The latter form shows longer distances between the alkyl groups of different ligands and consequently weaker interligand interactions and higher packing difficulties can be foreseen [2].

In ethanol the selective formation and precipitation of the Λ-(*R*,*R*)(*R*,*R*)(*R*,*R*) diastereoisomer (**I**) has been realized [1]. Evidently the packing energy contributes definitely to promote the stereoselective synthesis of this form (Λ) over the other (Δ): packing prevails over the steric factors and alky group interactions or on molecule–solvent interactions.

The obtained kinetic Δ-(*R*,*R*)(*R*,*R*)(*R*,*R*) diastereoisomer (**II**) is not produced in pure optical form using THF as solvent, because, subsequent to its formation, it inverts to the thermodynamically more stable Λ-(*R*,*R*)(*R*,*R*)(*R*,*R*) complex (**I**).

Electronic Absorbance and CD Spectra

The solubilization process of the isolated diastereoisomer **II** was monitored accurately by CD and Vis absorption spectroscopy. This complex is highly soluble in THF and in other solvents such as acetone, acetonitrile, benzene, ethanol, methylene chloride and chloroform where it shows, in the first instance, a negative Cotton effect in the range 660–675 nm. The intensity and frequency of this band change with time, reaching a steady state about 24 h later. Figure 4 shows the UV–Vis and CD spectra of the $\mathbf{I} \rightleftharpoons \mathbf{II}$ equilibrium in THF solution in the d–d (750–400 nm), charge transfer and intraligand band (400–200 nm) regions, immediately after solubilization.

In the d–d band region (750–400 nm) the Vis–absorption spectrum is similar to that of complex **I** showing in all solvents a stable band at 685 nm, $\epsilon = 329$, and an unresolved doublet at 535 nm, $\epsilon = 223$, and 518 nm, $\epsilon = 231$, which are assigned on the basis of an octahedral symmetry O_h in the complex Δ-(*R*,*R*)(*R*,*R*)(*R*,*R*) (**II**), to the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$, ${}^4A_{2g} \rightarrow {}^2T_{2g}$ transitions respectively [1, 8–11].

The CD spectrum in THF solution (Fig. 4) shows a negative Cotton effect at 665 nm, $\Delta\epsilon = -0.9$, $g = -3 \times 10^{-3}$ which could be assigned to the magnetic dipole allowed doubly-degenerate ${}^4A_2 \rightarrow {}^4E_a$ component. Owing to the splitting of the excited state for the lowering of the symmetry to D_3 by the influence of the ligand field in the tris-chelate complex, the ${}^4A_2 \rightarrow {}^4A_1$ component is completely over-

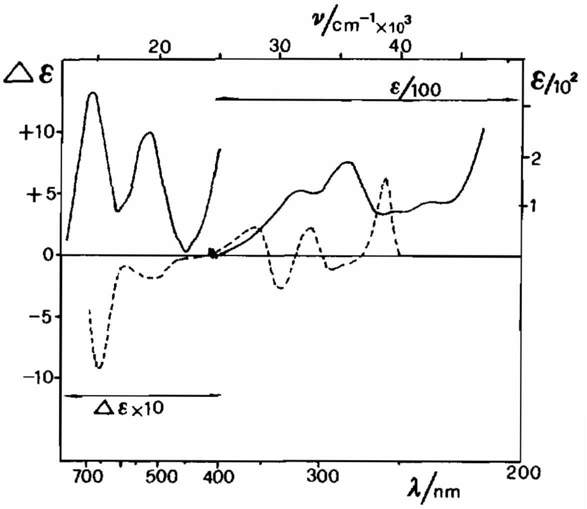


Fig. 4. UV and CD spectra of Δ-(+)$_{589}$Cr[(–)bdtp]$_3$ immediately after solubilization in THF.

lapped and cancelled by the dominant ^4E_a. The magnitude of this CD band suggests that a lower degree of optical purity has been reached in THF than in $CHCl_3$, where this complex shows at 665 nm a higher negative Cotton effect, $\Delta\epsilon = -1.6$, $g = -5 \times 10^{-3}$ [2].

In the spectral range 400–200 nm the absorption and CD spectra show the presence of many charge transfer and intraligand bands. The first of these at the lowest frequencies was evidenced clearly in CD spectra at 360 nm, even if the corresponding absorbance·band is unresolved under the continuous increasing absorbance line.

Absolute Configuration

The Δ-$(R,R)(R,R)(R,R)$ configuration was assigned on the basis of the negative CD component centred at 660–675 in the region of the allowed magnetic dipole $^4A_{2g} \rightarrow {^4T_{2g}}$ transitions [12]. The Λ-$(R,R)(R,R)(R,R)$ configuration has been tentatively assigned to $(-)_{589}$\{Cr[(–)bdtp]$_3$\} (**I**) on the basis of a positive CD Cotton effect at 675 nm [1].

It is interesting to note that the Δ-(+)Cr[(–)-bdtp]$_3$ complex (**II**) is optically labile in the solid state, and even in tetrahydrofuran, acetone and acetonitrile solutions it inverts though not completely to the diastereoisomer Λ-$(-)_{589}$Cr[(–)bdtp]$_3$ (**I**). The spectra show a diminishing of the 660 nm negative band and the progressive growth of a positive Cotton effect at 675–690 nm, $g = +1.4 \times 10^{-3}$, indicating the establishment of an equilibrium with the Λ-(R,R) form as the excess diastereoisomer.

In chloroform, dichloromethane and ethanol solution the Δ-(R,R) and Λ-(R,R) complex mixture changes slightly. In these solvents the spectra maintain a negative Cotton effect at 665 nm, and this is indicative of an excess at equilibrium of the Δ-(R,R) over the Λ-(R,R) form. The optical purity proves higher in chloroform ($g = -5 \times 10^{-3}$) than in the other solvents when the final steady state is reached.

These inversion processes demonstrate the higher thermodynamic stability of the Λ-(R,R) form in tetrahydrofuran, acetonitrile and acetone and of the Δ-(R,R) in chloroform, dichloromethane and ethanol.

The THF solvent does not contribute to stabilizing Δ-(R,R) in the same way as $CHCl_3$ does [2].

Steric factors can be envisaged as the driving force for the stereoselective synthesis of the Δ-$(R,R)(R,R)$-(R,R) diastereoisomer in THF solution.

Inversion of Configuration

The inversion processes in THF starting from the Δ-$(+)_{589}$\{Cr[(–)bdtp]$_3$\} or the Λ-$(-)_{589}$\{Cr[(–)-bdtp]$_3$\} diastereoisomer reach the same equilibrium state at similar rates, although it is richer in Λ- than in the Δ-$(R,R)(R,R)(R,R)$ form (Fig. 5).

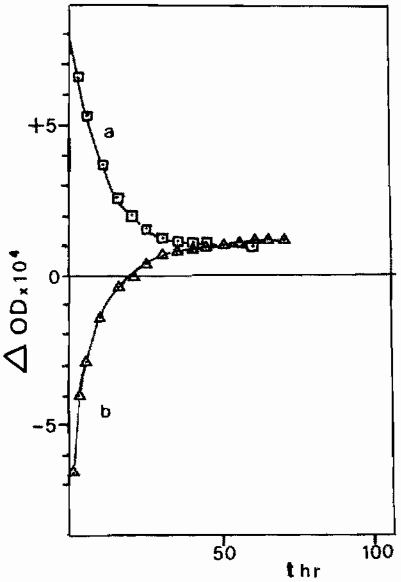


Fig. 5. Inversion reaction $\Lambda \rightleftharpoons \Delta$ in THF starting from: (a) Λ-$(-)_{589}$Cr[(–)bdtp]$_3$; (b) Δ-$(+)_{589}$Cr[(–)bdtp]$_3$.

The two inversion processes were studied kinetically at 25 °C following the CD variation of the $^4A_{2g} \rightarrow {^4T_{2g}}$ transition [2]. The rate constants prove identical $k_{\Delta \rightleftharpoons \Lambda}$ $(14.0 \pm 0.8) \times 10^{-4}$ s^{-1} and $k_{\Lambda \rightleftharpoons \Delta}$ $(13.0 \pm 0.9) \times 10^{-4}$ s^{-1}.

The values are similar to those obtained in $CHCl_3$, ($k_{\Lambda \rightleftharpoons \Delta}$ 16.1×10^{-4} s^{-1}) [2], and confirm the absence of strong interactions with the solvent during the rate determining step.

Thermodynamic Stability

The intensity of the Cotton effect, at 685 nm, at an equilibrium state, varies with temperature, indicating a change in the equilibrium constant. The measurements of ΔOD_e of the equilibrium solutions between 15 and 35 °C were used to determine the concentrations of the two diastereoisomers and the equilibrium constant K. $\Delta\epsilon = +6.7$ in the positive band at 675 nm of the pure diastereoisomer (**I**) was directly measured [2].

The K values at different temperatures and the thermodynamic parameters of equilibrium (1) in tetrahydrofuran are reported in Table I.

$$\Lambda\text{-}(R,R) \rightleftharpoons \Delta\text{-}(R,R) \qquad (1)$$

Heats of inversion were obtained from ln K *versus* $1/T$ 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 K results (0.8–0.95) are lower than those obtained in $CHCl_3$ equilibria (1.6–2.0) [2]. The thermodynamic stability of the two diastereoisomeric complexes changes significantly with the solvent.

TABLE I. Constants and Thermodynamic Parameters of the Equilibrium Λ-Cr[(−)bdtp]$_3 \rightleftharpoons \Delta$-Cr[(−)bdtp]$_3$ in THF Solution[a]

T (°C)	15	25	35
$K \pm 0.03$	0.85	0.88	0.91
$\delta \Delta H^\circ$ kJ mol^{-1}		1.5 ± 0.3	
$\delta \Delta G^\circ$ kJ mol^{-1}		0.30 ± 0.04	
$\delta \Delta S^\circ$ J mol^{-1} K^{-1}		4.0 ± 1.0	

[a] All errors are estimated at the 95% confidence level.

The Λ-(R,R) diastereoisomer has higher stability in THF, while Δ-(R,R) is strongly stabilized in $CHCl_3$. The positive differential energy values, $\delta\Delta G^\circ = +0.3$ k J mol^{-1}, between the two Λ-(R,R) and Δ-(R,R) diastereoisomers indicates that the prevalence of the Δ-$(+)_{589}$Cr[(−)bdtp]$_3$ is not obtainable in THF solution. Λ-(+)Cr[(−)bdtp]$_3$ is thermodynamically favoured in THF solution, compared with $\Delta(+)_{589}$Cr-[(−)bdtp]$_3$.

The stability constants grow with the temperature and it is calculable that K will be unity, with $\Delta G^\circ = 0$, at 102 °C. The positive but near to zero value of the standard entropy change ($\delta\Delta S^\circ = 4.0 \pm 0.1$ J mol^{-1} K^{-1}) indicates a small disorder production when the Λ-(R,R) form predominates over the Δ-(R,R) diastereoisomer. The slight ordered structure of the solvent due to the small interaction with the Δ propeller should be disturbed by the inversion of this diastereoisomer in the Λ-(R,R) form because the THF molecules are not able to order themselves over the Λ propeller and the solvent remains completely disordered. In this way a less favourable enthalpy change, due to the breaking of labile Δ-molecule–solvent contacts, could accompany higher solvent disorder.

Intramolecular interactions and/or packing energies are responsible for the stabilization of the Λ-$(R,R)(R,R)(R,R)$ form.

Molecule–solvent interactions stabilize the Δ-(R,R) diastereoisomer in chloroform or similar solvents. This type of interaction is lower in THF solution where the Λ-(R,R) diastereoisomer is stabilized by the interligand interactions.

The differential energy between the two forms may be due to dispersion interactions or intramolecular electrostatic repulsions between the ligands or molecule–solvent interactions, or to better crystal packing in one of the two diastereoisomers, as forecast and calculated by Craig [6] and Mason *et al.* [5]. This last factor prevails over the rest in the solid state and favours isolation by precipitation of the Λ-$(R,R)(R,R)(R,R)$ form in ethanol. In ethanol solution the molecule–solvent interaction seems however so high as to stabilize the Δ-(R,R) form.

Conclusions

The synthesis of the Δ-(R,R) diastereoisomer is favoured in THF, because the crystal packing energy, the dispersion forces and intramolecular electrostatic interactions give a lower contribution than the steric driving force. Unlike what occurs in ethanol where the Λ-(R,R) form is obtained by precipitation, in THF the two forms are equally soluble. The Δ-(R,R) diastereoisomer is kinetically synthesized since steric reasons favour the bonding of the three ligands to the metal ion in this form.

A stepwise formation reaction can be envisaged and the rate determining step is the bonding formation of the third ligand to the metal ion.

The preferential formation of the Δ-$(R,R)(R,R)(R,R)$ diastereoisomer could be due to the easier bonding insertion of the three ligands to form this configuration.

However the kinetic diastereoisomer inverts to the thermodynamically more stable complex Λ-(R,R).

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