

Circular Dichroism of Chromium(III) Hexadentate edta-type Complexes. Part II*. Ethylenediaminetetra-3-propionatochromate(III) Ion

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Abstract

The hexadentate Cr(III) complex with ethylenediaminetetra-3-propionate (edtp) ion has been prepared and resolved. Infrared, electronic absorption and CD spectra were used to characterize the $[\text{Cr}(\text{edtp})]^-$ complex. The CD data in the region of the d–d transitions are discussed in comparison with those of other edta-type Cr(III) complexes of known configuration. The $(+)_S$ - $[\text{Cr}(\text{edtp})]^-$ complex, having a positive (dominant) CD peak in the first spin-allowed d–d absorption band region, is tentatively assigned the Δ configuration.

Introduction

The $[\text{Co}(\text{edta})]^-$ complex (edta = ethylenediaminetetraacetate) has been investigated by absorption, CD and X-ray studies [2, 3]. The ligands are six-coordinate in $[\text{Co}(\text{edta})]^-$ and directly related $[\text{Co}(S\text{-pdta})]^-$ and $[\text{Co}(S,S\text{-cydta})]^-$ complexes [4–6] ($S\text{-pdta}$ = (S) -1,2-propanediaminetetraacetate; $S,S\text{-cydta}$ = $(1S,2S)$ -1,2-*trans*-cyclohexanediaminetetraacetate). The strain is presumably great enough for the larger Cr(III) ion so that the corresponding complexes of Cr(III) usually are pentadentate with one water molecule occupying the sixth coordination site [7–13]. However, the ^2H NMR studies [9, 10] for deuterated edta and the closely related amino polycarboxylate complexes in solution suggested possibilities of hexadentate edta coordination. Also, there is direct spectroscopic information to prove the hexadentate octahedral coordination in solution for the edta, $S\text{-pdta}$, and $S,S\text{-cydta}$ in Cr(III) complexes [11]. The chiroptical spectra for these complexes [11] were found to be more sensitive to the edta chelate coordination mode or to the change of the ligating atoms than are the ^2H NMR spectra. The corresponding hexadentates of Cr(III)

are formed in weakly acidic solutions (pH ~5.5) and these complexes, as suggested [9–13] in more strongly acidic solutions, are easily dissociated to form less-strained pentadentates having the same *cis*-equatorial configuration as $[\text{Cr}(\text{Hedta})(\text{H}_2\text{O})]$ [14]. The unstable Cr(III) hexadentates were isolated in the solid state and the expected strain of glycinate rings (G in-plane and R out-of-plane) is apparent in the crystal structure of $\text{K}[\text{Cr}(\text{edta})] \cdot 2\text{H}_2\text{O}$ [15] or $\text{Na}[\text{Cr}(\text{rac-cydta})] \cdot 4.5\text{H}_2\text{O}$ [16].

For the preparation of stable hexadentate edta-type Cr(III) complexes it was reasonable to use ligands structurally similar to edta but having longer carboxylate or diamine chains. Such complexes are of interest in the study of factors contributing to their chiroptical spectra [8].

The CD spectra of Co(III) complexes with edta analogues have been discussed in relation to their absolute configurations and theories of optical activity [8, 17, 18]. These complexes have been treated in terms of C_2 symmetry descending from trigonal (D_3) or tetragonal (D_{4h}) symmetry [8, 17–19].

The $[\text{Cr}(1,3\text{-pdta})]^-$ [20] and the $[\text{Cr}(\text{tdta})]^-$ [21] ($1,3\text{-pdta}$ = 1,3-propanediaminetetraacetate; tdta = tetramethylenediaminetetraacetate) were the first reported stable hexadentate edta analogues of Cr(III). In both cases the formation of complexes was attributed to the relief of strain because of the larger chain of the diamine backbone. All attempts at resolution of these hexadentate complexes were fruitless, but a crystallographic study [22] indicates the spontaneous resolution of the $[\text{Cr}(1,3\text{-pdta})]^-$ complex. Three isomers of $[\text{Cr}(1,3\text{-pddda})]^-$ (1,3-pddda is the hexadentate ligand 1,3-propanediamine- N,N' -diacetate- N,N' -di-3-propionate ion) have been reported [23] with a crystal structure of one of the isomers.

The CD spectra in the spin-forbidden d–d transitions of trigonal and tetragonal Cr(III) complexes have been elucidated in comparison with those in the first spin-allowed d–d transitions by using the theoretical relations between the rotational strengths

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[24–26]. The Cr(III) complexes with edta analogues such as, *trans*(O₅)-(–)₅₈₉-[Cr(eddda)][–] [1, 27], *trans*(O₅)-(+)₅₈₉-[Cr(S,S-edds)][–] [1] and (+)₅₈₉-[Cr(S,S-ptnta)][–] [28] (eddda = ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate; S,S-edds = (2*S*,2'*S*)-ethylenediamine-*N,N'*-disuccinate; S,S-ptnta = (2*S*,4*S*)-2,4-pentanediaminetetraacetate) represent the optical isomers of the stable hexadentate edta-type Cr(III) complexes of known Λ(ΛΔΛ) configuration. Their CD spectra in the spin-forbidden and spin-allowed transitions have been examined and discussed [1, 28].

The ethylenediaminetetra-3-propionate (edtp) ion is a hexadentate edta-type ligand in which four carboxylate groups are lengthened (each by one atom) with respect to the edta ligand. The hexadentate edtp complexes with Co(III) [17a] and Rh(III) [29] have been reported and their CD spectra discussed. This paper reports the preparation and the resolution of a new chiral [Cr(edtp)][–] complex. The IR, electronic absorption and CD spectra were used to characterize the complex. Preliminary reports of the absorption and CD spectra [30a] and ²H NMR [30b] have been presented for [Cr(edtp)][–].

Experimental

The H₄edtp ligand was prepared using previously described procedures [17a, 29]. Other reagent grade chemicals and solvents were obtained commercially and used without further purification. For exchange of the cation of the chromium(III) complex, Merck I Analytical Grade cation-exchange resin was used.

Two methods are used for the identification of optical isomers, the sign of the lowest energy CD peak in the ⁴T_{2g} region [(+) or (–)] and the sign of the optical rotation at 589 nm (sodium D line). Δ or Λ is the chirality assigned according to IUPAC rules [31].

Preparation of Lithium (Ethylenediaminetetra-3-propionato)chromate(III) Tetrahydrate, Li[Cr(edtp)]·4H₂O

H₄edtp (1.74 g, 0.005 mol) and NaOH (1.2 g, 0.03 mol) were dissolved with stirring in 100 ml of DMSO at 70 °C. To this solution, CrCl₃·6H₂O (1.33 g, 0.005 mol) was added. The resulting mixture was refluxed with stirring at the same temperature (70 °C) for 2 h (until the solution turned purple–red). After the mixture was left in the refrigerator for 5 h the red–violet crystals were collected from the mother liquor, washed with ethanol, then ether, and air-dried (2.2 g). The precipitate was dissolved in water (ca. 25 ml) and the solution was then introduced into a 5 × 60 cm column containing Dowex 1-X8 (200–400 mesh) anion-exchange resin in the Cl[–] form. The column was then washed with H₂O

and eluted with 0.1 M LiCl solution (ca. 0.5 ml/min). The eluate (red–violet) was evaporated to 10 ml and then was desalted by passage through a G-10 Sephadex column, eluting with distilled water. The eluate was concentrated to a volume of 2 ml and then to dryness in a vacuum desiccator over anhydrous CaCl₂. The crystals of Li[Cr(edtp)]·4H₂O were collected. Total yield: 1.2 g (50%). This complex was also obtained without desalting by addition of ethanol to the concentrated aqueous eluate and cooling in the refrigerator. *Anal. Calc.* for Li[Cr(edtp)]·4H₂O = LiCrC₁₄H₂₈N₂O₁₂ (Formula weight (FW) = 475.32): C, 35.37; H, 5.94; N, 5.89. Found: C, 35.30; H, 6.22; N, 6.06%.

For comparison, the corresponding Co(III) complex was prepared using a previously described procedure [17a]. The complex was converted to the Li⁺ salt using the column technique. *Anal. Calc.* for Li[Co(edtp)]·5H₂O = LiCoC₁₄H₃₀N₂O₁₃ (FW = 500.07): C, 33.61; H, 6.04; N, 5.60; H₂O, 18.00. Found: C, 32.92; H, 6.15; N, 5.96; H₂O, 18.37%.

Resolution of Lithium (Ethylenediaminetetra-3-propionato)chromate(III) Tetrahydrate, Li[Cr(edtp)]·4H₂O

The complex (0.95 g, 0.002 mol) was dissolved in 4 ml of water and converted from the Li⁺ to the Ag⁺ form by passing the solution through a cation-exchange column (Merck I Analytical Grade cation-exchange resin). To the eluate was added an equivalent amount of (–)₅₈₉-[Co(en)₂(ox)]Br·H₂O (0.73 g, 0.002 mol) and the mixture was stirred with heating (60 °C) for 40 min. The mixture was evaporated to a small volume (10 ml), the AgBr was removed by filtration, and washed with 2 ml of warm water. An equal volume of ethanol was added to the filtrate and the solution was cooled slowly to room temperature for 8 h. The precipitated less-soluble diastereoisomer, (–)₅₈₉-[Cr(en)₂(ox)]-(+) ₅₈₉-[Cr(edtp)]·xH₂O was removed by filtration, washed with ethanol and then ether, and air-dried (0.65 g). From the remaining filtrate, after addition of a small amount of ether and standing overnight in a refrigerator, the more soluble diastereoisomer, (–)₅₈₉-[Co(en)₂(ox)]-(–) ₅₈₉-[Cr(edtp)]·xH₂O crystallized. This diastereoisomer was collected and washed with ethanol, then ether and air-dried (0.62 g). Both diastereoisomers were crystallized from a (1:1) water–ethanol mixture to a constant value of optical rotation. Aqueous solutions (0.1%) gave [α]₅₈₉ = –300° for the less soluble and [α]₅₈₉ = –437° for the more soluble diastereoisomer.

The optical isomers in the form of the lithium salts were obtained using an ion-exchange column. The eluates were evaporated to 2 ml and then to dryness in a vacuum desiccator over anhydrous CaCl₂. [α]₅₈₉ = ±120° in 0.05% aqueous solution.

Anal. Calc. for $(+)_589\text{-Li}[\text{Cr}(\text{edtp})]\cdot 3\text{H}_2\text{O} = \text{LiCr}\cdot \text{C}_{14}\text{H}_{26}\text{N}_2\text{O}_{11}$ (FW = 457.30): C, 36.77; H, 5.73; N, 6.13. Found: C, 37.26; H, 5.74; N, 6.85%.

Physical Measurements

The $[\alpha]_{589}$ values were measured in a 1 dm tube at 20 °C on a Perkin-Elmer SP polarimeter.

Infrared spectra were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer using KBr disks.

Electronic absorption spectra were recorded on a Varian SuperScan 3 recording spectrophotometer. For these measurements 3.5×10^{-3} M aqueous solutions were used.

CD spectra were measured by a JASCO (J-500A) spectropolarimeter. For these measurements 1 to 2 mM aqueous solutions were used.

Analysis

Elemental microanalyses for carbon, hydrogen and nitrogen were performed by the Microanalytical Laboratory, Department of Chemistry, Faculty of Science, University of Belgrade, Belgrade, Yugoslavia.

Results and Discussion

Infrared Spectra

As was demonstrated for metal aminocarboxylic acid complexes [32, 33], the asymmetric stretching frequency of the carboxylate groups of the five-membered [32] rings lie at higher energy than the corresponding frequency of the six-membered chelate rings [33]. Later, this was supported by Neal and Rose [18a] and Douglas *et al.* [1, 34] who found that edta-type hexadentate complexes with mixed and equivalent (two five- and two six-membered) carboxylate arms, such as *trans*(O₅)-[M(S,S-edds)]⁻ [1, 18a, 34] and *trans*(O₅)-[M(eddda)]⁻ [1, 34] exhibit two very strong and well-separated bands in the asymmetric stretching carboxylate frequency region. This is in agreement with their C₂ molecular symmetry. The bands were assigned to the carbonyl stretching vibrations of the five-membered rings at higher energy and six-membered rings at lower energy.

As reported for the [Rh(edtp)]⁻ complex [29], both [Cr(edtp)]⁻ and the earlier reported [Co(edtp)]⁻ [17a] complexes exhibit very strong bands (nearly the same shape) in the asymmetric stretching carboxylate frequency region (*ca.* 1600 cm⁻¹, Fig. 1), indicating that all carboxylate groups are coordinated [35–37]. The acid forms of these complexes obtained by ion-exchange techniques show no evidence of protonated carboxylate groups in the expected spectral region (1700–1750 cm⁻¹) [37]. As expected [1], the energies of the coordinated

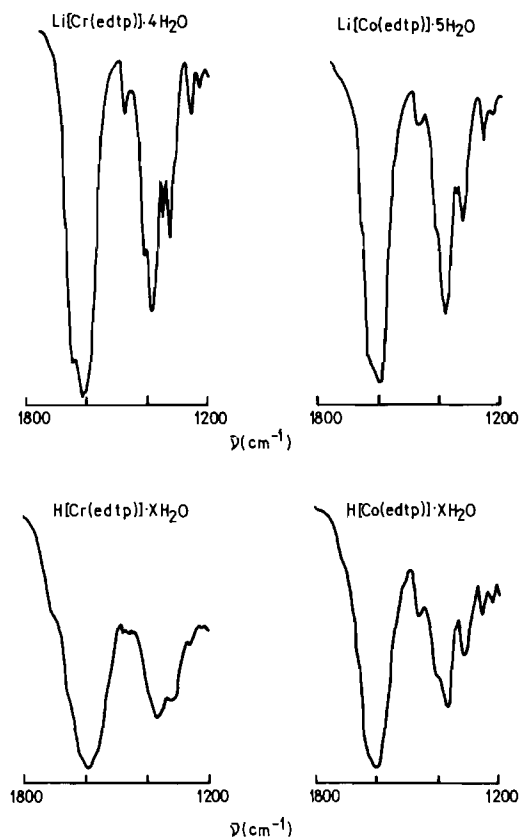


Fig. 1. Portions of the infrared spectra of [M(edtp)]⁻ complexes.

carboxylate bands differ slightly for Co(III) and Cr(III) complexes (at *ca.* 1590 cm⁻¹ for the Co(III) and 1600 cm⁻¹ for the Cr(III) complex, see Fig. 1).

Electronic Absorption and CD Spectra

In O_h symmetry the lower energy spin-allowed band for Cr(III) is ⁴A_{2g} → ⁴T_{2g} and the one at higher energy is ⁴A_{2g} → ⁴T_{1g}. The corresponding transitions for low-spin Co(III) are ¹A_{1g} → ¹T_{1g} and ¹A_{1g} → ¹T_{2g}, respectively. The symmetries of the spin-allowed transitions (cross products of ground and excited states) for these two systems are the same, T_{1g} and T_{2g} in order of increasing energy. The electronic absorption and CD data for the [Cr(edtp)]⁻ complex (Fig. 2, Table I) are compared to those of (-)₅₈₉-*trans*(O₅)-[Cr(eddda)]⁻, (+)₅₈₉-*trans*(O₅)-[Cr(S,S-edds)]⁻ and (+)₅₈₉-[Cr(S,S-ptnta)]⁻ complexes of known configuration [1, 27, 28].

The two symmetrical absorption bands suggest that the [Cr(edtp)]⁻ complex has pseudo-octahedral symmetry. The energies of the absorption bands of this complex observed at 18550 cm⁻¹ (ε₁ = 183, band I) and at 25110 cm⁻¹ (ε₂ = 71, band II) are lower with respect to those of other edta-type Cr(III) complexes (Table I). One way to compare the ligands

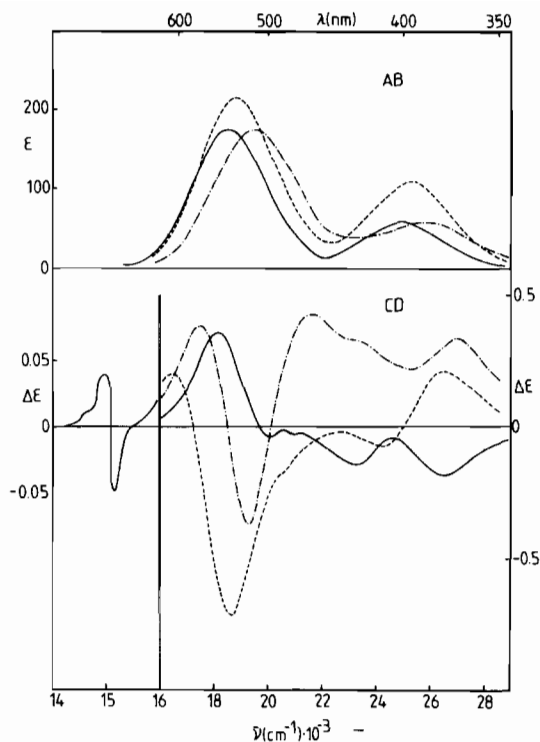


Fig. 2. Electronic absorption and CD spectra of: $\Lambda(-)_{589}\text{-trans}(\text{O}_5)\text{-[Cr(eddda)]}^-$ (---), $\Lambda(+)-_{589}\text{-trans}(\text{O}_5)\text{-[Cr(S,S-edds)]}^-$ (-·-·-), $\Delta(-)-_{589}\text{-[Cr(edtp)]}^-$ (·····), $\Delta(+)-_{589}\text{-[Cr(edtp)]}^-$ (—).

is to assume that each ligand provides an approximately cubic field for the Cr(III). Then clearly the Dq for edtp, representing the 'average' environment, is smaller than those for S,S -edds, S,S -ptnta, and eddda. This comparison suggests that edtp, with its four six-membered carboxylate rings and one five-membered diamine backbone ring represents a weaker-field ligand toward Cr(III) than these other ligands (Table I). The variations in energies and intensities of the spin-allowed bands for these complexes may arise from the structural characteristics involving the chelate rings, i.e. the different combination of the chelate rings (two O_5 - and two O_6 -carboxylate rings) in the 'tetragonal' plane (CrN_2O_2 -plane) and in the axial positions.

Although the absorption bands show no apparent splitting, $cis\text{-[Cr(N)}_2(\text{O})_4]$ type complexes have been treated successfully using holohedrized D_{4h} symmetry [38]. The splitting expected for the lower symmetry is apparent in the CD spectrum of $[\text{Co}(\text{edtp})]^-$. Since the energy of the maximum for the lower energy [$A_{2g} \rightarrow T_{2g}(\text{O}_h)$] absorption band corresponds closely with the energy of the lowest energy (dominant) spin-allowed CD peak, the lower energy ${}^4B_1 \rightarrow {}^4E_g(D_{4h})$ component must be dominant and determine the position of the absorption band. This case, with six-membered rings to the axial and in-plane oxygens, results in enhancement

of the intensity of the degenerate transition. The opposite pattern was noted for $cis\text{-[Cr(N)}_2(\text{O})_4]$ complexes with 5-6-5-membered chelate rings in the diamine plane [23].

The CD pattern in the lower energy spin-allowed absorption band for $\text{trans}(\text{O}_5)\text{-[Cr(S,S-edds)]}^-$ and $\text{trans}(\text{O}_5)\text{-[Cr(eddda)]}^-$ (Fig. 1) shows two prominent CD peaks of opposite sign with some indication of a shoulder at higher energy. Three components are expected for the proper C_2 symmetry. The expected complete removal of degeneracy is observed in some related complexes of Cr(III) [28] and Co(III) [2, 18c] with C_2 symmetry. Because of small splitting of the absorption bands, effective D_{4h} symmetry has been used for absorption spectra. This lowest energy CD components for hexadentate edta-type Co(III) complexes (A or $B(C_2)$ or $E(D_{4h})$) are positive for the $\Lambda(\Lambda\Delta\Lambda)$ configuration for Co(III) complexes [8, 17–19].

The lowest energy spin-allowed CD peak for Cr(III) edta-type complexes has been assigned ${}^4B(C_2)$ derived from ${}^4E_g({}^4T_{2g})$ with the same CD sign as the parent 4E_g [28] as for the corresponding Co(III) complexes [8, 17, 18, 39]. The next higher energy CD peak with opposite sign has nearly the same energy as the absorption maximum. For $[\text{Cr}(\text{edtp})]^-$ the lowest energy CD peak in the spin-allowed region dominates this region and corresponds closely ($18\,180\text{ cm}^{-1}$) with the absorption maximum ($18\,550\text{ cm}^{-1}$). This must correspond to the second CD peak of $\text{trans}(\text{O}_5)\text{-[Cr(S,S-edds)]}^-$ and $\text{trans}(\text{O}_5)\text{-[Cr(eddda)]}^-$. The lowest energy ${}^4B(C_2)$ CD peak is masked or cancelled in the case of $[\text{Cr}(\text{edtp})]^-$. Using the signs of the major peaks corresponding in energy to the absorption band, $(+)_{589}\text{-[Cr}(\text{edtp})]^-$ is assigned the Δ configuration, opposite to that of the other complexes shown in Fig. 1. The two negative CD peaks within the higher energy spin-allowed absorption band have opposite signs compared to $\Lambda\text{-[Cr(S,S-edds)]}^-$ and the more intense higher energy CD peak is opposite in sign to that of $\Lambda\text{-trans}(\text{O}_5)\text{-[Cr(eddda)]}^-$. There are two very weak negative CD peaks at $20\,080$ and $21\,010\text{ cm}^{-1}$. The one at $20\,080\text{ cm}^{-1}$ is probably the high-energy component of the ${}^4A_{2g} \rightarrow {}^4T_{1g}(\text{O}_h)$ transition. The other CD peak probably corresponds to the component of the spin-forbidden ${}^4A_{2g} \rightarrow {}^2T_{2g}(\text{O}_h)$ expected between the spin-allowed bands.

For the S,S -ptnta and S,S -edds M(III) complexes [$M = \text{Co(III)}$ or Cr(III)], the absolute configuration (Λ) based on the CD criteria is consistent with that determined from the stereospecific coordination of the hexadentate chiral ligands to M(III) [1, 17e, 18a, 28] (the S,S -edds and S,S -ptnta ligands are stereospecific giving only complexes with the Λ configuration). The CD spectra of the $(-)_{589}\text{-trans}(\text{O}_5)\text{-[Cr(eddda)]}^-$, $(+)_{589}\text{-trans}(\text{O}_5)\text{-[Cr(S,S-edds)]}^-$ and $(+)_{589}\text{-[Cr(S,S-ptnta)]}^-$ complexes with

TABLE I. Absorption (AB) and Circular Dichroism (CD) Data of Chromium(III) Hexadentate edta-type Complexes

Complex ion	AB		CD		Reference
	$\nu \times 10^3$ (cm^{-1})	ϵ	$\nu \times 10^3$ (cm^{-1})	$\Delta\epsilon^a$	
$\Lambda(+)_589\text{-trans}(\text{O}_5)\text{-[Cr(S,S-edds)]}^-$	19.60	175	17.54	+0.41 ^b	1, 28
			19.33	-0.39	
			21.83	+0.45	
	16.00	57	23.50sh	+0.34	
			26.99	+0.38	
$\Lambda(-)_589\text{-trans}(\text{O}_5)\text{-[Cr(eddda)]}^-$	18.90	214	16.53	+0.20 ^b	1, 28
			18.62	-0.77	
			20.33sh	-0.20	
	25.30	107	22.17sh	-0.05	
			24.10	-0.08	
		26.53	+0.23		
$\Lambda(+)_589\text{-[Cr(S,S-ptnta)]}^-$	19.64	110	18.00sh	+0.20 ^b	28
			19.67	+0.44	
			21.67	-0.06	
	25.97	77	24.00	+0.44	
			25.25sh	+0.27	
		29.66	-0.02		
$\Delta(+)_589\text{-[Cr(edtp)]}^-$	18.55	183	15.01	+0.04	
			15.20	-0.05	
			18.24	+0.37	
	25.11	71	20.08	-0.04	
			21.01	-0.02	
		23.20	-0.14		
		26.52	-0.18		

^aThe values are given in units of $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$. ^bThis band was assigned to the ${}^4\text{B}(\text{C}_2)$ state (ref. 28).

a Λ configuration (see Table I) give a positive CD component at the low frequency side of the first spin-allowed absorption band. This assignment has been verified crystallographically in the case of the $(-)_589\text{-trans}(\text{O}_5)\text{-[Cr(eddda)]}^-$ complex ion [27].

The CD spectra in the spin-allowed band region of the $(+)_589\text{-[Cr(S,S-ptnta)]}^-$ [28] and $(+)_589\text{-[Cr(edtp)]}^-$ complexes are much different from those of the corresponding Co(III) complexes [17a,e] whereas the CD spectra of the $(+)_589\text{-trans}(\text{O}_5)\text{-[Cr(S,S-edds)]}^-$ and $(-)_589\text{-[Cr(eddda)]}^-$ complexes [1] are similar in shape to those of the corresponding $\text{trans}(\text{O}_5)$ isomers of Co(III) complexes [17b, c, 18a, c].

The CD spectrum for $[\text{Cr(edtp)}]^-$ in the low-energy spin-forbidden region is not as detailed as the spectra observed [28] for $[\text{Cr(S,S-edds)}]^-$, $\text{trans}(\text{O}_5)\text{-[Cr(eddda)]}^-$ and $[\text{Cr(S,S-ptnta)}]^-$. No CD peak was observed near $14\,200 \text{ cm}^{-1}$ for $[\text{Cr(edtp)}]^-$, perhaps because of lower sensitivity of the CD instrument in comparison to Kaizaki's report. The two prominent CD peaks for $(+)_589\text{-[Cr(edtp)]}^-$ are at $15\,010 \text{ cm}^{-1}$ (positive) and $15\,200 \text{ cm}^{-1}$ (negative). These correspond to the negative CD

peaks at $14\,870 \text{ cm}^{-1}$ and positive peaks at *ca.* $15\,300 \text{ cm}^{-1}$ for $[\text{Cr(S,S-edds)}]^-$ and $\text{trans}(\text{O}_5)\text{-[Cr(eddda)]}^-$ as reported [28]. The signs for $(+)_589\text{-[Cr(edtp)]}^-$ are opposite those of corresponding peaks for the complexes with the Λ configuration reported by Kaizaki and Mori [28]. This is consistent with the assignment $\Delta(+)_589\text{-[Cr(edtp)]}^-$ based on the CD spectrum in the spin-allowed region.

As was reported recently [30b] the $[\text{Cr(edtp)}]^-$ complex ion appears to form three conformational isomers due to fixed 3-propionate (λ) conformation in the R(out-of-plane) rings. These combinations were denoted as: $\text{lel}_2(\delta\delta)$, $\text{lelob}(\delta\lambda)$, $\text{ob}_2(\lambda\lambda)$, where *lel* and *ob* denote the orientation of the 3-propionate ethylene C–C bonds with respect to the C_2 axis of the complex. Only one isomer was isolated in this work. We believe it to be the most stable lel_2 isomer reported [30b].

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