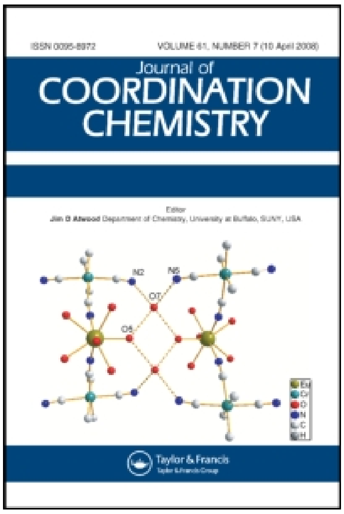

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CIRCULAR DICHROISM OF CHROMIUM(III) SEXADENTATE EDTA-TYPE COMPLEXES, PART I

(S,S)-Ethylenediamine-N,N′-disuccinatochromate(III) and Ethylenediamine-N,N′-Diacetato-N,N′-Di-3-Propionatochromate(III) Ions

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New sexadentate Cr(III) complexes with (S,S)-ethylenediamine-N,N′-disuccinic acid (S,S-H_4EDDS) and ethylenediamine-N,N′-diacetic-N,N′-di-3-propionic acid (H_4EDDDA) are reported. With both ligands only *trans*(O_5) geometrical isomers have been prepared. Infrared, electronic absorption, and CD spectra were used for characterizing the complexes. Because of the stereospecificity of the S,S-EDDS ligand the absolute configuration of the *trans*(O_5)-Cr(S,S-EDDS)$^-$ is known. The $(-)_{589}$-isomer of the *trans*(O_5)-Cr(EDDDA)$^-$ 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, by comparison of its CD spectrum to the CD spectrum of the corresponding *trans*(O_5)-Co(EDDDA)$^-$ and *trans*(O_5)-Cr(S,S-EDDS)$^-$ complexes of known absolute configurations.

INTRODUCTION

Cobalt(III) complexes of EDTA and structurally related ligands have been studied extensively in recent years. In Co(EDTA)$^-$ the two glyinate rings (G rings) in the plane of the diamine ring are considerably more strained than the other two glycinate rings (R rings).[1,2] The ligands are 6-coordinate in Co(EDTA)$^-$ and in Co(1,2-PDTA)$^-$ [3,4] (1,2-PDTA = 1,2-propylenediaminetetraacetate ion), but 5-coordinate in the corresponding Cr(III) complexes.[5–8] The strain is presumably great enough for the larger Cr(III) ion to prevent closure of the fifth chelate ring, so one water molecule occupies a sixth coordination site.

The Cr(1,3-PDTA)$^-$ complex[9] (1,3-PDTA = 1,3-propylenediaminetetraacetate ion) was the first reported sexadentate complex with Cr(III). The preparation of this complex was later repeated by Tanaka and coworkers[8] who gave a new method for the preparation of Cr(III)-EDTA complexes and reported the preparation of a new sexadentate Cr(TDTA)$^-$ complex (TDTA = tetramethylenediaminetetraacetate ion). Neither of the reported sexadentate complexes of Cr(III) was resolved. In both cases the formation of the sexadentate complexes was attributed to the relief of strain because of the longer chain of the diamine backbone.

Ligands, structurally similar to EDTA, having longer carboxylate chains, S,S-EDDS[10,11] [S,S-EDDS = (S,S)-ethylenediamine-N,N′-disuccinate ion] and EDDDA[12,13] (EDDDA = ethylenediamine-N,N′-diacetate-N,N′-di-3-propionate ion), have been studied and the CD spectra of their Co(III) complexes discussed. It was found[11,13,14] that these ligands preferentially form isomers having six-membered rings in the G plane. These are potentially sexadentate ligands for Cr(III). Since the optical activity of sexadentate Cr(III) complexes has not yet been studied, these ligands have been used for the preparation of Cr(III) complexes.

EXPERIMENTAL

S,S-H_4EDDS and H_4EDDDA ligands were prepared using previously described procedures.[10–13] Other reagents were obtained commercially and used without further purification.

For conversion of the chromium(III) complexes into salts of various cations, Rexyn 101 Analytical Grade cation-exchange resin was used.

Optical isomers are identified by the sign of the lowest energy CD band [(+) or (−)] or by the sign of

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† Research Associate, 1973–74

the optical rotation at the sodium D line. Δ or Λ is the chirality assigned according to IUPAC rules.[15]

Preparation of Silver (S,S)-Ethylenediamine-N,N′-disuccinatochromate(III) Hydrate, Ag[Cr(S,S-EDDS)] · H_2O

S,S-H_4EDDS · H_2O (3.10 g, 10 mmol) and 85% KOH (1.32 g, 20 mmol) were dissolved in 80 ml of water at 70°. To this solution $CrCl_3 \cdot 6H_2O$, (2.66 g, 10 mmol) was then added. Heating and stirring at the same temperature were continued until the solution turned purple-red. Then a new portion of 85% KOH (1.32 g, 20 mmol), which was previously dissolved in 10 ml water, was added dropwise and heating and stirring were continued for 3 hrs more. The resulting solution (*ca.* 20 ml, pH ≅ 7) yielded only one colored band by ion-exchange chromatography. A slight excess of $AgClO_4$ was added to this solution in order to precipitate AgCl and $KClO_4$. The filtrate was passed through a cation-exchange column in the Ag^+ form. The eluate was evaporated under vacuum at 30° to a volume of 10 ml and the solution was left overnight in the refrigerator. The precipitate of Ag[Cr(S,S-EDDS)] · H_2O was separated by filtration and washed with ethanol and acetone (1 g). The same volume of ethanol was added to the filtrate and the solution was again cooled overnight to obtain a second fraction of complex (0.6 g). Total yield: 1.6 g of Ag[Cr(S,S-EDDS)] · H_2O. This complex was recrystallized by dissolving it in a small amount of water, adding ethanol and cooling. $\Delta\epsilon_{572}$ + 0.40, $\Delta\epsilon_{518}$ − 0.39; $[\alpha]_D$ + 180° in 0.1% aqueous solution. *Anal.* Calcd for $(+)_D$-Ag[Cr(S,S-EDDS)] · H_2O (FW = 466.09): Ag, 23.14; C, 25.77; H, 3.02; N, 6.01; H_2O, 3.86. Found: Ag, 23.12; C, 25.97; H, 2.98; N, 5.89; H_2O, 3.84.

Preparation of Potassium Ethylenediamine-N,N′-diacetato-N,N′-di-3-propionatochromate(III) Dihydrate, K[Cr(EDDDA)] · $2H_2O$

To 100 ml of solution containing 5.28 g (80 mmol) of 85% KOH was added 12.8 g (40 mmol) of H_4-EDDDA. The solution was heated to 80° and then 10.66 g (40 mmol) of $CrCl_3 \cdot 6H_2O$ was added. This solution was heated with stirring for 1 hr. After that, 100 ml of water containing 5.28 g (80 mmol) of 85% KOH was added gradually and heating and stirring were continued at the same temperature for 16 hrs more. After the first 6 hrs of the reaction, the volume of the solution was reduced to *ca.* 60 ml. This volume was then maintained by periodic addition of hot water during the last 10 hrs of the reaction. To the resulting red-violet solution 60 ml of 95% ethanol was added. After the solution was left in the refrigerator for 2 days, the red-violet crystals of K[Cr(EDDDA)] · $2H_2O$ were collected from the mother liquor,† washed with ethanol, then acetone, and air-dried; yield: 11.5 g. This complex was recrystallized from a mixture of water and ethanol (1:1). *Anal.* Calcd for K[Cr(EDDDA)] · $2H_2O$ (FW = 443.39): C, 32.50; H, 4.54; N, 6.32; H_2O, 8.12. Found: C, 32.77: H, 4.45; N, 6.21; H_2O, 8.15.

Resolution of Potassium Ethylenediamine-N,N′-diacetato-N,N′-di-3-propionatochromate(III) Dihydrate, K[Cr(EDDDA)] · $2H_2O$

The resolution of this complex was accomplished using the corresponding silver salt, which was prepared via the cation-exchange technique. The Ag[Cr(EDDDA] · $2H_2O$ crystallized after the concentrated aqueous eluate had stood in the refrigerator overnight. *Anal.* Calcd for Ag[Cr(EDDDA)] · $2H_2O$ (FW = 512.16); Ag, 21.06; H_2O, 7.03. Found: Ag, 21.16; H_2O, 7.10.

$(-)_D$-[Co(en)$_2$ox]Br · $H_2$2O (1.82 g, 5 mmol) and Ag[Cr(EDDDA)] · $2H_2O$ (2.56 g, 5 mmol) were stirred together in 30 ml of warm water for several minutes. The AgBr was removed and washed with 2 ml of warm water. The warm filtrate was left standing in the refrigerator for 5 hrs. During that time a bulky precipitate of the less soluble diastereoisomer, $(-)_D$-[Co(en)$_2$ox]-$(-)_D$ [Cr(EDDDA)] · $2H_2O$ crystallized. The precipitate was separated by filtration, washed with a small amount of ethanol, then ether, and air-dried; yield: 1.2 g. The remaining filtrate was then evaporated to a volume of about 15 ml and allowed to stand in the refrigerator overnight. The more soluble diastereoisomer, $(-)_D$-[Co(en)$_2$ox]-$(+)_D$-[Cr(EDDDA)] · $5H_2O$ was collected by filtration, washed with ethanol, then ether, and air-dried; yield: 1 g. From the remaining

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†After removing ethanol from the mother liquor, ion exchange chromatography showed that it contains two complexes with −1 charge. The first complex eluted (red-violet) corresponds to the K[Cr(EDDDA)] · $2H_2O$ isolated, and the second complex (violet) is present in a much smaller amount. Purification and isolation of the violet complex is difficult. However, its electronic absorption spectrum shows maxima at 535 nm and 390 nm, suggesting that the complex is not an isomer of the sexadentate complex, but is most likely a quinquidentate species with a molecule of water occupying a sixth coordination site.

filtrate small amounts of both diastereoisomers were obtained by fractional crystallization. The diastereoisomers were crystallized from small amounts of warm water to constant values of optical rotation. Aqueous solutions (0.1%) gave $[\alpha]_D$ −730° and $[\alpha]_D$ − 212° for the less and more soluble diastereoisomers, respectively. The diastereoisomers' weight loss when dried under vacuum at 110° for 4 hrs was: less soluble, 5.70% (Calcd for $2H_2O$: 5.36%); more soluble, 12.20% (Calcd for $5H_2O$: 12.41%).

The optical isomers of the $Cr(EDDDA)^-$ complex were obtained by dissolving each of the diastereoisomers in water and passing the solutions through a cation-exchange column in the K^+ form. The eluates were evaporated under vacuum to volumes of 4 ml. The needle-like crystals of the enantiomers were formed after addition of several drops of ethanol and cooling. $\Delta\epsilon_{605} \pm 0.20$, $\Delta\epsilon_{535} \mp 0.78$; $[\alpha]_D \mp 340°$ in 0.05% aqueous solution. *Anal.* Calcd for $(-)_D$-K[Cr(EDDDA)] · $2.5H_2O$ (FW = 452.39): C, 31.86; H, 4.67; N. 6.19; H_2O, 9.95. Found: C, 31.73; H, 4.12; N, 5.94; H_2O, 10.20.

The enantiomers of the $Cr(EDDDA)^-$ complex were also isolated in the form of the lithium salts which crystallize better than the corresponding potassium salts. The lithium salts crystallize from water/ethanol solutions giving two different crystal forms. The crystal form containing five waters of crystallization has been analyzed. $[\alpha]_D \mp 338°$ in 0.05% aqueous solution. *Anal.* Calcd for $(-)_D$-Li [Cr(EDDDA)] · $5H_2O$ (FW = 465.27): C, 30.97; H, 5.63; N, 6.02; H_2O, 19.36. Found: C, 31.30; H, 5.41; N, 5.95; H_2O, 19.50.

Physical Measurements

$[\alpha]_D$ values were measured in a 1 dm tube at 20° on an O.C. Rudolph and Sons polarimeter.

Infrared spectra were recorded on a Perkin-Elmer 247 Grating Infrared Spectrophotometer using Nujol mulls.

Electronic absorption spectra were recorded on a Cary Model 14 recording spectrophotometer using a tungsten lamp. (3.5 x 10^{-3}M aqueous solutions).

The circular dichroism curves were measured at room temperature with a Cary 61 Recording CD Spectropolarimeter using a Xenon Arc Source.

Analyses Analyses were performed by Chemalytics Inc., Tempe, Arizona. The number of waters of crystallization was determined by both elemental analyses, and by weight loss on drying. Silver was determined gravimetrically as silver chloride.

RESULTS AND DISCUSSION

Because of the capability of forming two six-membered (β-alaninate) chelate rings, S,S-EDDS and EDDDA are likely to function as sexadentate ligands with Cr(III). The ligand SS-EDDS was found[11] to coordinate stereospecifically with Co(III). The stereospecificity results from the preparation of the ligand by joining two S-aspartic acid molecules by an ethylene linkage. Two isomers (I and II in Figure 1) are possible, but only I has been reported. This is the isomer expected, since the larger chelate rings in the G plane should relieve the strain present in $Co(EDTA)^-$. These isomers (I and II) have opposite absolute configurations, so identification of the isomer as *trans*(O_5)(I) or *trans*(O_6)(II) also establishes the absolute configuration. Three isomers are possible (Figure 2) for a sexadentate complex of EDDDA. The $Co(EDDDA)^-$ ion most readily forms I,[13] which should minimize the strain of the G rings. A second isomer (II) has been reported[14] for $Co(EDDDA)^-$, although it is formed in smaller amounts than I. Isomer III has not been isolated. Since ring strain seems to prevent EDTA from functioning as a sexandentate ligand with Cr(III) but not with Co(III), isomer I might be expected to be even more strongly favored for Cr(III) than for Co(III) with each ligand (Figures1 and 2).

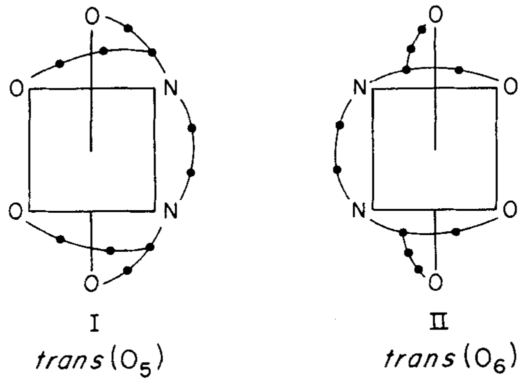

FIGURE 1 Absolute configurations of the two isomers of $[Cr(S,S\text{-}EDDS)]^-$.

Infrared Spectra and Geometrical Isomerism

The asymmetric carboxylate stretching frequencies have been established as criteria for distinguishing between protonated carboxylate groups (1700–1750 cm^{-1}) and carboxylate groups which are coordinated to metal ions (1600–1650 cm^{-1}) in

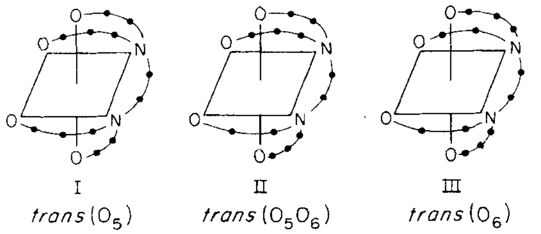

FIGURE 2 Three possible geometrical isomers of Λ-[Cr(EDDDA)]⁻.

metal aminopolycarboxylic acid complexes.[16-18] Also, it has been clearly demonstrated for tris(aminoacidato)cobalt(III) complexes that the asymmetric stretching frequency of the carboxylate groups of the five-membered[19] chelate rings lie at higher energy than the corresponding frequency of the six-membered[20] chelate rings. This was supported by Neal and Rose[11] who found that *trans*(O_5)-[Me(S,S-EDDS)]$^-$ complexes exhibit two very strong and well-separated bands in the asymmetric stretching carboxylate frequency region. Similar results were obtained[13] for *trans*(O_5)-[Co(EDDDA)]$^-$. The frequencies at higher energy were assigned to the asymmetric stretch of coordinated carboxylates contained in a glycine residue, and those at lower energy were assigned to belong to the moieties of the six-membered carboxylate arms.

The data reported here for Co(III) and Cr(III) complexes containing EDDDA and S,S-EDDS as ligands support the above trends regarding the asymmetric frequencies of five- and six-membered amino acid chelate rings. Infrared data for the complexes presently investigated are shown in Table I and Figure 3. For comparison, the corresponding values of other complexes are also given. As can be seen, all sexadentate complexes with EDTA-type ligands having glycinate arms show, in the 1600–1650 cm^{-1} region, only one very strong band corresponding to the coordinated carboxylate groups (Table I). The infrared spectra of the corresponding asymmetric carboxylate stretches of the other sexadentate complexes (Figure 3, Table I) containing the ligand with mixed (five- and six-membered) carboxylate arms (EDDDA and S,S-EDDS) are more complicated.

The geometrical isomerism of the *trans*(O_5)-[Co(EDDDA)]$^-$ and *trans*(O_5O_6) – [Co(EDDDA)]$^-$ complexes have been recently investigated,[14] but the infrared spectra were not reported. In the asymmetric carboxylate stretching region the *trans*(O_5)-[Co(EDDDA)]$^-$ isomer shows two very strong bands (at 1644 cm^{-1} and 1580 cm^{-1}) (Table I) which are separated by 64 cm^{-1}. This is in agreement with its C_2 molecular symmetry and the bands are assigned to the corresponding stretching vibrations of the five-membered carboxylate moieties at higher energy and six-membered carboxylate moieties at lower energy.

Trans(O_5O_6)-[Co(EDDDA)]$^-$, with C_1 molecular symmetry, has, as was expected, a more complicated infrared spectrum in this spectral region (Figure 3) than the *trans*(O_5)-isomer. The four bands are attributed to the four non-equivalent coordinated carboxylate groups. Two of them, at higher energy, are assigned as asymmetric stretching vibrations of the two non-equivalent coordinated glycinate rings, and the two at lower energy (1612 cm^{-1} and 1585 cm^{-1}) belong to the corresponding vibrations

TABLE I
Infrared asymmetric carboxylate stretching frequencies for some sexadentate Co(III) and Cr(III)-EDTA type complexes (cm^{-1}).[a,b]

Complex	COOM (five-membered) ring	COOM (six-membered) ring	Ref.
Na[Co(EDTA)] · $2H_2O$	1638 (vs)		4,16
Na[Co(S,S-EDDS)] · H_2O	1640 (vs)	1560 (vs)	11
trans(O_5)-K[Co(EDDDA)] · $2H_2O$	1644 (vs)	1580 (vs)	
trans(O_5O_6)-K[Co(EDDDA)] · $2H_2O$	1685 (vs)	1612 (vs) (?)	
	1630 (vs)	1585 (vs)	
Na[Cr(1,3-PDTA)] · $3H_2O$	1670 (sh)		9
	1630 (s)		
Na[Cr(TDTA)] · $4H_2O$	1630 (vs)		8
trans(O_5)-Ag[Cr(S,S-EDDS)] · H_2O	1652 (vs)	1570 (vs)	
trans(O_5)-K[Cr(EDDDA)] · $2H_2O$	1618 (vs)	1590 (vs)	

[a] Abbreviations: vs, very strong; s, strong; sh, shoulder.
[b] All spectra were obtained from Nujol mulls.

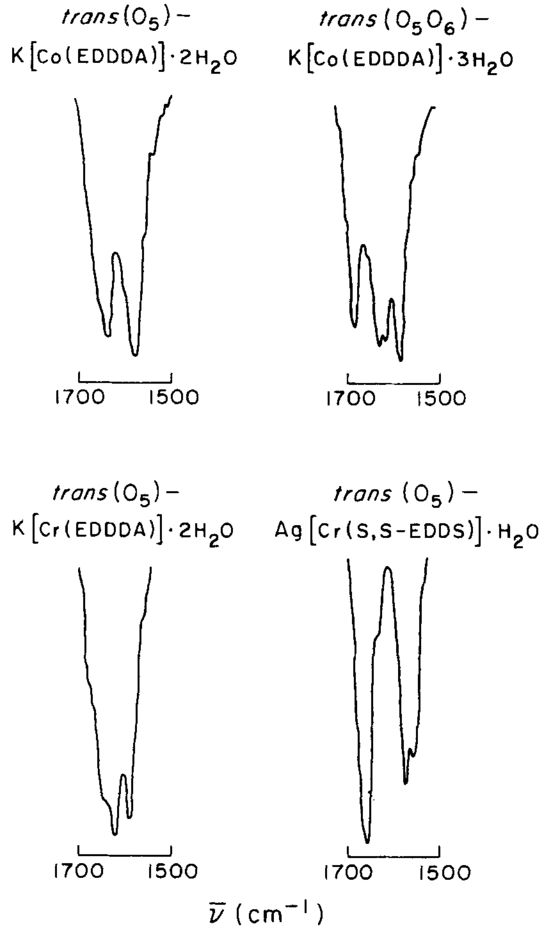

FIGURE 3 Portions of the infrared spectra of Co(III)-EDDDA, Cr(III)-EDDDA and Cr(III)-S,S-EDDS complexes in Nujol mulls.

of coordinated β-alaninate rings. The 1685 cm^{-1} band is at higher frequency than is usually observed for five-membered rings and the 1612 cm^{-1} band is also at higher energy than for the other six-membered rings.

Infrared data of the two new Cr(III) complexes are also given in Table I and Figure 3. Nujol mull spectra of the acid forms of these two complexes, prepared using the column technique and evaporating the eluates to dryness, show no evidence of protonated carboxylate groups in the expected (1700–1750 cm^{-1})[18] spectral region. Cr(EDDDA)$^-$ shows only two separate bands in the expected spectral region for coordinated carboxyl groups (at 1618 cm^{-1} and 1590 cm^{-1}), indicating that it is an isomer with C_2 molecular symmetry (Figure 2, Isomers I and III). From the results with the corresponding Co(III) complexes,[13,14] the Cr(III) complex is presumed to be the *trans*(O$_5$)-isomer, which is predicted to be formed preferentially. A smaller separation of these two bands occurs for *trans*(O$_5$)-[Cr(EDDDA)]$^-$ (28 cm^{-1}) than for the corresponding bands of *trans*(O$_5$)-[Co(EDDDA)]$^-$ (64 cm^{-1}).

Cr(S,S-EDDS)$^-$ also has two well-separated bands in the expected spectral region (1652 cm^{-1} and 1570 cm^{-1}) as was found for other S,S-EDDS complexes.[11] Earlier results with Co(S,S-EDDS)$^-$ showed that the stereospecifically coordinating S,S-EDDS ligand forms only one isomer having six-membered rings in the G plane[11,21] (Figure 1, Isomer I). This would suggest that the corresponding Cr(III) complex also has the *trans*(O$_5$) geometrical configuration. Both possible isomers of Cr(S,S-EDDS)$^-$ have C_2 symmetry (Figure 1), so the infrared results cannot distinguish between them. Since they are enantiomeric, the CD data (see follow) can relate the isomer obtained to Co(S,S-EDDS)$^-$ of known absolute configuration.

The energies of the coordinated carboxylate bands are more nearly the same for the Co(III) and Cr(III) S,S-EDDS complexes than for the corresponding EDDDA complexes (Table I). Presumably the difference in size of the metal ion has less effect on the bonding interactions for the more rigid, branched S,S-EDDS ligand.

Electronic Absorption and CD Spectra

The electronic absorption and CD data for *trans*(O$_5$)-Cr(EDDDA)$^-$ and *trans*(O$_5$)-Cr(S,S-EDDS)$^-$ are shown in Table II and Figure 4. The shapes of the absorption bands suggest that the complexes have pseudo-octahedral symmetry. The positions of the bands show that Dq for the latter complex is slightly greater than that of the former, as reported.[11,14] Both ϵ and $\Delta\epsilon$ values for these Cr(III) complexes are significantly lower than for the corresponding Co(III) complexes.[11,13,14]

The Cr(III) ion (d^3) has a ground state in a strong O_h field, $(t_{2g})^3$, which is formally similar to that for the $(t_{2g})^6$ configuration of a low-spin d^6 system. It would be expected that their electronic absorption and CD spectra should be qualitatively similar with respect to splittings of the spin-allowed d-d transitions. In O_h symmetry the lower energy spin-allowed band for Cr(III) is ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and the one at higher energy is ${}^4A_{2g} \rightarrow {}^4T_{1g}$. The corresponding transitions for low-spin Co(III) are ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$, respectively. Thus the symmetries of

TABLE II
Absorption and CD data for chromium(III) sexadentate EDTA-type complexes

Complex ion	Absorption peak position kK	ϵ	Circular dichroism peak position[a] kK	$\Delta\epsilon$
trans(O_5)-$[Cr(S,S\text{-}EDDS)]^-$	19.6	175	17.5	+0.40
			19.3	−0.39
			21.7	+0.44
	26.0	57	23.5 (sh)	+0.34
			26.9	+0.37
trans(O_5)-$[Cr(EDDDA)]^-$	18.9	214	16.5	+0.20
			18.7	−0.78
			~20.6 (sh)	−0.20
	25.3	107	24.3	−0.08
			26.7	+0.22

[a] sh = shoulder

the spin-allowed transitions (cross products of ground and excited states) for the two systems are the same, T_{1g} and T_{2g} in order of increasing energy. Several studies have been carried out on Cr(III) systems with D_3 symmetry.[22,26] The absolute configurations of the dissymmetric d^3 complexes have been assigned from a comparison of the CD signs in the spin-allowed absorption band region with the signs of the corresponding CD bands of $(+)_{546}$-$[Co(en)_3]^{3+}$ of known[27] absolute configuration. It has been shown that CD spectra of tris(diamine)chromium(III), [as well as Co(III)] complexes, show $E(D_3)$ and $A_2(D_3)$ CD components under the lower energy (T_g,O_h) absorption band. Further, by means of the ion-pairing effect on the CD spectra, the ^4E CD component has been found[25,26] to have a positive sign for $(+)_{546}$-$[Cr(en)_3]^{3+}$, which has the Λ configuration. The $(+)_D$-isomers of $Cr(oxalate)_3{}^{3-}$, and $Cr(malonate)_3{}^{3-}$ have the Λ configuration[28] and have dominant positive CD peaks in the first spin-allowed absorption band region. They show the same sign patterns for the CD peaks through the visible and ultraviolet region, but were originally assigned opposite absolute configurations.[23]

The relationship of CD spectra to absolute configurations of chromium(III) complexes with other symmetries has also been studied.[29–31] CD bands in both the spin-forbidden and spin-allowed regions have been used for the determination of the absolute configuration. It was found that assignments are consistent with Mason's empirical method[32,33] based on the CD bands in the first spin-allowed d-d absorption band region. For the $(+)_{546}$-$[Cr(en)_2ox]^+$ [29,31] and $(+)_{546}$-isomers of other structurally similar complexes,[30,31] all having the *cis*-$[CrN_4O_2]$ type structure, it has been found that the major bands in the first spin-allowed region have

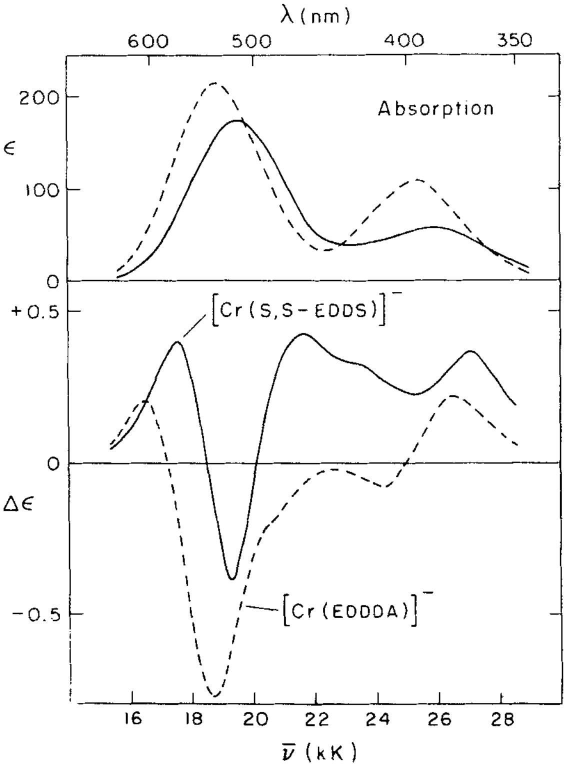

FIGURE 4 Electronic absorption and CD spectra of trans(O_5) geometrical isomers of the $(+)_D$-$Ag[Cr(S\text{-}S\text{-}EDDS)]\cdot H_2O$ and $(-)_D$-$K[Cr(EDDDA)]\cdot 2.5H_2O$

positive $^4E(D_3)$ components and, further, that these isomers have the Λ configuration. The $(+)_{546}$-isomers of the bis(oxalatao)-diamine complexes[31] of the *cis*-$[CrN_2O_4]$ type also have major positive CD bands in the first spin-allowed absorption band region and, therefore, these oxalato complexes were also assigned the Λ configuration.

Many Co(III) complexes[13,14,34-37] with EDTA-type ligands have been treated in terms of C_2 symmetry. Mason has shown[29] that the signs of the Cotton effects of the components under the lowest energy (O_h) band for compounds with C_2 symmetry are related to the signs of the Cotton effects of the parent levels in complexes with D_3 symmetry having the same configuration. The $A(C_2)$ component, having a positive Cotton effect for the Λ configuration, for the *cis*-$[Co(en)_2ox]^{n+}$ complexes, was considered[29] to retain the sign of the $E_a(D_3)$ component for $Co(en)_3{}^{3+}$.

The Co(III) complex of S,S-EDDS is known[11,21] to be *trans*(O_5)-$[Cr(S,S\text{-}EDDS)]^-$ with the absolute configuration (I) shown in Figure 1. The CD spectrum of $Cr(S,S\text{-}EDDS)^-$ shows three peaks (+,–,+) under the first absorption band (Figure 4). The sign pattern and general shape of the CD curve corresponds to that[11] of *trans*(O_5)-$[Co(S,S\text{-}EDDS)]^-$ throughout the spectral region covered. It is reasonable that their splitting patterns and signs of rotational strengths correspond, and that they have the same geometrical and absolute configuration. Because of the optically active S,S-EDDS, each geometrical isomer shown in Figure 1 can have only the absolute configuration shown. From comparison of the CD spectrum of $Co(S,S\text{-}EDDS)^-$ with related EDTA-type complexes,[38] it would appear that the positive lowest energy CD peak is probably the $A(C_2)$ component for which the sign correlates with the absolute configuration.

From the infrared data, it was concluded that the $Cr(EDDDA)^-$ complex isolated is the *trans*(O_5)-isomer. The CD spectrum (Figure 4) in the first absorption band region corresponds to that of *trans*(O_5)-$[Co(EDDDA)]^-$ in shape and sign pattern,[13,14] so presumably they have the same absolute configuration. The Λ configuration (Figure 2, I) was assigned for the $(-)_D$-*trans*(O_5)-$[Co(EDDDA)]^-$ complex ion with the corresponding CD curve.[13,14] Here again the corresponding Co(III) and Cr(III) complexes are presumed to have the same splitting and sign patterns. For both cases the lowest energy positive CD peak is presumed to be the $A(C_2)$ component, indicative of the Λ configuration. The close similarities between the CD spectra of the Co(III) and Cr(III) complexes of S,S-EDDS and EDDDA and the similarity between the CD spectra for the two ligands with each metal ion lend support to the tentative spectral assignments.

The isomers reported here are assigned the configurations expected to be most favorable from the consideration of chelate ring strain. The $(-)_D$-isomers of the *trans*(O_5)-EDDDA complexes of both Co(III) and Cr(III) were isolated from the less soluble diastereoisomers using $(-)_D$-$[Co(en)_2ox]^+$ as resolving agent. This lends support to the assignment of the same absolute configuration for these isomers.[39]

There is good general correspondence between the CD curves for the Cr(III) and Co(III) complexes.[11,13,14] The CD peaks are less than one-half as intense for the Cr(III) complexes. As in the case of the Co(III) complexes,[11,13,14,40] the CD intensities of the Cr(III) complexes are probably due mainly to configurational effects, with only small contributions[40] to the CD of the asymmetric nitrogens (RR) for the Λ configurations.

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