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Chiral Discrimination of Complexes with D_3 Symmetry. Synthesis and Characterization of Tris{*O,O′*-bis[(+)(*S*)-2-methylbutyl] dithiophosphato}chromium(III) Complexes (ΛΔ){Cr[(+)(*S*)(*S*)Mebdtp]$_3$} and Λ-(−)$_{589}$- and Δ-(+)$_{589}${Cr[(+)(*S*)(*S*)Mebdtp]$_3$} and Crystal Packing of Racemic Tris{*O,O′*-diethyl dithiophosphato}chromium(III), Cr[ddtp]$_3$

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Synthesis of the title chiral complex (ΛΔ){Cr[(+)(*S*)(*S*)Mebdtp]$_3$}, with (+)(*S*)(*S*)Mebdtp$^-$ = (+)[(*S*)-(CH_3CH_2-$CHCH_3CH_2O$)$_2PS_2$]$^-$, *O,O′*-bis[(+)(*S*)-2-methylbutyl] dithiophosphate ion, as the ligand, was accomplished in solution with various solvents giving rise in all cases to a higher production of Λ-(−)$_{589}$ {Cr[(+)(*S*)(*S*)Mebdtp]$_3$} diastereoisomer than Δ-(+)$_{589}${Cr[(+)(*S*)(*S*)Mebdtp]$_3$}. The formation reaction was followed by absorption and CD spectroscopy. The Λ-(*S,S*)(*S,S*)(*S,S*) diastereoisomer proved to have higher stability in all the solvents employed (ethanol, acetone, acetonitrile, benzene, dichloromethane, chloroform, and water). Crystal packing forces seem to favor an equal mixture assembly of Λ- and Δ-{Cr[(+)(*S*)(*S*)Mebdtp]$_3$}, as is evident from CD characterization of the solid precipitated from solutions with a slight excess of the Λ(−)-isomer. Configurational inversion was observed in solution and even in the solid state after a long time if the solid was kept at higher temperature and under vacuum, although the chirality favored was different in the two phases. The molecular structure and crystal-packing mode of the related title complex {Cr[ddtp]$_3$}, ddtp$^-$ = (C_2H_5O)$_2PS_2^-$, ($C_{12}H_{30}CrO_6P_3S_6$, formula weight 607.64) were determined from single-crystal X-ray diffraction data and refined by full-matrix least squares methods to $R = 0.065$. Crystals are monoclinic, with $a = 14.512(8)$ Å, $b = 13.657(3)$ Å, $c = 14.350(2)$ Å, $\beta = 90.42(3)°$, $V = 2844(2)$ Å^3, $Z = 4$, and space group *C2/c* (No. 15). The crystals contained a racemic mixture of Λ- and Δ-Cr[ddtp]$_3$ enantiomers. The discussion based on the structural information of this compound extends to chiral discrimination in the formation reaction, configurational inversion reaction, molecular structure, and crystal packing of (ΛΔ){Cr[(+)-(*S*)(*S*)Mebdtp]$_3$}.

Chiral discrimination in the formation of diastereoisomeric octahedral tris-chelate complexes can be considered as the difference in the interaction of the chiral ligand molecules with the two prochiral forms or chiral intermediate complexes. The stereochemical features of the ligand molecules lead to diastereoselectivity in the formation reaction of the metal complexes. The structure of the resulting complexes as a whole determines thermodynamic stability of the diastereoisomers as well as chiral discriminations/recognitions between the molecules and hence the mode of crystal packing.[1−4]

Previously we have studied the diastereoselective synthesis of chiral octahedral metal complexes, tris[(−)cyclo-*O,O′*-(1(*R*)-2(*R*)dimethylethylene) dithiophosphato]chromium(III) complexes. Depending on the solvents, either Λ-(−)$_{589}$- or Δ-(+)$_{589}$-{Cr[(−)(*R*)(*R*) bdpt]$_3$} was preferentially synthesized.[5−8] We have determined the molecular structure and crystal-packing mode of Λ-(−)$_{589}${Cr[(−)(*R*)(*R*)bdtp]$_3$} and related the absolute configuration at the metal center to the positive Cotton effect assigned to the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition.[5,8]

Chiral discrimination occurs during the formation reaction and crystallization of the complexes. Our interest is to reveal the influence of the chiral ligand stereochemistry on the kinetics and thermodynamics of the formation reaction of the diastereoisomers as well as on the crystal-packing mode. In this paper, we report the synthesis and characterization of the title complexes and a preliminary kinetic study of their formation and configuration inversion reactions, as studied by CD spectroscopy. Effects of the ligand chirality and the absolute configuration at the metal center on the molecular structure are also discussed on the basis of the crystal structure of the analogous chromium complex, [Cr(ddtp)$_3$].

Experimental Section

Preparation of the Compounds. Hydrated chromium(III) chloride, 2-methyl-1-butanol, and phosphorus pentasulfide (C. Erba) were used without further purification. Solvents were purified by standard methods.

***O,O′*-Bis[(S)(+)-2-methylbutyl] Dithiophosphinic Acid, (+)(*S*)-(*S*)MebdtpH (I), and Potassium *O,O′*-Bis[(*S*)(+)-2-methylbutyl]**

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1995.

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Dithiophosphate, (+)(*S*)(*S*)MebdtpK (II) and MebdtpK (III). (+)-(*S*)-2-Methyl-1-butanol was obtained by repeated distillation of molasses from sugar refineries, using a 3 m distillation column filled with Raschig rings, until a maximum value of $[\alpha]_D$ was recorded: bp 129 °C; $[\alpha]_D = -5.74$ (neat, l = 0.1 dm).

Under a nitrogen atmosphere (+)(*S*)-2-methyl-1-butanol (8.18 g, 93 mmol) was added with magnetic stirring to 4.9 g (22 mmol) of phosphorus pentasulfide. The reaction was completed by heating the flask gently on a sand bath. When the phosphorus pentasulfide had dissolved completely (2–3 h), a clear oily solution was obtained.

One part of the oil was distilled and identified as (+)(*S*)(*S*)MebdtpH (I): bp (1 mmHg) = 85–106 °C; $[\alpha]_D = +5$ (C = 1.3 g/100 mL, ethanol); ^{1}H NMR in CCl_4 showed three multiplets and one singlet at 3.98 ppm (4H, m, $2CH_2O$), 3.02 ppm (1H, s, SH), 1.48 ppm (6H, m, $2CH_2CH$), 0.92 ppm (12H, m, $4CH_3$); infrared (IR) spectrum (in CsI pellets) showed bands at 2456 cm^{-1} (S–H), 994 (P–O asym), 874 (P–O sym), 671 (P–S asym), 530 (P–S sym) cm^{-1}.

To the remaining clear acidic oil an excess of anhydrous potassium carbonate was added. The stirring and heating were continued to the point of complete neutralization of the mixture, which was then extracted with acetone. The boiling acetone solution was filtered to separate the unreacted potassium carbonate. On cooling and slow evaporation of the solvent under vacuum a residual oil was obtained. This was washed with anhydrous petroleum ether until a white solid product was separated. The solid was filtered and maintained 2 h under vacuum at 50 °C and identified as the ligand (+)(*S*)(*S*)MebdtpK (II): 7.94 g (yield 58.5%); mp 165–67 °C; $[\alpha]_D = +14.5$ (C = 0.42 g/100 mL, $CHCl_3$). Anal. Found: C, 38.4; H, 8.5. Calcd for $C_{10}H_{22}O_2PS_2K$: C, 38.9; H, 7.2. The higher analytical results for H could be due to some solvent or water molecules included in the compound. The ^{1}H NMR spectrum in CCl_4 showed three multiplets at 3.8 ppm (4H, m, $2CH_2O$), 1.4 ppm (6H, m, $2CH_2CH$), and 1.0 ppm (12H, m, $4CH_3$). The IR spectrum (in CsI pellets) showed strong bands at 1000 (P–O asym), 834 (P–O sym), 686 (P–S asym), and 574 (P–S sym) cm^{-1}. The optically inactive compound, MebdtpK (III), was obtained by the same method apart from starting from racemic (*S*)- and (*R*)-2-methyl butanol: 6.44 g, yield 60%; mp 164–66 °C. The reaction yielded an optically inactive mixture of the racemic and meso compounds: (*S*)(*S*)MebdtpK/(*R*)(*R*)MebdtpK, 1:1, and (*S*)(*R*)MebdtpK.

Tris{*O,O'*-bis[(+)(*S*)-2-methylbutyl] dithiophosphato}chromium(III), (ΛΔ){Cr[(+)(*S*)(*S*)Mebdtp]$_3$} (IV), and Λ-(−)$_{589}${Cr[(+)(*S*)(*S*)Mebdtp]$_3$} (V) and Δ-(+)$_{589}${Cr[(+)(*S*)(*S*)Mebdtp]$_3$} (VI). A 0.97 g (3 mmol) amount of (+)(*S*)(*S*)MebdtpK was dissolved by gentle heating in 100 mL of absolute ethanol in a three-necked 250 mL flask fitted with a reflux condenser (with a calcium chloride guard tube), a dry nitrogen inlet tube, and a dropping funnel. When dissolution was completed, chromium trichloride hexahydrate (0.284 g, 1 mmol) in absolute ethanol was dropped in, while the solution was heated to gentle refluxing. After 3 h of stirring and heating, the violet hot solution was filtered from the solid potassium chloride. The solvent was evaporated in part, and the residual solution was cooled to −20 °C. The precipitated complex was separated by filtration: 0.63 g, mp 160–161 °C; yield 73%. The initial $[\alpha]_D = +30.7$ (c = 0.23 g/100 mL, $CHCl_3$) changed quickly to a final $[\alpha]_D = -138$. The complex was crystallized by dissolution in ethanol and slow evaporation of the solvent. The violet crystals were identified as (ΛΔ)-{Cr[(+)(*S*)(*S*)-Mebdtp]$_3$} (IV). Anal. Found: C, 41.0; H, 8.9; S, 21.7. Calcd for $C_{30}H_{66}O_6P_3S_6Cr$: C, 41.9; H, 7.7; S, 22.4. The higher analytical results for H could be due to some water molecules adsorbed. The IR spectrum in CsI pellets showed strong bands at 991 (P–O asym), 873 (P–O sym), 645 (P–S asym), 563 (P–S sym), and 319 (Cr–S) cm^{-1}. The CD spectrum of **IV** in a Nujol mull shows no appreciable Cotton effect between 750 and 350 nm.

An excess of the Λ-(−)$_{589}${Cr[(+)(*S*)(*S*)Mebdtp]$_3$} diastereoisomer (V) was formed in solution through a configurational inversion process on the coordinating metal ion. When the (ΛΔ) solid **IV** was dissolved, a new equilibrium between the Δ- and the Λ- isomers was established after 24 h with an excess of the Λ-form. The equilibrium was further shifted toward the Λ-(*S,S*) diastereoisomer (**V**), on lowering the temperature of the solution (from +20 to −80 °C). It is known that to establish the concentration of the diastereoisomeric excess, C_{de}, one needs to know the differential extinction coefficient, $\Delta\epsilon_\Lambda$, of the pure diastereoisomer **V**. Until now it has not been possible to isolate this pure diastereoisomer and measure its $\Delta\epsilon$, but in ethanol solution its concentration grows with the lowering of the temperature as shown by the monotonic growth of the proportional positive differential optical density, ΔOD. In the range of temperature explored there were no indications of any change in the gradient of the curve or of a stabilization of these values. So by utilization of the observed ΔOD values at various temperatures, a graphical extrapolation from −80 to −273 °C simulating a sigmoid curve was realized. A value of $\Delta\epsilon = +3.5$ and a chirality factor $g = +1 \times 10^{-2}$ were calculated for the maximum value of ΔOD obtained. Assuming that at the lowest temperature the equilibrium was shifted almost entirely toward the Λ-(*S,S*) form (**V**), the extrapolated value, so obtained, was taken as a first convenient approximation to be $\Delta\epsilon_\Lambda$ so as to calculate the concentration of the excess diastereoisomer, $C_{de} = \Delta OD/[\Delta\epsilon l]$, and the optical purity or diastereoisomeric excess, de%, as follows: de% = 2(dp%) − 100%; dp%(diastereoisomeric purity) = $(C_\Lambda/C_T)100$; $C_{de} = C_\Lambda - C_\Delta$. Here C_Λ and C_Δ are the concentrations of the Λ- and Δ-diastereoisomers, respectively, and C_T is the total concentration ($C_T = C_\Lambda + C_\Delta$).

On the other hand, Δ-(+)$_{589}${Cr[(+)(*S*)(*S*)Mebdtp]$_3$} (**VI**) was obtained, as an excess over the Λ-form (**V**), when the achiral solid complex **IV** was kept under vacuum at 100 °C for many hours (see Results and Discussion).

Tris{*O,O'*-bis[2-methylbutyl] dithiophosphato}chromium(III), Cr[Mebdtp]$_3$ (VII). Starting from MebdtpK (**III**), compound **VII** was obtained by a method similar to that for **IV** and identified by elemental analysis, IR, and visible–ultraviolet (UV–vis) spectra. The compound was optically inactive and proved to be a mixture of the racemic Λ- and Δ-(*S,S*)(*S,S*)(*S,S*) and Δ- and Λ-(*R,R*)(*R,R*)(*R,R*) diastereoisomers, as well as mixtures of all the possible complexes of chromium with the meso, (*R,S*)-, and/or racemic (*S,S*)- and (*R,R*)-Mebdtp$^-$ ligands present in the formation reaction mixture. In an approximately 1/1 ethanol/D(−)-diethyl tartrate solution the optically inactive complex **VII** inverted one of the two configurations at the metal center and after some hours showed a negative Cotton effect with $g = -0.2 \times 10^{-3}$, which characterizes an excess of the Δ-{Cr[Mebdtp]$_3$} diastereoisomers. The signal remained unaltered for a long time, though on addition of more chiral solvent some of complex **VII** was crystallized in achiral form and the negative Cotton effect of the solution increased to reach a chirality factor of $g = -0.3 \times 10^{-3}$, probably due to the stronger interactions of the D(−)-chiral solvent with the Δ-diastereoisomers.

In a 1/1 ethanol/L(+)-diethyl tartrate solution the same compound (**VII**) showed a positive Cotton effect with $g = +0.2 \times 10^{-3}$. When the chiral solvent was further added, the signal grew to $g = +0.3 \times 10^{-3}$ indicating the stabilization of the major diastereoisomer Λ-{Cr-[Mebdtp]$_3$} as a result of the interaction with the L(+) chiral solvent. When the ethanol was evaporated from the solutions, some of the complex crystallized in an inactive form, while in the solution remained a diastereoisomeric excess of the Λ-complex.

Tris{*O,O'*-diethyl dithiophosphato}chromium(III), Cr[ddtp]$_3$ (VIII). The compound was obtained as described,[9] as well as from a trans-esterification reaction of compound **IV**. The last reaction was achieved in a boiling ethanolic solution containing chromium ion and *O,O'*-bis[(*S*)(+)-2-methylbutyl] dithiophosphinic acid, (+)(*S*)(*S*)-MebdtpH (I), as ligand. Under high-temperature conditions, the acid-catalyzed trans-esterification of the chiral diastereoisomer, substituting the chiral (+)(*S*)-2-methylbutyl groups of the ligands in the complex with ethyl groups from ethanol, forms the racemic complex Cr[ddtp]$_3$: violet; mp 157 °C. The IR spectrum in CsI pellets showed strong bands at 969 (P–O$_{asym}$), 814 (P–O$_{sym}$), 660 (P–S$_{asym}$), 537 (P–S$_{sym}$), and 314 (Cr–S) cm^{-1}. Formation of this compound was confirmed by the X-ray structure determination.

Spectroscopic Measurements. IR spectra between 4000 and 200 cm^{-1} were obtained on a Perkin-Elmer 225 spectrophotometer using Nujol and hexachlorobutadiene mulls and CsI windows.

UV–vis spectra of solutions in various solvents were measured between 750 and 200 nm with a Jasco UVIDEC 650 spectrophotometer. Circular dichroism (cd) spectra of Nujol mulls and solutions were

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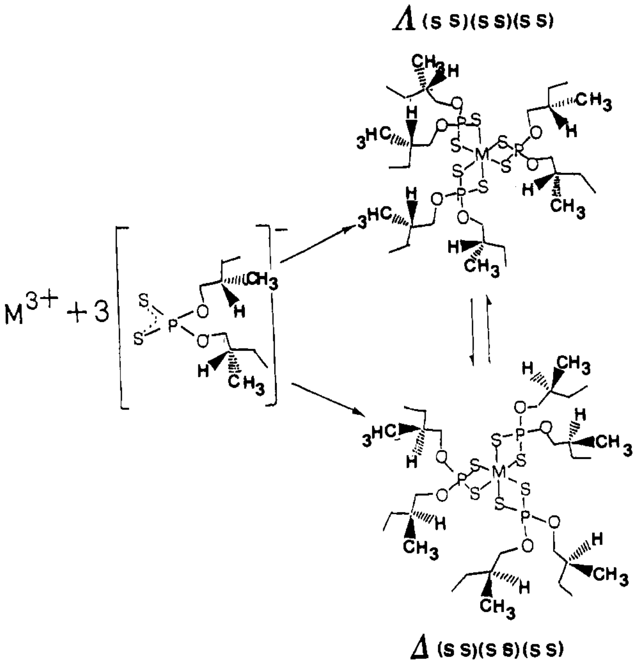
Table 1. Analytical Data for the Compounds

no.	compd	color	mp (°C)	$[\alpha]_D$ (*c*%, $CHCl_3$)	% exptl (% calcd) C	H	S
I	(+)(*S*)(*S*)MedtpH		85–106[d]	+5.0 (0.006)			
II	(+)(*S*)(*S*)MedtpK	white	165–67	+14.5 (0.42)	38.4 (38.9)	8.5 (7.2)	(20.8)
III	MedtpK	white	164–66				
IV	Cr[(+)(*S*)(*S*)Medtp]$_3$	violet	160–61	+30.7 (0.23) [a]	41.0 (41.9)	8.9 (7.7)	21.7 (22)
V	Λ-(−)$_{589}$Cr[(+)(*S*)(*S*)Medtp]$_3$	violet		*b*			
VI	Δ-(+)$_{589}$Cr[(+)(*S*)(*S*)Medtp]$_3$	violet		*c*			
VII	Cr[Medtp]$_3$	violet	158–60				
VIII	Cr[ddtp]$_3$	violet	157–58				

[a] Optical activity immediately after the dissolution of the sample. After a long time, at equilibrium state, $[\alpha]_D = -138.0$. [b] Compound **V** was not isolated as a solid sample, but it was identified in solution by CD: $\Delta\epsilon_{(675)} = +3.5$ (ethanol, extrapolated at 0 K)}. [c] A solid sample of **IV** shows, after heating at 100 °C under vacuum, a de = 4% of the diastereoisomer identified by CD: $\Delta\epsilon_{(675)}$ = negative (optically unstable in ethanol). [d] Bp, 1 mmHg, oil.

Scheme 1. Formation Reaction of Λ-(−)$_{589}$- and Δ-(+)$_{589}$Cr[(+)(*S*)(*S*)Mebdtp]$_3$ and Λ ⇌ Δ Configurational Inversion in Ethanol



obtained between 750 and 200 nm on a Jasco J-500 A spectropolarimeter. Magnetic circular dichroism (MCD) spectra of $CHCl_3$ solutions were obtained on a Jasco J-500 A spectropolarimeter equipped with an electromagnet working at 15 100 G. The calibration was obtained with a 1 M solution of $CoSO_4 \cdot 7H_2O$ using the data reported.[10]

Crystallographic Results. The crystal structure of Cr[(ddtp)$_3$] (**VIII**) was determined by single crystal X-ray diffractometry.

A purple crystal, 0.50 × 0.12 × 0.20 mm, monoclinic, was examined by Mo Kα radiation (λ = 0.710 69 Å) with a Rigaku four-circle AFC5S diffractometer. Of the 3477 reflections collected with $2\theta < 55°$, 3344 were unique (R_{int} = 0.035). The intensities of three representative reflections measured after every 150 reflections remained constant throughout the data collection indicating crystal and electronic stability.

Structure Determination. The structure was solved by direct methods[11] and refined with anisotropic temperature factors using the program system TEXSAN.[12] Out of 3344 unique reflections only 897 satisfied $I > 3\sigma(\mathbf{I})$, resulting in poor quality of the structure obtained. This may be related to the high flexibility of the terminal part of the ligand. An empirical absorption correction using the program DIFABS[13] was applied. Hydrogen atoms were generated at their ideal positions and kept fixed during the refinement. The final R and R_w factors were 0.065 and 0.072, respectively. $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)]^{1/2}$, where $w = 4F_o^2/\sigma^2(F_o^2)$. All computations were carried out on a VAX station 3200.

Results and Discussion

Formation Reaction. Table 1 reports analytical data, colors, and optical rotation data for the compounds **I-VIII.** Anisotropic thermal parameters and additional crystal data are available as supplementary material.

The chiral *O,O'*-bis[(+)(*S*)-2-methylbutyl] dithiophosphate ion, (+)(*S*)(*S*)Mebdtp$^-$, reacted with $CrCl_3 \cdot 6H_2O$ at room temperature in chloroform, acetone, ethanol, and water, eventually arriving, after many days and in solution, at Λ(−)$_{589}$ {Cr[(+)(*S*)(*S*)Mebdtp]$_3$} (*V*) as the major complex (see Scheme 1).

The formation reaction could be carried out at the boiling point of the solvent using the potassium salt of the ligand ion (+)(*S*)(*S*)MebdtpK (**II**) or at room temperature (20 °C) using the dithiophosphinic acid (+)(*S*)(*S*)MebdtpH (**I**).

Formation of the complex at room temperature was carefully monitored by vis and CD spectroscopy as the complex is highly soluble in the solvents used, except for water. A small positive CD signal at 675 nm was observed soon after the addition of the chromium salt, and the peak grew during the course of reaction. Simultaneously an absorption band at ~680 nm, which partially overlaps the spectrum of the solvated chromium(III) ion, increased in intensity (Figure 1).

Figure 2 reports the variation in optical density, OD, differential optical density, ΔOD, and chirality factor, g = ΔOD/OD, of the transition at 675 nm, observed up to 24 h (Figure 2a) and up to 40 days (Figure 2b), of the reaction. During the first hours both OD and ΔOD as well as g grew rapidly. Saturated OD values indicate that the formation of the complex at room temperature was complete in 1 or few days, depending on the reactant concentrations. In contrast, the chirality (positive g and ΔOD) kept increasing for many days after the end of the formation reaction.

Using the values OD and ϵ as well as ΔOD and $\Delta\epsilon_\Lambda = +3.5$ (the hypothetical $\Delta\epsilon$ value for the Λ-isomer; see Experimental Section), the total concentration (C_T) and the approximate concentrations of the excess diastereoisomer (C_{de}) and of the single diastereoisomers, C_Λ and C_Δ, were calculated at various times after the initiation of the reaction (Figure 3).[6,7] Under typical experimental conditions a diastereoisomeric excess of ca. 22% was estimated. These results indicate the sure prevalence of the Λ-(*S,S*)(*S,S*)(*S,S*) diastereoisomer over the Δ-(*S,S*) form during the formation reaction as well as in the equilibrium state. This can be achieved by taking one or both of the following pathways: (i) a kinetically diastereoselective

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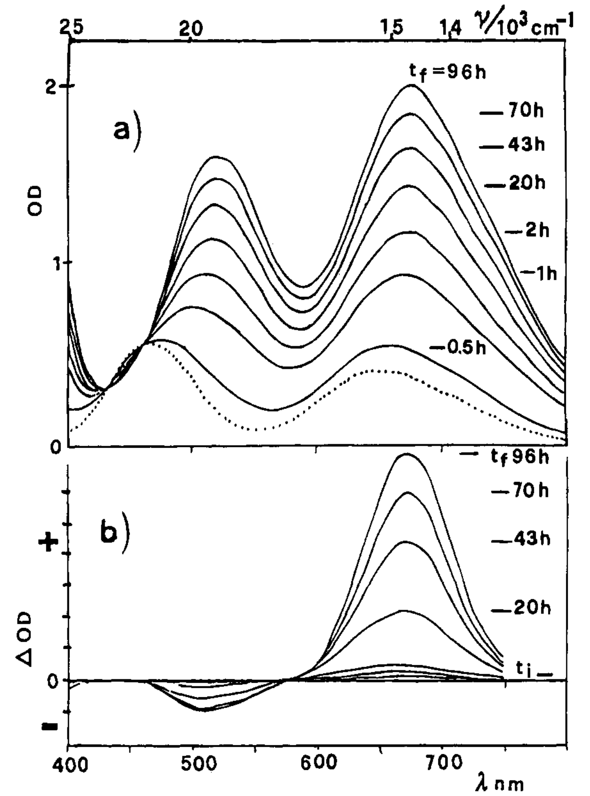


Figure 1. Formation of the Λ-(−)Cr[(+)(*S*)(*S*)Mebdtp]$_3$ diastereoisomer (t_i, starting time; t_f, final time) followed by UV−vis (a) and CD (b) in a cold ethanol reaction solution. The UV−vis spectrum of $CrCl_3 \cdot 6H_2O$ in ethanol is shown (• • •).

formation of the Λ-(*S,S*)(*S,S*)(*S,S*) form; (ii) formation of the two diastereoisomers in a 1:1 mixture accompanied by a parallel or consecutive fast configurational inversion from the Δ- to the Λ-form (toward the right-hand side in eq 1. Even when a 1:1

$$\Delta\text{-}(+)_{589}\{\mathrm{Cr}[(+)(S)(S)\mathrm{Mebdtp})_3]\} \rightleftharpoons \Lambda\text{-}(-)_{589}\{\mathrm{Cr}[(+)(S)(S)\mathrm{Mebdtp}]_3\} \quad (1)$$

mixture of the Δ- and Λ-forms is formed or an excess of the Δ- diastereoisomer is formed, the ensuing conversion reaction can bring the system to the final equilibrium state where the Λ-form is thermodynamically more stable.

It is difficult to say what is happening immediately after the initiation of the reaction. The low positive *g* factor grew during the formation reaction. The increase continued after the end of the complex formation (*i.e.* after OD became constant), though at a much slower rate, and reached an equilibrium after several days. Judging from the slow rate of configuration conversion after the end of the formation reaction, the formation reaction itself may be slightly diastereoselective, giving a slight excess of the Λ-diastereoisomer. Detailed quantitative work is necessary to understand the mechanism of chiral discrimination in the formation reaction.

Configuration Inversion. When the solution was evaporated or cooled to −20 °C, or when the reaction was carried out in water, solid compound **IV** was deposited. The CD spectrum of **IV** in a Nujol mull showed no appreciable Cotton effect between 750 and 350 nm, thus it was identified as a 1/1 mixture of diastereoisomers **V** and **VI**. After dissolution in $CHCl_3$ or ethanol, **IV** antiracemized at the metal center as was evident from the time-course CD spectroscopy: CD spectra in many solvents showed no signals immediately after the dissolution, though, after a few minutes, a very low positive Cotton effect appeared at 675 nm and grew with time to reach an equilibrium of a chirality factor, *g* = ΔOD/OD, varying in the range +2.7 × 10^{-3} ≤ *g* ≤ +4.7 × 10^{-3}, depending on the type of solvent. The UV−vis absorption spectrum did not show any peak apart from the one at *ca.* 680 nm (ε = 349). The change indicates

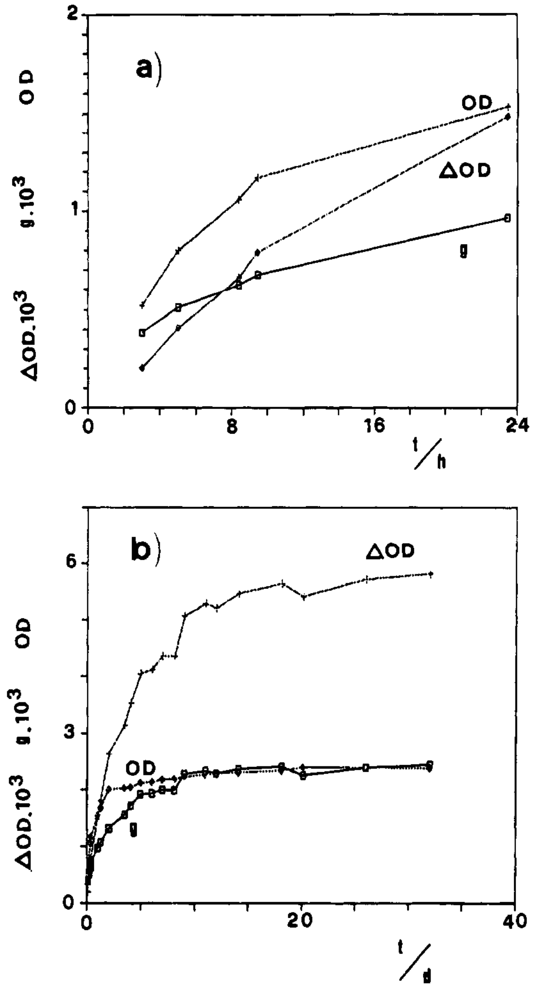


Figure 2. Variation at 675 nm of the differential optical density ΔOD (- - -) the chirality factor *g* = ΔOD/OD (—), and the optical density OD (• • •) during the formation reaction of {Cr[(+)(*S*)(*S*)Mebdtp]$_3$} in ethanol solution in 0−24 h (a) and 0−40 days (b).

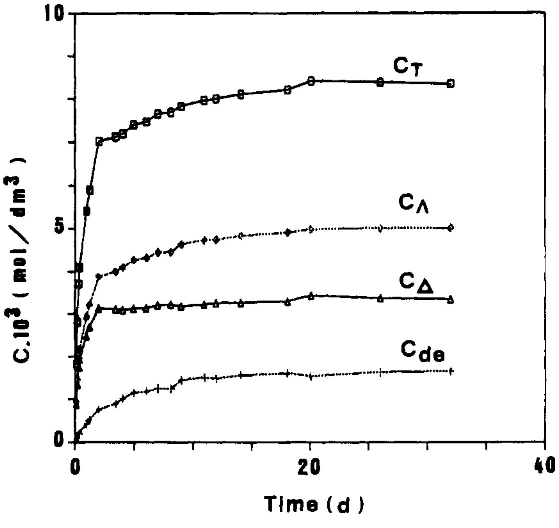


Figure 3. Variation of the concentration of complexes {Cr[(+)(*S*)(*S*)-Mebdtp]$_3$} during the formation reaction: total concentration, C_T (−); concentration of the Λ-(*S,S*)(*S,S*)(*S,S*) diastereoisomer, C_Λ (• • •); concentration of the Δ-(*S,S*)(*S,S*)(*S,S*) diastereoisomer, C_Δ (- - -); concentration of the diastereoisomer that is in excess, $C_{de} = 2C_\Lambda - C_T$ (- • -).

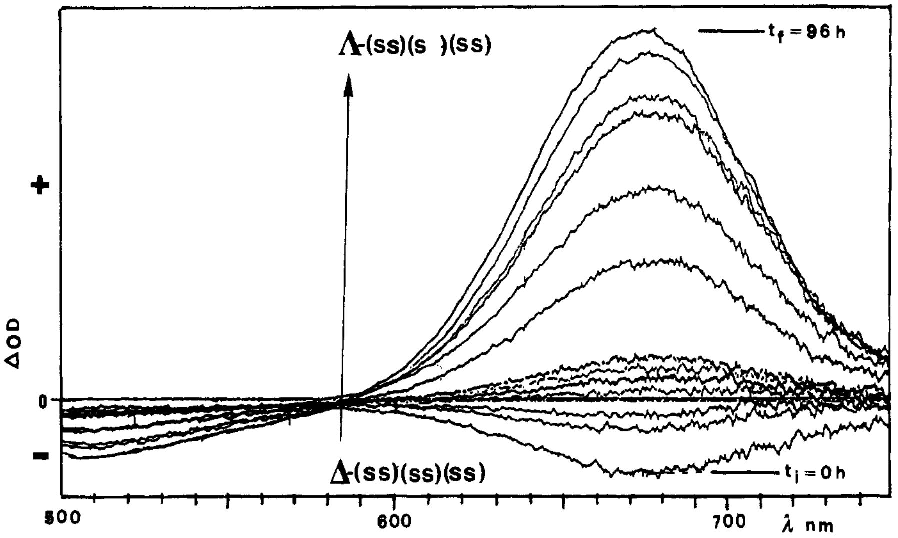


Figure 4. CD spectra of a chloroform solution of complex **IV**. The solution was made after the solid had been kept at 100 °C under vacuum. The spectrum labeled $t_i = 0$ h was obtained immediately after dissolution and shows that Δ-$(+)_{589}$$\{Cr[(+)(S)(S)Mebdtp]_3\}$ is the major diastereoisomer: de = 4%. The spectrum labeled $t_f = 96$ h was obtained after 96 h and shows that Λ-$(-)_{589}$ $\{Cr[(+)(S)(S)Mebdtp]_3\}$ is the major diastereoisomer.

that configurational inversion occurred and the Δ-isomer (**VI**) was converted to the Λ-diastereoisomer (**V**) preferentially over the Λ-isomer conversion to Δ.

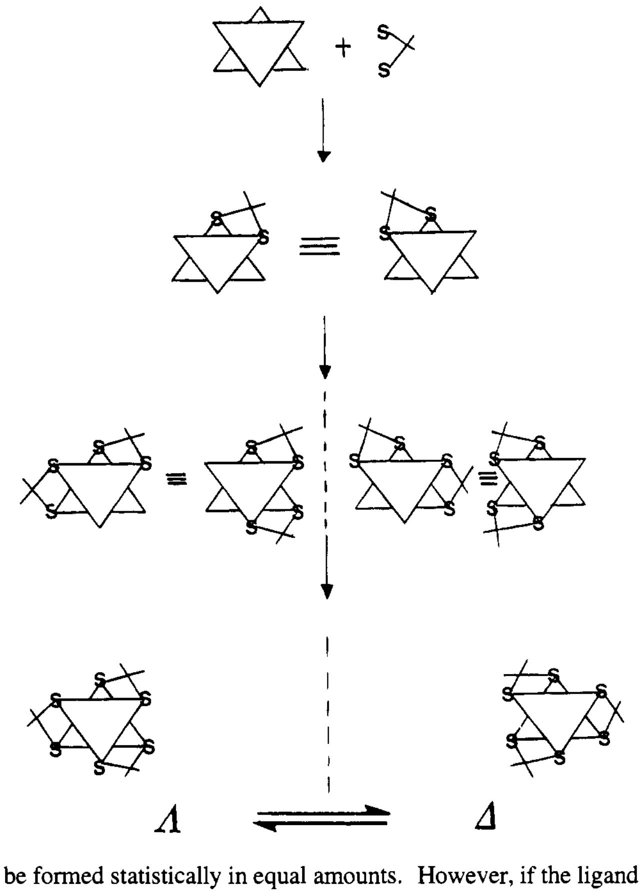
When the achiral solid complex **IV** was maintained under vacuum at 100 °C for several hours, it began to exhibit a negative Cotton effect at 670−675 nm in a Nujol mull CD spectrum. No change in the CsI pellet IR spectrum or in the melting point was observed. The negative peak was also observed immediately after the dissolution of the solid in $CHCl_3$ or other solvents. These results indicate that the configurational conversion from the Λ- to the Δ-diastereoisomer occurred in the solid state at a high temperature and under vacuum. The negative peak observed for the fresh solution decreased in intensity with time, inverted sign in a few minutes, and reached an equilibrium state after 24 h with an excess of the Λ-(*S*,*S*)(*S*,*S*)(*S*,*S*) diastereoisomer, $g = +2.0 \times 10^{-3}$ (Figure 4). Thus, the preferred diastereoisomer is opposite in the solution and the high-temperature solid state.

Light radiation and temperature promote the Λ-(*S*,*S*)(*S*,*S*)(*S*,*S*) → Δ-(*S*,*S*)(*S*,*S*)(*S*,*S*) inversion reaction in solution, shifting the original equilibrium toward equimolar mixture of the two diastereoisomers. When an ethanol solution of the Λ-$(-)_{589}$-$\{Cr[(+)(S)(S)Mebdtp]_3\}$, with $g = +4.6 \times 10^{-3}$, was irradiated with an enlarged 514.5 nm argon laser beam for a few minutes, a very fast Λ → Δ configuration inversion was observed with the fast decrease in intensity of the 675 nm Cotton effect. On interruption of the irradiation of the sample, a new inversion process Δ → Λ restored the solution to the initial equilibrium.

At different temperatures the system attains different equilibrium states as shown by the solution CD spectra. Using the Δε values, quantitative analysis of the inversion reaction 1 can be carried out, which will be reported elsewhere.[14]

Chiral Discrimination. The addition of the ligand to solvated metallic ions in solution may occur in a typical three-step mechanism for octahedral tris-bidentate complexes (Scheme 2). Three chelate rings coordinated to a metal ion form a left-handed (Λ) or a right-handed (Δ) helix. Two-ligand intermediates are already chiral and form a segment of helices, if the two ligands act as bidentate and do not form a common mean plane. With an achiral ligand or a racemic mixture of a chiral ligand, tris-chelate complexes of Δ and Λ configurations should be formed statistically in equal amounts. However, if the ligand is chiral, as in this case, chiral discrimination operates between the third ligand and the two helical segments of the bis-chelate intermediates; hence, Δ and Λ forms should be synthesized in an unequal ratio. If the formation rate or stability of the bis-chelate intermediates is different for the Δ and Λ helical forms, this could also lead to an unequal formation of the tris-chelate diastereoisomers. However, this is less likely as the interactions between the ligands are less severe in the bis-chelate state. The third ligand addition may be the key step in the unequal formation of the two diastereoisomers.

Scheme 2



Thermodynamically the Λ-form is more stable than the Δ-(*S*,*S*) diastereoisomer in solution. Configurational inversion

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(14) Kuroda, R.; Biscarini, P. Manuscript in preparation.

produces a thermodynamic equilibrium with an excess of the Λ-form, even starting from an excess of the Δ-(*S*,*S*) diastereoisomer. The discrimination can be driven by the difference in intramolecular interactions between the alkyl chains in the two diastereoisomers, although we cannot completely neglect the possibility of solvent involvement. The discriminatory ability in the current complex is much lower than in the case of {Cr[(−)(*R*)(*R*)bdtp]$_3$} where the ligand (*R*)(*R*)bdtp$^-$ is sterically rigid.[5−7] In this case stereoselective synthesis of the Λ-(*R*,*R*) diastereoisomer was achieved in THF or CH_3CN, though the Δ-(*R*,*R*)(*R*,*R*)(*R*,*R*) form was favored in $CHCl_3$ solution. In the current complex, {[Cr[(*S*)(*S*)Mebdtp]$_3$}, the long alkyl chains are conformationally flexible and thus it would be difficult to exert a strong chiral discrimination either kinetically or thermodynamically.

Crystal Packing. The solubility of the two diastereoisomers appears to be similar, and complex **IV**, a 1:1 mixture of **V** and **VI**, crystallizes from the reaction solution with g ~ $+3.0 \times 10^{-3}$. The crystallization occurs on cooling the solution to −20 °C, evaporating the solvent slowly at 35 °C, or fast evaporation of the solvent under vacuum. A CD spectrum of the solution after filtration of the solid complex shows the presence of an excess of the Λ-form with a chirality factor g = $+2 \times 10^{-3}$. On the other hand, the solid showed no CD signals.

The stereochemistry of the ligands and ligand−ligand or ligand−solvent interactions thermodynamically favor Λ-(*S*,*S*)-(*S*,*S*)(*S*,*S*) diastereoisomer **V** in solution but hinder homochiral crystal packing. As the crystals with an equimolecular mixture of **V** and **VI** were formed from the solution containing a slight excess of the Λ-(*S*,*S*)(*S*,*S*)(*S*,*S*) diastereoisomer, the chiral discrimination energy which favors the Λ-form formation in solution must be smaller than the difference in crystal packing energies. A CD spectrum of the residual solution after filtration of the solid complex also shows the presence of an excess of the Λ-(*S*,*S*)(*S*,*S*)(*S*,*S*) epimer with a chirality factor g = $+2.0 \times 10^{-3}$.

By warming of the solid **IV** to 100 °C under vacuum for some hours, a solid compound with an excess of the Δ-(*S*,*S*)-(*S*,*S*)(*S*,*S*) diastereoisomer (**VI**) was obtained (Figure 4). It is interesting to speculate what is actually happening in the solid state at high temperature. When the solid separates from solution, solvent molecules might be trapped thereby contributing to the higher stability of the 1:1 heterochiral packing. When the solid is heated under vacuum, either some or all solvent molecules might be removed and a new crystal packing mode achieved after configurational inversion. Another model which does not involve solvent molecules can be proposed. Moreover, as the prevalence of the Λ-diastereoisomer is independent of the type of solvent, this seems more likely. In solution the equilibrium was shifted toward the Λ-diastereoisomer on lowering the solution temperature from 20 to −80 °C. Thus, it is not entirely unreasonable to assume that the Δ-form is somehow more stable than the Λ-form at higher temperature and the tendency may be accelerated under vacuum. If the crystal packing is loose and the crystal lattice has enough room for configurational inversion to take place, the inversion reaction at high temperature might have led to an excess of the Δ-(*S*,*S*) diastereoisomer. X-ray crystal structures of the high- and the low-temperature forms should reveal the crystal packing and hence the mechanism of configurational inversion and chiral discrimination. At the moment, we have not been successful in obtaining reasonable crystals for X-ray structural analysis despite many attempts.

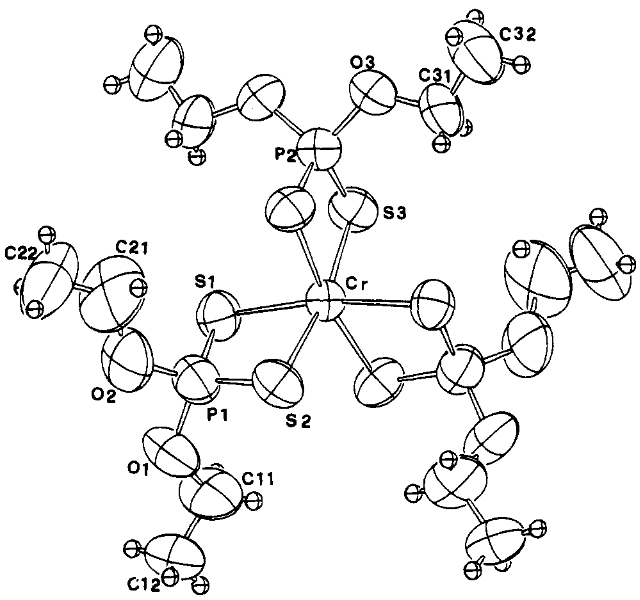

Figure 5. ORTEP drawing of the molecular structure {Cr[ddtp]$_3$} with the numbering scheme employed.

Table 2. Crystallographic Data for Cr[(ddtp)$_3$] (**VIII**)

chem formula $C_{12}H_{30}CrO_6P_3S_6$
monoclinic
$a = 14.512(8)$ Å
$b = 13.657(3)$ Å
$c = 14.350(2)$ Å
$\beta = 90.42(3)°$
$V = 2844(2)$ Å^3
$Z = 4$

fw 607.64
space group *C2/c* (No. 15)
$T = 20$ °C
$\lambda = 0.71069$ Å
$\varrho_{obsd} = 1.42$ g cm^{-3}, $\varrho_{calcd} = 1.419$ g cm^{-3}
$\mu = 10.05$ cm^{-1}
$R(F_o)^a = 0.065$
$R_w(F_o) = 0.072$

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)]^{1/2}$, $w = 4F_o^2/\sigma^2(F_o^2)$.

Trans-Esterification and Model Molecular Structure of {Cr[(+)(S)(S)Mebdtp]$_3$}. When the reaction between the chromium ion and *O*,*O'*-bis[(*S*)(+)-2-methylbutyl] dithiophosphinic acid, (+)(*S*)MebdtpH (**I**), as ligand was carried out in a boiling ethanol solution, the racemic complex Cr[ddtp]$_3$ (**VIII**) was obtained. The color, melting point, and UV-vis spectrum of this complex were very similar to those of complex **IV**, though compound **VIII** showed no optical activity in solution, and all the IR stretching frequencies were different from the corresponding values for **IV**, *e.g.* ν(Cr−S)= 314 and 319 cm^{-1} for **VIII** and **IV**, respectively. Thus, it can be assumed that, at high temperature, the acid catalyzes a reaction of trans-esterification and during the process the chirality of the solution disappeared, as the ethyl groups of the solvent substituted the (+)(*S*)-2-methylbutyl groups of the ligands in complex **IV**. X-ray structure determination of the isolated violet crystals confirmed that trans-esterification indeed occurred at high temperature in an acidic medium as catalyst. The work revealed the molecular structure and crystal packing of the racemic octahedral complex **VIII**, which helps to understand the structure of the two diastereoisomers **V** and **VI**.

The molecular structure of [Cr(ddtp)$_3$] is shown in Figure 5. Atomic coordinates and relevant atomic distances and angles are listed in Table 2.

The molecule lies on a crystallographic C_2 axis. The alkyl chain of the ligand is flexible. Thus, its atoms exhibited large temperature factors and, as a consequence, terminal C−C distances appeared very short. The structure is similar to that reported earlier.[15] There are no unusually close intermolecular contacts; the shortest distance is 3.66(2) Å between the O and methyl C atoms.

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(15) Vincents, H.; Jensen, F. D.; Hazel, R. G. *Acta Chem. Scand.* **1972**, *26*, 135.

Table 3. Positional Parameters and *B*(eq) Values (a) and Relevant Bond Distances (b) and Angles (c) for $\{Cr[ddtp]_3\}$ (**VIII**)

(a) Positional Parameters and *B*(eq) Values[a]

atom	*x*	*y*	*z*	*B*(eq)
Cr	1.0000	0.1817(2)	$^3/_4$	5.2(2)
S(1)	1.0808(3)	0.1673(3)	0.8974(3)	7.1(2)
S(2)	1.1138(2)	0.0626(3)	0.7005(3)	7.4(2)
S(3)	0.9088(3)	0.3145(3)	0.8134(3)	7.1(2)
P(1)	1.1647(3)	0.0748(3)	0.8301(3)	7.9(3)
P(2)	1.0000	0.4032(4)	$^3/_4$	7.7(4)
O(1)	1.1773(7)	−0.0286(8)	0.8819(8)	10.1(7)
O(2)	1.2706(7)	0.107(1)	0.837(1)	11.8(9)
O(3)	0.9510(7)	0.4818(6)	0.6828(8)	9.8(7)
C(11)	1.102(1)	-0.090(1)	0.904(1)	11(1)
C(12)	1.140(1)	-0.179(1)	0.943(1)	9(1)
C(21)	1.303(2)	0.202(2)	0.819(2)	18(2)
C(22)	1.387(2)	0.223(2)	0.848(2)	16(2)
C(31)	0.884(2)	0.452(1)	0.614(1)	14(2)
C(32)	0.860(1)	0.531(1)	0.558(1)	14(2)

(b) Intramolecular Distances Involving the Non-Hydrogen Atoms[b]

Cr−S(1)	2.420(4)	P(2)−O(3)	1.605(9)
Cr−S(2)	2.428(4)	O(1)−C(11)	1.42(2)
Cr−S(3)	2.426(4)	O(2)−C(21)	1.40(2)
S(1)−P(1)	2.007(5)	O(3)−C(31)	1.44(2)
S(2)−P(1)	2.003(6)	C(11)−C(12)	1.44(2)
S(3)−P(2)	2.016(5)	C(21)−C(22)	1.31(3)
P(1)−O(1)	1.60(1)	C(31)−C(32)	1.39(2)
P(1)−O(2)	1.60(1)		

(c) Intramolecular Bond Angles Involving the Non-Hydrogen Atoms[b]

S(1)−Cr−S(2)	82.8(1)	S(3)−P(2)−S(3′)	106.1(3)
S(3)−Cr−S(3″)	83.3(2)	S(3)−P(2)−O(3)	112.5(4)
Cr−S(1)−P(1)	85.5(2)	S(3)−P(2)−O(3′)	114.8(4)
Cr−S(2)−P(1)	85.4(2)	O(3)−P(2)−O(3′)	96.1(8)
Cr−S(3)−P(2)	85.3(2)	P(1)−O(1)−C(11)	123(1)
S(1)−P(1)−S(2)	106.2(2)	P(1)−O(2)−C(21)	124(1)
S(1)−P(1)−O(1)	113.5(5)	P(2)−O(3)−C(31)	121(1)
S(1)−P(1)−O(2)	112.3(5)	O(1)−C(11)−C(12)	107(1)
S(2)−P(1)−O(1)	113.4(5)	O(2)−C(21)−C(22)	117(2)
S(2)−P(1)−O(2)	115.5(6)	O(3)−C(31)−C(32)	109(2)
O(1)−P(1)−O(2)	96.1(7)		

[a] $B(eq) = (^4/_3)[\Sigma_i\Sigma_j B_{ij}a_ia_j]$. [b] Distances and angles are in Å and deg, respectively, with esd's given in parentheses.

As is seen in Figure 5, the three independent chains (chains 1, 2, and 3) of a molecule adopt similar conformations. They take *trans(anti-periplanar)* conformations with P−O−C−C torsion angles of 175(1), 165(2), and 173(2)°. The S−P−O−C angles are slightly different for the three chains: chain 1 has the dihedral angle of 57° as compared with 73 and 71° for the other two chains. The O−P−O angles of 96.1(7) and 96.1(8)° are slightly smaller than the corresponding angles of 97.6(4) and 97.8(4)° in $\Lambda(-)_{589}\{Cr[(-)(R)(R)bdtp]_3\}$.[8] The average inner-cycle S−P−S angle is 106.2(2) and 107.2(2)° for **VIII** and $\Lambda(-)_{589}\{Cr[(-)(R)(R)bdtp]_3\}$, respectively. The bite dimensions S•••S are 3.21 and 3.18 Å for the two compounds. The three four-membered chelate rings in a molecule are almost perpendicular to each other with dihedral angles of 83.4 and 97.1°. All the C_3 axes of the metal complexes lie in the *ac plane* and are parallel to each other due to the space group symmetry (*i.e.* inversion and translation).

On the basis of the molecular structure of $[Cr(ddtp)_3]$, *i.e.*, by means of adding CH_3 and C_2H_5 groups to the last carbon atom of the ethyl group of **VIII** and assuming the same C_2 molecular symmetry, the structure of $\{Cr[(+)\text{-}(S,S)(Mebdtp)]_3\}$ can be generated (Figure 6). The methylbutyl chain can adopt numerous conformations. However, if we assume the usual lowest-energy conformation about the $Cn1-Cn2$ bonds (n = 1, 2, and 3 for chain 1, 2, and 3, respectively) with the three torsion angles of −60 (*gauche*), +60 (+*gauche*), and 180° (*trans*), three possible conformations for the (*S*) configuration can be generated depending on whether methyl (case 1), ethyl (case 2), or hydrogen (case 3) takes the *trans* position. Thus, coupling with the absolute configuration about the metal center, six conformations are considered: Δ-case 1, Δ-case 2, Δ-case 3, Λ-case 1, Λ-case 2, and Λ-case 3, which are shown in Figure 6.

These models show a different topological arrangement of the methyl and the ethyl groups in the Λ- and Δ-(*S,S*)(*S,S*)(*S,S*) diastereoisomers. When all the hydrogen atoms take the trans position (case 3), the methyl groups are located around the equatorial part of the metal complex, in the case of the Δ-isomer, while they stick out in the C_3 direction in the Λ-diastereoisomer (Figure 6c). In case 2, the methyl groups are located in the equatorial part for the Λ, while they stick out in the C_3 direction in the Δ (Figure 6b). Case 1 is the combination of the two cases, and the methyl and ethyl groups are located either in the equatorial or the outskirt parts depending on the absolute configuration around the metal. It is quite difficult to explain how these topological differences are related to the difference in the thermodynamic stability of the diastereoisomers. Particularly the alkyl chains are flexible, and hence the methyl or the ethyl groups can easily take on one of the three conformations or any conformation in between. Moreover the two alkyl chains joined at a phosphorus atom are completely independent of each other and free to move around causing a high conformational flexibility.

In the case of $\{Cr[(-)(R)(R)bdtp]_3\}$ where the chiral center is in the rigid ligand, absolute configuration of the metal coordination cluster affects the conformation of the ligand more precisely. In this case, the methyl group is in the equatorial position for the Λ-(*R,R*)(*R,R*)(*R,R*) diastereoisomer, while it is in the axial position in the Δ- case. The crystal packing force favored the homochiral packing of the Λ configuration, and the Λ-homochiral crystals were obtained from solution where the Δ-isomer was also present.[8] In contrast a racemic crystal was obtained for $[Cr(ddtp)_3]$. It is difficult to predict the crystal packing mode of $\{Cr[(+)(S)(S)Mebdtp]_3\}$ based on that of $[Cr(ddtp)_3]$ as there is no chiral center in the latter ligand.

Electronic Absorbance, CD, and MCD Spectra. The process of enantiomeric equilibrium attainment in solution was monitored accurately by CD and UV−vis absorption spectroscopy by dissolving the isolated complex $(\Delta\Lambda)\{Cr[(+)(S)(S)\text{-}Mebdtp]_3\}$ (**IV**) in various solvents. Figure 7 shows the UV−vis and CD spectra of $Cr[(+)(S)(S)Mebdtp]_3$ in $CHCl_3$ solution in the d−d (750−400nm), charge-transfer, and intraligand band (400−200 nm) regions, 1 h after dissolution and at final equilibrium (eq 1).

The vis-absorption spectrum remains unchanged with time, showing a stable band at 690 nm (ϵ = 349) and an unresolved doublet at 535 and 520 nm (ϵ = 249), which are assigned[16−18] on the basis of octahedral symmetry O_h to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$, $^4A_{2g} \rightarrow {}^2T_{2g}$ transitions, respectively.

The CD spectrum of $CHCl_3$ solution is almost flat immediately after dissolution, though, after a few minutes, it shows a positive Cotton effect at 670 nm, which grows with time reaching $\Delta\epsilon = +0.3$ and $g = +1.1 \times 10^{-3}$. This band was assigned to the magnetic dipole-allowed doubly-degenerate $^4A_2 \rightarrow {}^4E_a$ component. The excited state was split due to the lowering of the symmetry to D_3 under the influence of the ligand

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(16) Tomlinson, A. A. *J. Chem. Soc. A* **1971**, 1409.
(17) Jϕrgensen, C. K. *J. Inorg. Nucl. Chem.* **1962**, *24*, 1571.
(18) McCaffery, A. J.; Mason, S. F.; Ballard, R. E. *J. Chem. Soc.* **1965**, 2887.

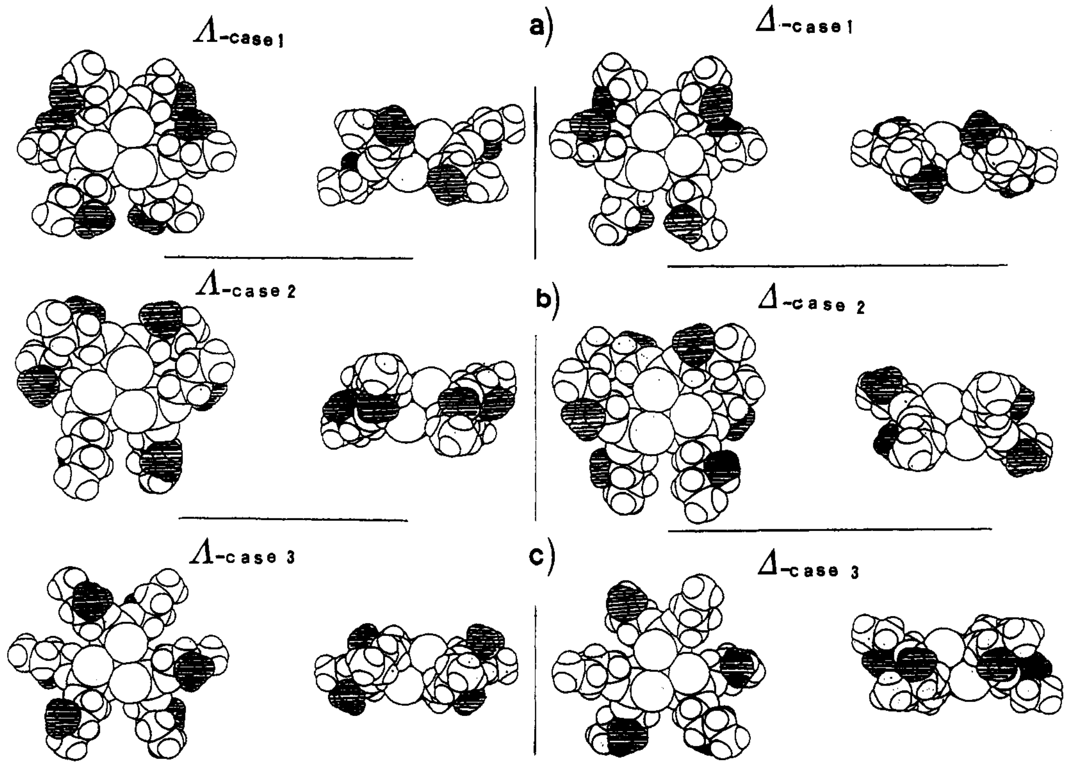

Figure 6. Three-dimensional views along C_3 and along C_2 of (a) Λ-(−)$_{589}${Cr[(+)(*S*)(*S*)Mebdtp]$_3$} and (b) Δ-(+)$_{589}${Cr[(+)(*S*)(*S*)Mebdtp]$_3$} structural models, showing the different arrangement of the CH_3 groups, equatorial and axial, with respect to the plane containing the Cr and three P atoms.

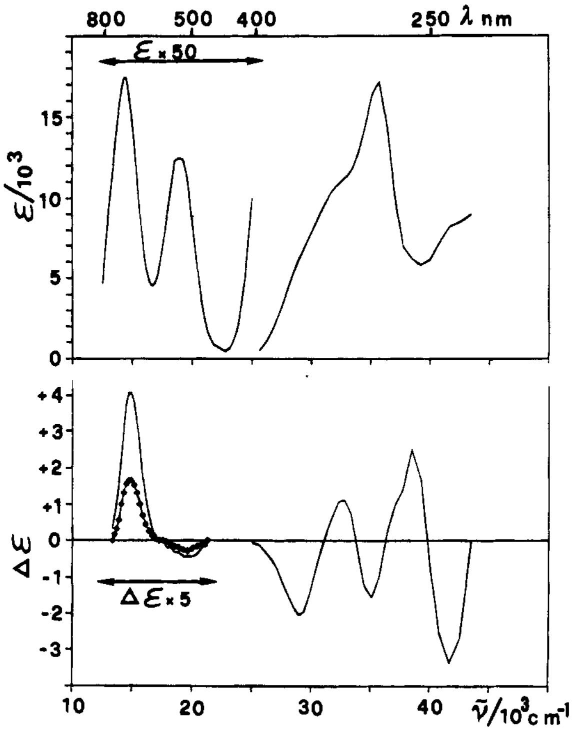

Figure 7. UV−vis and CD spectra of {Cr[(+)(*S*)(*S*)Mebdtp]$_3$} (**IV**) in chloroform solution 1 h after its dissolution (•••) and at final equilibrium (—).

field. The second $^4A_2 \rightarrow {}^4A_1$ component is completely overlapped and canceled by the dominant ^4E_a.

This transition is not observable in the magnetic circular dichroism spectrum (MCD) of the related optically inactive complex {Cr[Mebdtp]$_3$} (**VII**). Two Faraday terms at 540 and 525 nm, respectively, with molar ellipticity $[\Theta]_M = -8 \times 10^{-3}$ and $+2.8 \times 10^{-2}$ deg dL dm^{-1} mol^{-1} per Gauss unit were observed at the broad doublet absorption band and can be assigned to the $^4A_{2g} \rightarrow {}^4T_{1g}$ and $^4A_{2g} \rightarrow {}^2T_{2g}$ transitions.[16]

The CD spectrum in the same range shows a broad, scarcely resolved band at 535−510 nm with a *g* factor of $\sim 10^{-4}$, which confirms the magnetic dipole-forbidden character of these transitions.[1] 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 is shown clearly in the CD spectra at 345 nm, and the corresponding absorption band is submerged under the continuous increasing curve.

Complex **IV** is scarcely soluble in water, but in solvents such as ethanol, acetonitrile, acetone, benzene, and dichloromethane it shows spectra similar to that in chloroform. The CD spectra in all the solvents show little signal in the 750−500 nm region, immediately after dissolution. However, a positive Cotton effect soon appears at ~670 nm and the intensity grows with time reaching a steady state after about 24 h. By contrast, absorption due to the d−d transition measured along with the CD spectra remains constant in each solvent. The chirality factor *g* varies in the range $+4.6 \times 10^{-3}$ to $+2.7 \times 10^{-3}$ following the order of ethanol > acetonitrile > benzene > acetone > dichloromethane > chloroform. The solvents may not strongly discriminate the two diastereoisomers as Λ-(*S*,*S*) predominates in all the above mentioned solvents, although the *g* factor at equilibrium is slightly different from solvent to solvent.

Chiral solvents such as L(+)- and D(−)-diethyl tartrate, L-(+)DET and D(−) DET, stabilize the Λ-(*S*,*S*) and Δ-(*S*,*S*) diastereoisomers, respectively, at a *g* value of $+0.3 \times 10^{-3}$ and -0.3×10^{-3}. An enantiomerization process at the metal center is shown when the optically inactive complex {Cr[Mebdtp]$_3$} (**VII**) is dissolved in 1/1 ethanol/L(+)DET or 1/1 ethanol/D(−)DET mixed solvents. The deracemization processes give a diastereoisomeric excess of Λ- or Δ-{Cr[Mebdtp]$_3$}, with a $g = +0.22 \times 10^{-3}$ or $g = -0.16 \times 10^{-3}$, respectively. The process confirms that the chiral solvent recognizes the chirality of the metal complex and Λ-{Cr[Mebdtp]$_3$}·L(+)DET is more stabilized than Δ-{Cr[Mebdtp]$_3$}·D(−)DET. After evaporation of the ethanol from the solution, a part of the complex crystallizes in an optically inactive form (ΛΔ){ Cr[Mebdtp]$_3$}- and the chirality factor of the residual in the chiral solvent increases to $g = +1.0 \times 10^{-3}$ and $g = -0.3 \times 10^{-3}$ for L(+)-DET and D(−)DET, respectively.

Absolute Configuration. The Λ-(*S*,*S*)(*S*,*S*)(*S*,*S*) absolute configuration is assigned to (−)$_{589}$ {Cr[(+)(*S*)(*S*)Mebdtp]$_3$} (**V**) on the basis of the positive CD component at 670 nm in the region of the allowed magnetic dipole $^4A_{2g} \rightarrow {}^4T_{2g}$ transitions. The same assignment was given to Λ-(−)$_{589}${Cr[(−)bdtp]$_3$},[5] whose absolute configuration was established by X-ray structure determination.[8]

Conclusions

This study has shown that a chiral center located at the end of a flexible aliphatic chain can exert a small chiral discrimination at the metal center. Thermodynamically and possibly kinetically as well, Λ-{Cr[(+)(*S*)(*S*)Mebdtp]$_3$} is favored over Δ-{Cr[(+)(*S*)(*S*)Mebdtp]$_3$} in solution, although light radiation and a higher temperature shift the equilibrium toward the Δ-(*S*,*S*)(*S*,*S*)(*S*,*S*) diastereoisomer.

Crystals of {Cr[(+)(*S*)(*S*)Mebdtp]$_3$} obtained from all solvents used contain a 1/1 mixture of the Λ-(*S*,*S*)(*S*,*S*)(*S*,*S*) and Δ-(*S*,*S*)(*S*,*S*)(*S*,*S*) diastereoisomers. This indicates that the crystal packing energy favors heterochiral rather than the homochiral recognition, although at higher temperature the equilibrium shifts slightly toward the Δ- isomer even in the solid state. The crystal structure and the conformational analysis of {Cr[(+)(*S*)(*S*)-Mebdtp]$_3$} will help to understand the different kinetic and thermodynamic behavior of the diastereoisomers and the mechanism of the configuration inversion in solution and in the high-temperature solid state. We are currently trying to obtain crystals of the complex suitable for X-ray structure determination, as well as quantitative analysis of the formation and configuration inversion reactions.

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Supporting Information Available: Tables giving crystal data and details of the structure determination, atom coordinates and *B* values, bond lengths, bond angles, and anisotropic thermal parameters (6 pages). Ordering information is given on any current masthead page.

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