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Circular dichroism of chromium(III) hexadentate edta-type complexes Part III*. Ethylenediamine-*N*-acetato-*N*,*N*′,*N*′-tri-3-propionatochromate(III) ion

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Abstract

A new hexadentate chromium(III) complex with ethylenediamine-*N*-acetic-*N*,*N*′,*N*′-tri-3-propionic acid [H_4eda3p) is reported. Only one (*trans*(O_5O_6)) geometrical isomer of the [Cr(eda3p)]$^-$ complex ion was prepared and resolved into optical isomers. IR, electronic absorption and CD spectra were used for characterizing the complex. 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 $(-)_{589}$-isomer of the *trans*(O_5O_6)–[Cr(eda3p)]$^-$ complex, having a positive CD peak at lowest energy in the first spin-allowed d–d absorption band region, is tentatively assigned the Λ configuration.

Introduction

Spectral and X-ray data for the [Co(edta)]$^-$ complex (edta = ethylenediaminetetraacetate ion) are known [3, 4]. This system, having a diamine backbone ring (E ring) with two different pairs of glycinate rings (G rings in equatorial positions and R rings in axial positions), was found to be strained [4]. Both G rings of this complex are more strained than the R glycinate rings. Similar results can be expected in the directly related [Co(*S*-pdta)]$^-$ and [Co(*S*,*S*-cydta)]$^-$ complexes [5, 6] containing six-coordinate ligands forming only five-membered rings (*S*-pdta = (*S*)-1,2-propanediaminetetraacetate ion; *S*,*S*-cydta = (1*S*,2*S*)-1,2-*trans*-cyclohexanediaminetetraacetate ion).

The strain is great enough for the larger Cr(III) ion so that the corresponding Cr(III) complexes are usually pentadentate [7–13]. However, there is direct spectroscopic information to prove hexadentate coordination in solution for the edta, *S*-pdta and *S*,*S*-cydta Cr(III) complexes [11]. These hexadentates are formed in weakly acidic solutions (pH ~ 5.5). Hexadentates in strongly acidic solutions are reported [9–13] to be dissociated to form less-strained pentadentates having the *cis*-equatorial configuration such as [Cr(Hedta)(H_2O)] [14]. Very strained hexadentate complexes of Cr(III), with ligands forming only five-membered rings, have been isolated and expected strain of the glycinate rings is apparent in the crystal structure of K[Cr(edta)]·$2H_2O$ [15] or Na[Cr(*rac*-cydta)]·$4.5H_2O$ [16].

Factors determining structural types of edta and related complexes have been discussed in detail in terms of the d-electron configuration of and the size of the central metal ion M, and the difference in bond lengths between the M–N and M–O bonds involved [17].

Complexes less strained than [M(edta)]$^-$ contain ligands that are structurally similar to edta but have a longer diamine backbone or carboxylate chains. Studies of these complexes were directed to determine the influence of various structural changes of the ligand, relative effects of these structural changes, and other factors on their optical activity [8].

These [Co(edta-type)]$^-$ complexes have been treated in terms of C_2 symmetry and their CD spec-

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tra were discussed in relation to their absolute configurations and theories of optical activity [8, 18–20].

Two complexes, $[Cr(1,3\text{-pdta})]^-$ [21] and $[Cr(tdta)]^{-1}$ [22] (1,3-pdta = 1,3-propanediaminetetraacetate ion; tdta = tetramethylenediaminetetraacetate ion), were the first reported stable hexadentates of Cr(III) and their stability was attributed to the relief of strain because of the longer chain of the diamine backbone. Neither of these reported complexes was resolved. However, a crystallographic study [23] indicates the spontaneous resolution of the $[Cr(1,3\text{-pdta})]^-$ complex. The $[Cr(1,3\text{-pddadp})]^-$ complex (1,3-pddadp = 1,3-propanediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate ion) also contains a stable hexadentate ligand. The complex was prepared and separated into the three geometrical isomers with respect to the N–O chelate ring size: (*trans*(O_5), *trans*(O_5O_6) and *trans*(O_6)). These isomers were characterized through the combined use of ^2H NMR, magnetic circular dichroism, and single-crystal X-ray diffraction analysis [24].

Circular dichroism spectral changes throughout the region of d–d transitions for trigonal and tetragonal Cr(III) complexes, including spin-forbidden transitions, have been discussed based upon theoretical considerations of rotational strengths [25–27]. Optical isomers of the stable hexadentate of known $\Lambda(\Lambda\Delta\Lambda)$ configuration have been established for *trans*(O_5)–$(-)_{589}$-$[Cr(eddadp)]^-$ [1, 28, 29], *trans*-(O_5)–$(+)_{589}$-$[Cr(S,S\text{-edds})]^-$ [1] and $(+)_{589}$-$[Cr(S,S\text{-ptnta})]^-$ [29] (eddadp = ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate ion; *S*,*S*-edds = (2*S*,2′*S*)-ethylenediamine-*N*,*N*′-disuccinate ion; *S*,*S*-ptnta = (2*S*,4*S*)-2,4-pentanediaminetetraacetate ion). Using the assumption of effective C_2 symmetry for complexes of this type, the lowest-frequency CD component in the first band region was assigned to the $^4B(C_2)$ state, for which CD signs are considered to be the same as those for the $^4B(C_2)$ state with $^4E(^4T_{2g})$ trigonal parentage or with $^4E(^4T_2g)$ tetragonal parentage as in the case of $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions for Co(III) complexes [8, 18].

The $[Cr(edtp)]^-$ complex (edtp = ethylenediaminetetra-3-propionate ion) [30] appears to form three conformational isomers due to a fixed 3-propionate (λ) conformation in the R (out-of-plane) rings: $lel_2(\delta\delta)$, lelob ($\delta\lambda$), $ob_2(\lambda\lambda)$ (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 (the most stable lel_2) isomer of this complex was resolved [2, 31]. The $(+)_{589}$-$[Cr(edtp)]^-$ with positive major CD peaks corresponding in energy to the absorption band was assigned the Δ configuration, as confirmed crystallographically [31].

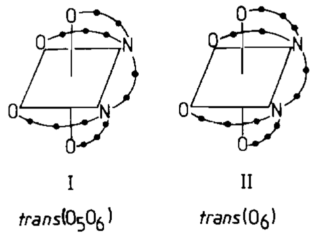

Fig. 1. Two possible geometrical isomers of Λ-$[Cr(eda3p)]^-$.

The unsymmetrical edta-type ligand, ethylenediamine-*N*-acetate-*N*,*N*′,*N*′-tri-3-propionate ion (eda3p), on hexadentate coordination, forms two five-membered and three six-membered rings. Two geometrical isomers with respect to the N–O chelate ring size can be expected: *trans*(O_5O_6) (I) and *trans*(O_6) (II) (Fig. 1). Only one, the *trans*(O_5O_6) geometrical isomer of the $[Co(eda3p)]^-$ complex, has been prepared and resolved [18f]. This paper deals with the preparation and resolution of the corresponding *trans*(O_5O_6)–$[Cr(eda3p)]^-$ complex. IR, electronic absorption and CD spectra were used to characterize the complex. The isomer reported here has the configuration expected to be most favorable, from considerations of chelate ring strain.

Experimental

Ethylenediamine-*N*-acetic-*N*,*N*′,*N*′-tri-3-propionic acid (H_4eda3p) was prepared according to the procedure described in the literature [18f]. Other reagents were obtained commercially and used without further purification.

Optical isomers are identified by (+) or (−), corresponding to the sign of the lowest energy CD peak in the $^4T_{2g}$ region, or by the sign of the optical rotation at 589 nm (sodium D line). Chirality is designated as Δ or Λ according to IUPAC rules [32].

Preparation of the trans(O_5O_6) geometrical isomer of lithium(ethylenediamine-N-acetato-N,N′,N′-tri-3-propionato)chromate(III) trihydrate, Li[Cr(eda3p)]·3H_2O

For the preparation of this complex the ligands synthesis product containing a mixture of acids (H_4edtp + H_4eda3p) [18f] was used. H_4edtp + H_4eda3p (3.48 g, ~0.01 mol) and NaOH (2.00 g, 0.05 mol) were dissolved with stirring in 100 ml of DMSO at 80 °C. To this solution $CrCl_3 \cdot 6H_2O$ (2.66 g, 0.01 mol) was added. The mixture turned purple–red when the solution was refluxed with stirring at 80 °C for 3 h. The mixture was allowed to cool to room temperature and then cooled to 0 °C and allowed to stand for 5 h. Red–violet crystals were collected, washed with ethanol and then ether, and air-dried (*c*. 3 g). The precipitate was dissolved in water (*c.* 25 ml) and the solution was passed through a 5 × 60 cm column containing Dowex 1-X8 (200–400 mesh) anion-exchange resin in the Cl^- form. Two red–violet bands were obtained (*c.* 3:1) when the column was washed with H_2O and eluted with a 0.1 M LiCl solution. The first and second eluates were evaporated to 10 ml and desalted by passage through a G-10 Sephadex column, eluting with distilled water. Each eluate was concentrated to a volume of 3 ml and then to dryness in a vacuum desiccator over anhydrous $CaCl_2$. Red–violet crystals were collected. Yield: 2 g of $Li[Cr(edtp)]\cdot 4H_2O$ [2] (the first band) and 0.6 g of Li(*trans*(O_5O_6)[Cr(eda3p)]$\cdot 3H_2O$ (the second band). These complexes were also obtained without desalting by gradual addition of small amounts of ethanol to concentrated solutions and cooling in the refrigerator. *Anal.* Calc. for *trans*(O_5O_6)–Li[Cr(eda3p)]$\cdot 3H_2O = LiCrC_{13}H_{24}N_2O_{11}$ (formula weight (FW) = 443.27): C, 35.22; H, 5.45; N, 6.32. Found: C, 34.30; H, 5.00; N, 6.39%.

For comparison, the corresponding complex of Co(III) of known (*trans*(O_5O_6)) configuration [18f] was also prepared.

Resolution of the trans(O_5O_6) geometrical isomer of lithium(ethylenediamine-N-acetato-N,N′,N′-tri-3-propionato)chromate(III) trihydrate, Li-trans(O_5O_6)[Cr(eda3p)]$\cdot 3H_2O$

The complex (0.44 g, 0.001 mol) was dissolved in a small amount of water and converted from the Li^+ to the Ag^+ form by using a cation-exchange column (Merck I Analytical Grade cation-exchange resin was used for that purpose). An equivalent amount of $(-)_{589}$-$[Co(en)_2(ox)]Br\cdot H_2O$ (0.37 g, 0.001 mol) was then added to the eluate and the mixture was stirred with heating (60 °C) for 30 min. AgBr was removed by filtration and washed with 2 ml of water. The combined filtrate and washing was reduced on a steam bath to a volume of 10 ml and allowed to stand at room temperature overnight. The precipitated less-soluble diastereoisomer, $(-)_{589}$-$[Co(en)_2(ox)]$–$(-)_{589}$-[Cr(eda3p)]$\cdot 3H_2O$ was removed by filtration, washed with ethanol and then ether, and air-dried (0.34 g). Two volumes of ethanol and some ether was then added to the filtrate and the solution was left to stand at room temperature for several hours. The precipitate (a mixture of both diastereoisomers) was removed (0.1 g). The remaining filtrate was then allowed to stand in the refrigerator for several days. The more soluble diastereoisomer, $(-)_{589}$-$[Co(en)_2(ox)]$–$(+)_{589}$-[Cr(eda3p)]$\cdot 3H_2O$ was collected by filtration, washed with ethanol and then ether, and air-dried (0.28 g). Both diastereoisomers were crystallized from water (or water–ethanol (1:2) mixture) to constant values of optical rotation. Aqueous solutions (0.1%) gave $[\alpha]_{589} = -599°$, $[\alpha]_{546} = -653°$ and $[\alpha]_{589} = -245°$, $[\alpha]_{546} = -390°$ for the less and more soluble diastereoisomers, respectively. Corresponding enantiomers in the form of the lithium salt were obtained by dissolving each of these diastereoisomers in water and passing their solutions through a cation-exchange column in the Li^+ form. These eluates were evaporated to a volume of 3 ml and then to dryness after standing in a desiccator over $CaCl_2$. $[\alpha]_{589} = \mp 240°$, $[\alpha]_{546} = \mp 175°$ in 0.05% aqueous solution. *Anal.* Calc. for $(-)_{589}$-$[Co(en)_2(ox)]$–$(-)_{589}$-[Cr(eda3p)]$\cdot 3H_2O = CoCrC_{19}H_{40}N_6O_{15}$ (FW = 703.48): C, 32.44; H, 5.73; N, 11.95. Found: C, 32.61; H, 5.96; N, 12.42%. *Anal.* Calc. for $(-)_{589}$-$[Co(en)_2(ox)]$–$(+)_{589}$-[Cr(eda3p)]$\cdot 3H_2O = CoCrC_{19}H_{40}N_6O_{15}$ (FW = 703.48): C, 32.44; H, 5.73; N, 11.95. Found: C, 32.87; H, 5.68; N, 12.55%. *Anal.* Calc. for $(-)_{589}$-*trans*(O_5O_6)–Li[Cr(eda3p)]$\cdot 3H_2O = LiCrC_{13}H_{24}N_2O_{11}$ (FW = 443.27): C, 35.22; H, 5.45; N, 6.32. Found: C, 35.47; H, 5.32; N, 6.34%.

Physical measurements

Measured $[\alpha]_\lambda$ values were obtained in a 1 dm tube at 20 °C on a Perkin-Elmer SP polarimeter.

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

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

Circular dichroism (CD) spectra were recorded at room temperature with a Jobin-Yvon Dichrographe III using a Xenon Arc Source.

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

The edta-type ligands forming six-membered (β-alaninate) chelate rings (*S,S*-edds, eddadp, edtp and eda3p ligands) are likely to function as hexadentate ligands with Co(III) or even with the larger Cr(III). The ligand *S,S*-edds was found to coordinate stereospecifically giving only one (*trans*(O_5)) geometrical isomer of known *Λ* configuration [1] (also a *trans*(O_6) isomer is possible in this case). Three isomers are possible (*trans*(O_5), *trans*(O_5O_6) and *trans*(O_6)) for a hexadentate complex of eddadp. The favored *trans*(O_5) geometrical isomer was found to dominate in complexes of Co(III) [18b, c] or Cr(III) [1, 28].

In both cases *trans*(O_5) isomers might be favored since larger chelate rings in the G plane should relieve the strain present in $[M(edta)]^-$ [4, 15].

Isomers of the $[M(eda3p)]^-$ complex (Fig. 1) differ in the position of the glycinate ring: the glycinate ring in an axial position (R ring), *trans*(O_5O_6), and the glycinate ring in an equatorial position (G ring), *trans*(O_6). Both isomers have a rhombic ligand field and C_1 molecular symmetry. These isomers also have pseudo-D_{4h} (holohedrized) symmetry with quasi-C_4 axes being perpendicular to the plane containing the diamine ring. Because of the observed larger strain for G rings [4, 15] than for the corresponding R rings it was expected that the *trans*(O_5O_6) isomer (Fig. 1, isomer **I**) with larger (six-membered) chelate rings in the G plane should form preferentially. This favored isomer (*trans*(O_5O_6)) was the one reported with Co(III) [18f] for which the geometry was assigned on the basis of its ^1H NMR spectrum. Based on the metal ion size (Co < Cr) the formation of *trans*(O_5O_6) geometrical isomers might be expected to be even more strongly favored for Cr(III) than for Co(III).

IR spectra and geometry of complexes

In the asymmetric carboxylate stretching region, as was found for metal aminocarboxylic acid complexes [33, 34], the frequency assigned to five-membered rings [33] lies at higher energy than the corresponding frequency of six-membered chelate rings [34]. This has been clearly demonstrated in $[M(edta\text{-}type)]^-$ complexes containing ligands with mixed (five- and six-membered) carboxylate arms, such as *trans*(O_5)–$[M(S,S\text{-}edds)]^-$ [1, 19a, 35] and *trans*(O_5)–$[M(eddadp)]^-$ [1, 35]. These complexes with C_2 molecular symmetry exhibit two very strong and well-separated bands in the asymmetric stretching carboxylate frequency region which were assigned to carbonyl stretching vibrations of five-membered rings at higher energy (~1640 cm^{-1}) and six-membered rings at lower energy (~1570 cm^{-1}).

For $[M(eda3p)]^-$ complexes both expected isomers (Fig. 1) have the same C_1 molecular symmetry (acid solutions of these complexes show no evidence of protonated carboxylate groups in the expected spectral region (1700–1750 cm^{-1}) [36]. As seen in Fig. 2, both Co(III) and Cr(III) complexes exhibit only one very strong band in the asymmetric stretching carboxylate frequency region (*c*. 1590 cm^{-1}), indicating that all carboxylate groups are coordinated [36–38]. Frequencies of these bands are nearly the same for both complexes and there is no evidence of their resolution. Possibly even four frequencies could appear because of their C_1 molecular symmetry with four non-equivalent coordinated carboxylate groups. However, each complex (see Fig. 2) exhibits one band having nearly the same shape indicating that $[Cr(eda3p)]^-$ has the same (*trans*(O_5O_6)) geometrical configuration (Fig. 1, isomer **I**) as found for $[Co(eda3p)]^-$ [18f].

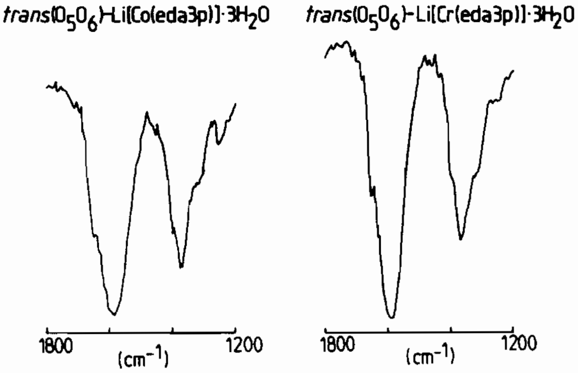

Fig. 2. Portions of IR spectra of $[M(eda3p)]^-$ complexes.

Electronic absorption and CD spectra

Electronic absorption and CD spectra should be qualitatively similar with respect to splittings of spin-allowed d–d transitions for strong O_h fields for Cr(III) $(t_{2g})^3$ and low-spin Co(III) $(t_{2g})^6$ complexes. The lower energy spin-allowed absorption band for Cr(III) in O_h is $^4A_{2g} \rightarrow {}^4T_{2g}$ and the one at higher energy is $^4A_{2g} \rightarrow {}^4T_{1g}$, corresponding for low-spin Co(III), to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1T_{1g} \rightarrow {}^1T_{2g}$, respectively. Symmetries of the transitions for these two systems are the same, T_{1g} and T_{2g} in order of increasing energy.

Electronic absorption and CD spectra for the $(-)_{589}$-*trans*(O_5O_6)–$[Cr(eda3p)]^-$ complex are shown in Fig. 3 in comparison to those of the Λ-$(-)_{589}$-*trans*(O_5)–$[Cr(eddadp)]^-$ [1, 28, 29] and Λ-$(+)_{589}$-*trans*(O_5)–$[Cr(S,S\text{-}edds)]^-$ [1]. Corresponding numerical data for these and other related edta-type complexes are summarized in Table 1. Absorption spectra of these and other edta-type Cr(III) complexes (Fig. 3, Table 1) are very similar with two bands corresponding to transitions to the $^4T_{2g}$ and $^4T_{1g}(O_h)$ states. Bands I and II are symmetrical showing no obvious splitting.

The edtp ligand [2], with its four six-membered carboxylate rings, represents a weaker-field ligand toward Cr(III) than these other edta-type ligands (Table 1). Variation in energies and intensities of spin-allowed bands for these complexes may arise from changes in the local symmetry at the metal center from different combinations of chelate rings (O_5- and O_6-carboxylate rings) in the planar (CrN_2O_2 plane) and axial positions. Absorption bands for complexes shown (Table 1) shift to lower energy on going from $[Cr(S,S\text{-}ptnta)]^-$, having four glycinate rings, to $[Cr(edtp)]^-$, having four 3-propionate rings. Absorption energies of the *trans*(O_5O_6)–

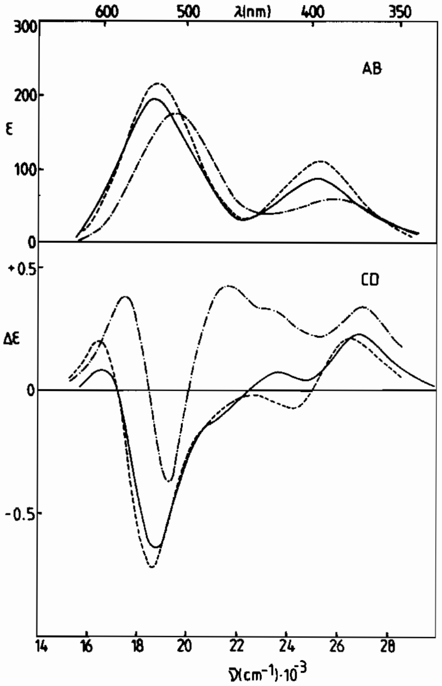

Fig. 3. Electronic absorption and CD spectra of: Λ-$(-)_{589}$-*trans*(O_5)–$[Cr(eddadp)]^-$ (– – –), Λ-$(+)_{589}$-*trans*(O_5)–[Cr-(*S*,*S*-edds)$]^-$ (– · –), Λ-$(-)_{589}$-*trans*(O_5O_6)–$[Cr(eda3p)]^-$ (——).

$[Cr(eda3p)]^-$ complex, containing one glycinate and three 3-propionate rings (the bands at 18 690 cm^{-1}, $\epsilon_1 = 194$, and at 25 120 cm^{-1}, $\epsilon_2 = 86.6$), are closer to those of $[Cr(edtp)]^-$ than to those of $[Cr(eddadp)]^-$. The observed trend regarding positions of absorption maxima for these complexes is in accordance with the decrease in ligand field strengths on going from the *S*,*S*-ptnta to the edtp ligand (edtp < eda3p < eddadp < *S*,*S*-edds ~ *S*,*S*-ptnta). Both ϵ and $\Delta\epsilon$ values for edta-type Cr(III) complexes are significantly lower than for the corresponding Co(III) complexes [8, 18, 19a]. As might be predicted [39, 40], the less-strained complexes related to $[Cr(edta)]^-$, with expected less distortion from O_h symmetry because of the decrease in ring strain ($[Cr(edtp)]^- < [Cr(eda3p)]^- < [Cr(eddadp)]^-$), have lower intensities for visible absorption bands and their CD spectra show decreases in net rotational strength.

CD spectra of these complexes given in Table 1, as usual, exhibit resolution of spectral components of these absorption bands. By comparison of positions of CD peaks and distinct shoulders within the envelope of the corresponding absorption band maxima, there are indications of three CD components under the first spin-allowed d–d absorption band for all of these complexes (Table 1). The complete removal of the degeneracy of the triplet state (O_h parentage) is expected for the actual symmetry of these complexes as was observed in some complexes of Cr(III) [29] and Co(III) [3, 19c] having C_2 symmetry.

Circular dichroism spectra in the spin-allowed band region for the $(+)_{589}$-[Cr(*S*,*S*-ptnta)$]^-$ [29] and $(+)_{589}$-$[Cr(edtp)]^-$ [2] complexes are much different from those of corresponding Co(III) complexes [18a, e], whereas CD spectra of complexes shown in Fig. 3 are similar in shape to those of corresponding isomers of Co(III) complexes [18b, c, f, 19a, c].

The 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, 18–20]. In the case of the *S*,*S*-ptnta and *S*,*S*-edds M(III) complexes, the absolute configuration $\Lambda(\Lambda\Delta\Lambda)$ based on the CD criteria is consistent with that determined from the stereospecific coordination of these hexadentate chiral ligands to M(III) [1, 18e, 19a, 29].

The CD pattern in the lower energy spin-allowed absorption band for $(+)_{589}$-*trans*(O_5)–[Cr(*S*,*S*-edds)$]^-$ [1, 29], $(+)_{589}$-[Cr(*S*,*S*-ptnta)$]^-$ [29] and $(-)_{589}$-*trans*(O_5)–$[Cr(eddadp)]^-$ [1, 29] complexes (Table 1) show 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 and the lowest energy spin-allowed CD peak for these complexes has been assigned $^4B(C_2)$ derived from $^4E_g(^4T_{2g})$ [2, 29] as for the corresponding Co(III) complexes [8, 18, 19, 41]. The $(+)_{589}$-*trans*(O_5)–[Cr(*S*,*S*-edds)$]^-$ [1, 29], $(+)_{589}$-[Cr(*S*,*S*-ptnta)$]^-$ [29] and $(-)_{589}$-*trans*(O_5)–$[Cr(eddadp)]^-$ [1, 29] complexes with a Λ configuration give a positive CD component at the lowest energy side of the first spin-allowed absorption band. This was verified crystallographically in the case of Λ-$(-)_{589}$-*trans*(O_5)-$[Cr(eddadp)]^-$ [28]. The lowest energy $^4B(C_2)$ CD peak is masked or cancelled in the case of $(+)_{589}$-$[Cr(edtp)]^-$ [2] which was assigned the Δ configuration from the sign of the major peak corresponding in energy to the absorption band. This has been confirmed crystallographically [31].

The CD pattern in the lower energy spin-allowed absorption band for the $(-)_{589}$-*trans*-(O_5O_6)–$[Cr(eda3p)]^-$ complex also exhibits two CD peaks of opposite sign with some indication of a shoulder at higher energy. This complex (Fig. 3, Table 1) has a positive CD sign of the lowest energy spin-allowed CD peak ($^4B(C_2)$ component derived from $^4E_g(^4T_{2g})$) indicative of the Λ configuration as was the case for $(+)_{589}$-[Cr(*S*,*S*-ptnta)$]^-$ [29], $(+)_{589}$-*trans*(O_5)–[Cr(*S*,*S*-edds)$]^-$ [1, 29] and $(-)_{589}$-

TABLE 1. Absorption (AB) and circular dichroism (CD) data of chromium(III) hexadentate edta-type complexes

Complex Ion	AB		CD		Reference
	ν ($\times 10^3$ cm^{-1})	ϵ	ν ($\times 10^3$ cm^{-1})	$\Delta\epsilon$[a]	
Λ-$(-)_{589}$-*trans*(O_5)–[Cr(eddadp)]$^-$	18.90	214	16.53	+0.20[b]	1, 28, 29
			18.62	−0.77	
			20.33sh	−0.20	
	25.30	107	22.17sh	−0.05	
			24.10	−0.08	
			26.53	+0.23	
Λ-$(-)_{589}$-*trans*(O_5O_6)–[Cr(eda3p)]$^-$	18.69	194	16.58	+0.09[b]	this work
			18.76	−0.64	
			21.05sh	−0.14	
	25.12	86.6	23.53	+0.07	
			26.67	+0.23	
Δ-$(+)_{589}$-[Cr(edtp)]$^-$	18.55	183	18.24	+0.37	2
			20.08	−0.04	
			21.01	−0.02	
	25.11	71	23.20	−0.14	
			26.52	−0.18	
Λ-$(+)_{589}$-*trans*(O_5)–[Cr(*S*,*S*-edds)]$^-$	19.60	175	17.54	+0.41[b]	1, 29
			19.33	−0.39	
			21.83	+0.45	
	26.00	57	23.50sh	+0.34	
			26.99	+0.38	
Λ-$(+)_{589}$-[Cr(*S*,*S*-ptnta)]$^-$	19.64	110	18.00sh	+0.20[b]	29
			19.67	+0.44	
			21.67	−0.06	
	25.97	77	24.00	+0.44	
			25.25sh	+0.27	
			29.66	−0.02	

[a] Values are given in units of mol^{-1} dm^3 cm^{-1}. [b] These peaks are presumed to be $^4B(C_2)$ components, indicative of the Λ configuration (ref. 2, 29 and this work).

trans(O_5)–[Cr(eddadp)]$^-$ [1, 28, 29] complexes of known (Λ) absolute configuration.

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