Stereoselective Synthesis and Characterization of Cyclic O,O′-1(R)2(R)(–)-dimethylethylene Dithiophosphate Complexes of Chromium(III): Λ-Cr[(–)bdtp]$_3$

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Abstract

The chiral octahedral tris((–)cyclic O,O′-1(R)-2(R) dimethylethylene dithiophosphato)chromium(III) complex was obtained stereoselectively in ethanol in the diastereoisomeric form, Λ-(–)$_{589}$-{Cr[(–)bdtp]$_3$}, (I), with (–)bdtp$^-$ = 1(R)2(R)-(–)$C_4H_9O_2PS_2^-$. The complex was characterized in pure optical form through its chiroptical properties and is optically labile: $[\alpha]_D = -816$, in $CHCl_3$, changing quickly to $[\alpha]_D = +209$. The achiral Cr(bdtp)$_3$ complex was also synthesized separately and its isotropic absorbance and MCD spectra compared with UV-Vis. and CD spectra of the isolated diastereoisomer. CD spectra of (I) in various solvents show a configuration inversion which gives diastereoisomeric equilibria Λ-(R,R)(R,R)(R,R) ⇌ Δ-(R,R)(R,R)(R,R), with an excess of the Λ-(R,R) or Δ-(R,R) forms, depending on the solvent. The thermodynamic stability of Λ-(R,R) diastereoisomer changes with the solvent in the order THF > CH_3CN > $(CH_3)_2CO$ > C_6H_6 > EtOH > CH_2Cl_2 > $CHCl_3$.

Introduction

The tris(chelate)metal(III) complexes, ML$_3$, being dissymmetric at the metal centre, may exist in two enantiomeric forms of Λ and Δ absolute configuration. There has been much interest in the synthesis, resolution and energy discriminations between the enantiomers as well as in the dynamic stereochemistry of this type of transition-metal complexes [1, 2]. Chiral energy discrimination of Λ and Δ-tris(chelate)metal(III) complexes have been the subject of CD studies [3].

Induced CD activity by a chiral environment compound in $M^{III}S_6$ chromophores allowed their absolute configuration to be inferred [4]. However, it is necessary to isolate the enantiomers of the complexes to determine the preferred association structures and to measure the chiral discrimination energies, so that the $\Delta\epsilon_{max}$ values for the estimation of an enantiomeric excess could be available.

The aim of this work is the synthesis and characterisation of optically active chromium(III) complexes containing chiral dithiophosphate ligands. Chiral sulphur ligands would allow the synthesis of optically active complexes and enable the stereochemical and chiroptical properties of the ($M^{III}S_6$) chiral chromophoric group to be studied. In fact, when an optically active ligand of (R) or (S) configuration is used, two pairs of diastereoisomers of opposite chirality are possible: Λ-(R) and Δ-(R) or Λ-(S) and Δ-(S). Employing a (–)chiral dithiocarbamate, a unique diastereoisomer, Λ-(–), of $Co^{III}L_3$ complex has been obtained [5].

The chiral dithiophosphate ligand, (R)(R), (–)-bdtp$^-$, derived from active 2(R),3(R)-butanediol [6], is also expected to yield a single diastereoisomer forming stereospecifically the corresponding tris-chelate complex, Cr[(–)bdtp]$_3$.

Experimental

Spectroscopic Measurements

Infrared (IR) spectra were obtained on a Perkin-Elmer 225 spectrometer in nujol and hexachlorobutadiene mulls between 4000 and 200 cm^{-1}, using NaCl and CsI windows.

Visible and ultraviolet (UV-Vis.) spectra were measured with Cary 14 and 17 spectrometers in various solvents, between 750 and 200 nm.

Circular dichroism (CD) spectra were obtained in freshly prepared solutions between 750 and 200 nm on Jasco J-500 A and J-40 CS spectropolarimeters.

Magnetic circular dichroism (MCD) spectra in $CHCl_3$ solution were obtained on a Jasco J-500 A spectropolarimeter equipped with an electromagnet working at 15100 G. The calibration was obtained with a ~1 M solution of $CoSO_4 \cdot 7H_2O$ using the data reported [7].

Preparation of the Compounds

Potassium(–)cyclic O,O′-1(R),2(R)dimethylethylene dithiophosphate

(–)bdtpK, and the corresponding achiral ligand, bdtpK, were prepared as described [6].

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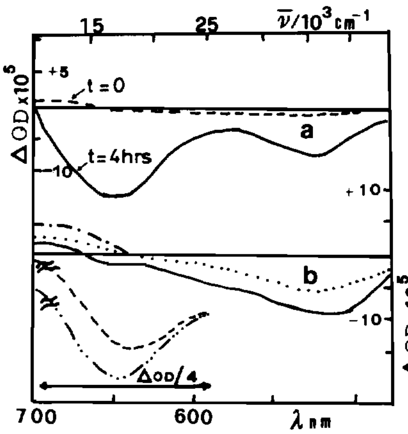


Fig. 1. CD spectra *in situ* of: a) the boiling ethanol solution immediately after precipitation of the Λ-(−)$_{589}${Cr[(−)-bdtp]$_3$} and 4 h later; b) the cold ethanol reaction solution at different times since the start.

Tris(−)cyclic O,O′-1(R),2(R) dimethylethylene dithiophosphate chromium(III), Λ-(−)$_{589}${Cr[(−)-bdtp]$_3$}, (I)

In a three-necked 500 ml flask fitted with a reflux condenser with a calcium chloride guard tube, a dry nitrogen inlet tube and a dropping funnel, 1.35 g (6 mmol) of (−)bdtpK were placed and dissolved by minimal heating in 200 ml of absolute ethanol. When the dissolution was completed, and while heating to gentle refluxing, a solution of 0.53 g (2 mmol) of chromium trichloride hexahydrate in absolute ethanol was dropped in, which caused the solution to become violet. After 1 h of stirring and heating the reaction mixture was filtered and the separated solid was dissolved in anhydrous methylene chloride followed by filtration from the white solid potassium chloride. The filtrate was concentrated to one-fourth of the original volume and upon addition of ethyl ether, the violet product, 0.6 g, m.p. >360, $[\alpha]_D$ = −816 (C = 0.48, $CHCl_3$), separated. This changed quickly to $[\alpha]_D$ = +209. CD spectra in nujol mulls show a positive Cotton effect at 690 nm, g = +0.8 × 10^{-2}. In $CHCl_3$ the spectrum shows a positive Cotton effect at 675 nm which inverts to negative values. The compound was maintained under vacuum at 150 °C many hours and identified as Λ-(RR)(RR)(RR), (I). Found: C, 23.80; H, 4.25%. Required for $C_{12}H_{24}O_6P_3S_6Cr$: C, 23.95; H, 4.0%.

The IR spectrum (nujol mulls) shows strong bands at 1040 (P–O asym), 935 (P–O sym), 870, 815, 660, 635 (P–S asym), 565 (P–S sym), 410, 370, 330, 310 (Cr–S) cm^{-1}.

The CD spectrum of the residual mother solution shows after a long time a negative Cotton effect at 665 nm, g = −2 × 10^{-3}. Upon adding petroleum ether to the ethanol solution until a 10/1 ratio, the intensity of this band grows to a g value of −1 × 10^{-2}.

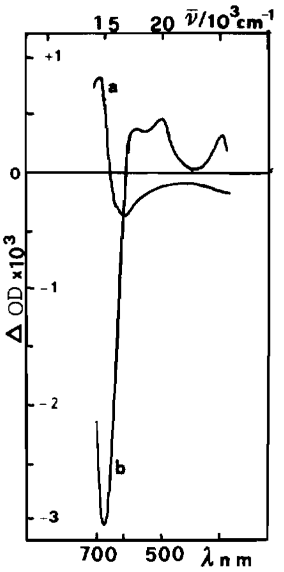


Fig. 2. CD spectra in nujol mulls: a) (−)$_{589}$Cr[(−)bdtp]$_3$; b) (+)$_{589}$Cr[(−)bdtp]$_3$ and (−)$_{589}$Cr[(−)bdtp]$_3$ mixture.

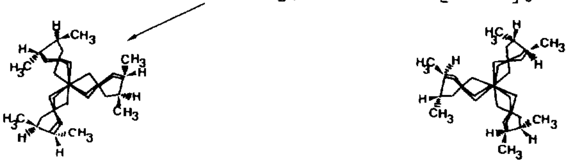
The mother liquor of the reaction mixture was evaporated under vacuum without heating, so that it yielded a solid residue, identified as a mixture of the two diastereomers. CD spectra in nujol mulls show a broad negative Cotton effect below 650 nm, g = −0.2 × 10^{-2}. The residual washed with petroleum ether results richer in the diastereoisomer Δ-(RR)(RR)(RR), (II). In $CHCl_3$, CD(−)675 nm, g = −2.7 × 10^{-3} which grows with time to g = −4.5 × 10^{-3}.

Tris cyclic O,O′-1,2-dimethylethylene dithiophosphate chromium(III), Cr(bdtp)$_3$, (III)

The compound was obtained as (I), starting from the achiral ligand bdtpK, and identified as (III) by elemental analyses, IR and UV-Vis. spectra.

Results and Discussion

The chiral ion (−)bdtp reacts in ethanol solution with $CrCl_3 \cdot 6H_2O$ to give a solid complex (−)$_{589}${Cr[(−)bdtp]$_3$}, (I), in the Λ-(RR) configuration (see Scheme 1).



(I) Λ-(RR)(RR)(RR)

(II) Δ-(RR)(RR)(RR)

Scheme 1.

In principle one might expect two diastereomers to be formed when a chiral ligand reacts with the prochiral chromium ion, but the two diastereoisomers (I) and (II) should possess different physical and energetic properties because they are not formed in equal amounts. It seems that a stereoselective reaction occurs, which favours the formation of only one diastereoisomer.

The formation reaction of the precipitate solid, (I), takes place immediately in the ethanolic boiling solution. The resulting clear solution gives no appreciable particular CD effects in the spectral range (750–650 nm), (Fig. 1a), where at 688 nm a Vis-absorption band (ϵ = 330) characteristic of chromium complexes has been registered, and where a CD effect could be foreseeable for the expected chiral complexes. This fact could either be indicative of the presence in solution of the equilibrium of the two diastereoisomeric forms in equimolecular amounts, or could be due to the fast racemisation of the first formed Cr(III) chiral centre. This last hypothesis was confirmed when soon after (in the solution) a progressive increase of a large negative Cotton effect at ~660 nm was observed.

However, when the reaction was performed at room temperature, careful monitoring of the changes in the CD spectra during the course of the reaction showed, immediately after the addition of the chromium salt (½ hr), a weak resultant positive CD curve between 700 and 650 nm, which disappears slowly during the formation of the precipitate, being substituted by a negative CD curve, (250 h), (Fig. 1b).

In nujol mulls, where it is optically stable, the isolated complex (I) shows a very high positive Cotton effect at 690 nm, $g \cong +10^{-2}$, and a broad negative CD band with a minimum at ~610 nm extending to lower wavelengths (Fig. 2a).

The filtered ethanol reaction solution from the isolated product eventually shows a changed CD spectrum, with a negative CD band at 671 nm, $g = -7 \times 10^{-3}$ while the Vis-absorption spectrum is maintained unaltered. Evaporation of the solvent leaves a solid mixture of the two diastereoisomers Λ-(RR) and Δ-(RR), characterized by a nujol mull spectrum with a CD band at ~660 nm. A part of complex (I) can be separated from this mixture by dissolution in chloroform and fractionated precipitation by petroleum ether. The addition of a strong excess of petroleum ether to the reaction solution determines a fast growth of the negative CD band at 665 nm and a stabilization of the g factor at ~−1 × 10^{-2}. The complete elimination of the solvent leaves a solid residual with a strong negative CD band at 675 nm (Fig. 2b), which is identified as a mixture richer in the complex, (+)$_{589}${Cr[(−)-bdtp]$_3$}, (II).

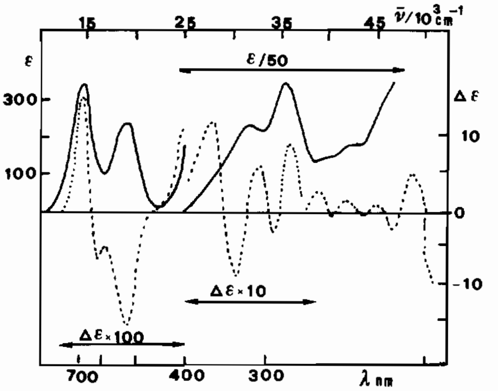


Fig. 3. The absorption ——— and CD ······· spectra of (−)$_{589}$Cr[(−)bdtp]$_3$ in CH_3CN after standing for 24 h since solubilization.

The CD observations in ethanol solution may indicate the beginning of an inversion process of the first formed complex (I), which in part yields the thermodynamically stable second diastereoisomeric complex, (II). A thermodynamic equilibrium between the two diastereoisomers is established, the second being higher than the first in concentration. Thus the kinetically fast process of stereoselective formation and precipitation of the first complex takes place before its inversion, which occurs on the species in solution. We conclude that we might have isolated one, (I), of the diastereoisomers of a racemic mixture by a selective, kinetically-controlled precipitation, followed by the partial inversion of the residual complex to the thermodynamically more stable form (II) in the ethanol solution.

The solubilization process of the isolated diastereoisomer (I) was monitored accurately using various solvents by CD and Vis absorption spectroscopy. The complex (I) is obviously scarcely soluble in ethanol, but in chloroform solution and in other solvents such as acetonitrile, acetone, deuterochloroform, methylene chloride and tetrahydrofuran, it shows a positive Cotton effect in the range 675–690 nm. The intensity and frequency of this band change with time, reaching a steady state about 24 h later.

Spectroscopic and chiroptical data of the obtained complex (I) and of the (I) + (II) complexes mixture are reported in Table I. Figure 3 shows the UV-Vis. and CD spectra of the (I) $\rightleftharpoons$ (II) equilibrium in CH_3CN solution in the d–d (750–400 nm), charge transfer and intraligand bands (400–200 nm) regions. Figure 4 shows the spectra at 5 °C in $CHCl_3$ immediately after the solubilization, and after 24 h.

In the d–d band region (750–400 nm) the Vis-absorption spectrum shows in all solvents a stable band at 688 nm. ϵ = 329, and an unresolved doublet

TABLE I. Absorption and CD Spectra of the Chiral Λ-(−)$_{589}${Cr[(−)bdtp]$_3$} immediately after the Dissolution (in parentheses) and after Standing for 24 h.

Assignments (O_h) $^4A_{2g}$ →	λ, nm	$\bar{\nu}/10^3$ cm^{-1}	ε	Nujol		CHCl$_3$		CH$_3$CN	
				Δε	$g \times 10^4$	Δε	$g \times 10^4$	Δε	$g \times 10^4$
$^4T_{2g}$	695							+0.15	+4.6
	690				+80				
	688	14.5	329						
	675					(+6.7)	(+200)		
	660				+118^a	−2	−60		
	635							−0.09	−4.7
$^4T_{1g}$	535	18.7	223			−0.13	−6	−0.17	−7.6
	520	19.2	231			(−0.36)	(−16)	−0.17	−7.4
	515	19.4				−0.13	−5.7		
	510	19.6			−66^a	(−0.48)	(−21)		
C.T.	365	27.4				+1.14	+5.8		
	355	28.2		+5.3	+12			+1.8	
	328	30.5				−0.9	−1		
C.T.	315	31.7	11720	−1.8	−1.5	+0.4	+0.3		
	307	32.6		−1.2	−1	+0.59	+0.3	−1.13	
	293	34.1				−0.34	−0.12		
C.T.	282	35.5	18880	+3.5	+1.8	+0.8	+0.14	+1.13	
	270	37.0		−0.6	−0.5			−12	
	259	38.6		−5.6	−7.5	+2.4	+4	−28	
C.T.	252	39.7	7600			−0.2	−0.26		
	238	42.0	9400			+1	+1	+28.6	
	223	44.8				+0.4	+0.6		
I.L.	215	46.5				−2.6	−1.7		
	208	48.0				+4.3	+2.0		
I.L.	204	49.0	21200						

^{a}In Voltalef mulls.

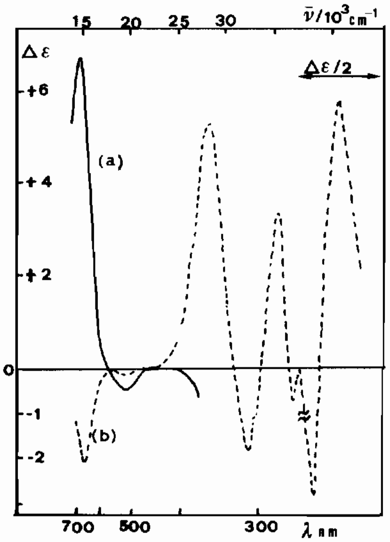


Fig. 4. CD spectra of (−)$_{589}$Cr[(−)bdtp]$_3$ in CHCl$_3$ at 5 °C: a) immediately after solubilization; b) after standing for 24 h since solubilization.

at 535 nm, ε = 223, and 518 nm, ε = 231 (Fig. 3). The comparison with the reported Cr(dtp)$_3$ spectrum allows us to assign the bands on the basis of an octahedral symmetry O_h in the complex (I), to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$, $^4A_{2g} \rightarrow {}^2T_{2g}$ transitions respectively [4, 8–10].

The influence of the ligand field as occurs in tris chelate complexes lowers the symmetry to D_3 and both the excited states of the octahedral symmetry split [1, 4, 11]. The CD spectra in CH$_3$CN and in CHCl$_3$ solutions (Figs. 3 and 4) show a positive Cotton effect at 695, $\Delta\epsilon = +0.15$, $g = +4.6 \times 10^{-4}$, and at 675 nm, $\Delta\epsilon = +6.7$, $g = +2 \times 10^{-2}$, respectively, which could be assigned to the magnetic dipole-allowed doubly-degenerate $^4A_2 \rightarrow {}^4E_a$ component. The $^4A_2 \rightarrow {}^4A_1$ component is completely overlapped and cancelled by the dominant ^4E_a. The magnitude of this CD band in chloroform suggests that a high degree of optical purity is present in the complex (I).

This transition is not observable in the MCD spectra of the corresponding achiral racemic complex, Cr(bdtp)$_3$, (III), where two Faraday terms at

545 and 526 nm respectively, with molar ellipticity, $[\theta]_M = -3 \times 10^{-3}$ and -1.8×10^{-2} degrees deciliter dm^{-1} mol^{-1} per unit gauss, and two small shoulders at higher and lower wavelengths, have been observed.

The registered MCD extrema are very similar to that of the reported Cr(dtp)$_3$, and likewise could be assigned to the $^4A_{2g} \rightarrow {}^4T_{1g}$ and $^4A_{2g} \rightarrow {}^2T_{2g}$ transitions. The CD spectra in the same range show a broad, scarcely-resolved band at 535–515 nm, with a g factor value $\sim 10^{-3}$ which confirms the magnetic dipole-forbidden character of these transitions [1].

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

The Λ-(R,R)(R,R)(R,R) configuration has been tentatively assigned to the (−)$_{589}${Cr[(−)bdtp]$_3$}, (**I**), on the basis of the large positive CD component centred at 675–695 nm in the region of the allowed magnetic dipole $^4A_{2g} \rightarrow {}^4T_{2g}$ transitions [11]. The negative CD band at 665 nm in the same region should characterize the Δ-(R,R)(R,R)(R,R) configuration.

In view of the claimed optical stability of the dithiocarbamates, Cr[dtc]$_3$ [2], it is interesting to note that Λ-(−)$_{589}${Cr[(−)bdtp]$_3$} is optically labile.

In chloroform as well as in deuterochloroform and dichloromethane solution (**I**) inverts quickly, though not completely, to the diastereoisomer (+)$_{589}${Cr[(−)bdtp]$_3$}, (**II**) having a Δ-(RR)(RR)(RR) configuration. The spectra show in fact a lowering of the 675 nm positive band and the progressive growth of a negative Cotton effect at 665 nm, $g = -6 \times 10^{-3}$, indicating the establishment of an equilibrium with the Δ-(RR) form as the excess diastereomer (Fig. 4) [12].

In acetonitrile, acetone, benzene and tetrahydrofuran solutions the Λ-(R,R) complex changes similarly and a steady state is reached after 24 h without a complete inversion reaction. In these solvents the spectra maintain a positive but lower Cotton effect at ~690 nm, $g = +10^{-4}$, and two negative Cotton effects at 630 and 530 nm (Fig. 3) and this is indicative of an excess at equilibrium of the Λ-(RR) over the Δ-(RR) form.

The solvent appears to play a noteworthy role in determining the stability of the two diastereoisomers. The intensity of the changeable CD band at 690–665 nm permits us to establish the diastereoisomeric excess of the Λ-(R,R) $\rightleftharpoons$ Δ-(R,R) equilibrium, and consequently to calculate the diastereoisomeric equilibrium constant, $K = C_{\Delta\text{-(R,R)}}/C_{\Lambda\text{-(R,R)}}$.

We have found an equilibrium mixture of 53% and 47% in THF, 51% and 49% in CH$_3$CN and 37% and 63% in CHCl$_3$ solution of the Λ-(R,R) and Δ-(R,R) diastereoisomers respectively.

A rough determination of K at room temperature (~21 °C) shows values between 0.8 and 1.7 in different solvents, indicating an order of thermodynamic stability of the Λ-(RR) diastereoisomer in tetrahydrofuran > acetonitrile > acetone > benzene and of the Δ-(R,R) diastereoisomer in chloroform > dichloromethane > ethanol solution.

Solutions of Λ-(−)$_{589}${Cr[(−)bdtp]$_3$} in the two di-ethyltartrate chiral solvents (±)DET show indefinitely stable spectra with a positive band at 690 nm, $g = +5 \times 10^{-3}$. Upon dilution of the solution with chloroform a process of inversion begins and, after 15 h, a negative band at about 640 nm is registered with $g = -1 \times 10^{-2}$. Evaporation of the chloroform restores the solution to its initial conditions with a spectrum showing a positive band at 688 nm.

These observations confirm that the solvent contributes to operate the diastereoisomeric discrimination. It is known that chloroform, as well as dichloromethane and benzene, interact strongly with tris dithiocarbamate or carbodithioate metal(III) complexes, both in the solid state and in solution, through hydrogen-bonding with ligand sulphur atoms or other strong static interactions with the ligand [13–16]. Similar interactions should be largely responsible of the stabilization of the Δ-(R,R) with respect to the Λ-(R,R) diastereoisomer. The energy differences between the two diastereoisomers should be small, but the molecular structures should be sufficiently different to justify the particular stabilization of the Λ-(R,R) or of the Δ-(R,R) form operated by the various solvents.

The molecular models in the Δ-(R,R) form show an axial disposition of the ligand alkyl groups with respect to the plane containing the chromium and phosphorus atoms (Scheme 1), which could favour its stabilization and the packing of solvent molecules between the blades of the propeller. On the other hand the equatorial disposition of the alkyl tails in the Λ-(R,R) shape should favour the packing of this diastereoisomer in the solid state.

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