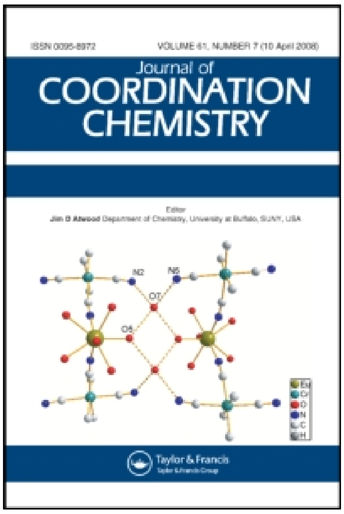

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CIRCULAR DICHROISM AND ELECTRONIC ABSORPTION OF RHODIUM(III) EDTA-TYPE COMPLEXES:
Ethylenediamine-*N*,*N*′-diacetato-*N*,*N*′-di-3-propionatorhodate(III) and (*S*,*S*)-Ethylenediamine-*N*,*N*′-disuccinatorhodate(III) Ions

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Electronic absorption and CD spectra are reported for the sexidentate complexes, *trans*(O_5)-Rh(EDDDA)$^-$, *trans*(O_5O_6)-Rh(EDDDA)$^-$, and *trans*(O_5)-Rh(*S*,*S*-EDDS)$^-$ (EDDDA) = ethylenediamine-*N*,*N*′-di-3-propionate; *S*,*S*-EDDS = (*S*,*S*)-ethylenediamine-*N*,*N*′-disuccinate). Because of the sterospecific coordination of the *S*,*S*-EDDS ligand the absolute configuration of $(+)_D$-*trans*(O_5)-Rh(*S*,*S*-EDDS)$^-$ is known to be Λ. By comparison of their CD spectra to that of the $(+)_D$ isomer of *trans*(O_5)-Rh(*S*,*S*-EDDS)$^-$, the absolute configurations of the $(-)_D$EDDDA complexes are assigned tentatively.

INTRODUCTION

X-ray crystal structure data of the EDTA-Co(III) chelate system[1] show that the glycinate rings (G-rings) lying in the plane of the diamine ring are considerably more strained than the out-of-plane rings (R rings). While the Co(EDTA)$^-$ complex is sexidentate, corresponding complexes with the larger Cr(III)[2–4] and Rh(III)[3,5] ions are quinquedentate with one water molecule occupying the sixth coordination site. A sample of sexidentate Rh(EDTA)$^-$ in solution has been reported[6] but there is no further information concerning isolation of the solid complex.

The *trans*(O_5) and *trans*(O_5O_6)-Rh(EDDDA)$^-$ (EDDDA = ethylendiamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate ion) complexes[7] have been characterized by ^{13}C and ^1H NMR and IR. The preparation of the Rh(*S*,*S*-EDDS)$^-$(*S*,*S*-EDDS = (*S*,*S*)-ethylenediamine-*N*,*N*′-disuccinate ion) complex and its ^1H NMR and IR spectra have been reported also.

The *S*,*S*-EDDS[8–11] and EDDDA[12,13] ligands are structurally similar to EDTA but have two longer carboxylate chains. The formation of their sexidentate Rh(III) complexes could be attributed to the relief of strain of chelate rings. Such complexes are of interest in the study of the influence of chelate ring size of multidentate ligands on the arrangement of rings about a central metal ion and the relative effects of this and other factors on optical activity. The CD spectra of the *S*,*S*-EDDS[14,15] and EDDDA[13,15,16] M(III) chelate systems (M = Co and Cr) have been studied. In this paper we describe the preparation and optical resolution and the visible electronic absorption and CD spectra of the two Rh(III) EDDDA complexes and the visible absorption and CD spectra of Rh(*S*,*S*-EDDS)$^-$.

EXPERIMENTAL SECTION

Reagents:

EDDDA and *S*,*S*-EDDS ligands were prepared using previously described procedures[9–13]. All other reagent-grade chemicals and solvents were obtained commercially and used without further purification.

For conversion of the rhodium(III) complexes into salts of various cations, Merck I Analytical Grade cation-exchange resin was used.

Optical isomers are identified by the sign of the optical rotation at a wavelength, λ [$(+)_\lambda$ or $(-)_\lambda$]. The Δ or Λ is the chirality assigned according to IUPAC rules.

Preparation of Complexes:

Preparation of the Trans(O_5) and Trans(O_5O_6) Geometrical Isomers of Sodium Ethylenediamine-N,N'-diacetato-N,N'-di-3-propionatorhodate(III), Na[Rh(EDDDA)]. – Rhodium trichloride trihydrate (1.32 g, 5 mmol) was dissolved in 1 ml of water in a Pyrex tube. To this mixture, a solution obtained by dissolving 1.6 g (5 mmol) H_4EDDDA in 5 ml 4M of sodium hydroxide (20 mmol) was added, the tube sealed and the mixture heated at 145°C on a oil-bath for 7 hr. After cooling to room temperature, the tube was chilled in ice and opened carefully. The yellow solution (pH ~ 4) was filtered off and a little rhodium metal removed. The filtrate was then introduced into a 5 cm x 70 cm column containing QAE A-25 Sephadex anion exchange resin in the Cl^- form. After the column was washed with H_2O, 0.1M NaCl solution was used for elution (*ca.* 0.5 ml/min.). Two yellow colored bands representing *trans*(O_5) and *trans*(O_5O_6) geometrical isomers of $Rh(EDDDA)^-$ were obtained (*ca.* 3:2) in addition to a third which was more strongly bound to the column and later eluted with 0.2M NaCl. This complex polymerizes and could not be isolated in pure form. Its electronic absorption spectrum suggests the presence of a $[Rh(EDDDA)(OH)]^{2-}$ complex. The eluates of the first and second bands were evaporated under vacuum at 40°C to a volume of 4 ml and then cooled overnight in a refrigerator. The deposited NaCl was removed and filtrates desalted by passage through a G – 10 Sephadex column (2.5 cm x 40 cm) eluting with distilled water. Then each eluate was concentrated to a volume of 2 ml. After addition of 2 to 3 ml of ethanol, the solutions were left in a refrigerator for two days. The yellow crystals were collected, washed with ethanol, then acetone and air-dried. Yield: *trans*(O_5), 0.6 g and *trans*(O_5O_6), 0.4 g. *Anal* Calcd for *trans*(O_5)-Na[Rh(EDDDA)] · $2H_2O$ = $NaRhC_{12}H_{20}N_2O_{10}$(FW = 478.19): C, 30.14; H, 4.21; N, 5.86. Found: C, 30.42; H, 4.43; N, 6.43; and for *trans*(O_5O_6)-Na[Rh-(EDDDA)] · $3H_2O$ = $NaRhC_{12}H_{22}N_2O_{11}$(FW = 496.21): C, 29.04; H, 4.47; N, 5.64. Found: C, 28.37; H, 4.70; N, 5.93.

Resolution of the Trans(O_5)Geometrical Isomer of Sodium Ethylenediamine-N,N'-diacetato-N,N'-di-3-propionatorhodate(III) Dihydrate, Na[Rh(EDDDA)] ·$2H_2O$. – This complex (0.96 g, 2 mmol) was dissolved in 4 ml of water and converted from the Na^+ to the Ag^+ form by passing the solution through a cation-exchange column (2.5 cm x 40 cm) in the Ag^+ form. To the eluate heated to 60°C an equivalent amout of $(-)_D$-$[Co(en)_2(ox)]$-Br · H_2O (0.73 g, 2 mmol) was added. Stirring with heating at the same temperature was continued for 15 min. The AgBr was removed by filtration and washed with 2 ml of warm water. The filtrate was evaporated to a volume of 4 ml and allowed to stand at room temperature for 1 hr. The precipitated less soluble diastereoisomer, $(-)_D$-$[Co(en)_2(ox)]$-$(-)_D$-[Rh(EDDDA)] · x H_2O, was removed by filtration, washed with a small amount of ethanol, then ether and air-dried (0.5 g). The remaining filtrate was then evaporated to a volume of 2 ml and left again to stand at room temperature for 2 hr. An additional amount of less soluble diastereoisomer was removed (0.2 g). Total yield: 0.7 g. From the remaining filtrate, after standing overnight in a refrigerator, the more soluble diastereoisomer, $(-)_D$-$[Co(en)_2(ox)]$-$(+)_D$-[Rh-(EDDDA)] · x H_2O, crystallized. This diastereoisomer was collected and washed with ethanol and ether (0.32 g). After addition of ethanol to the filtrate and cooling the mixture in the refrigerator, more of this diastereoisomer crystallized (0.21 g). Total yield: 0.53 g. Both diastereoisomers were crystallized from warm water to constant values of optical rotation. Aqueous solutions (0.1% gave $[\alpha]_D = -401°$ and $[\alpha]_D = -345°$ for the less and more soluble diastereoisomers, respectively.

The enantiomers of the $Rh(EDDDA)^-$ complex were isolated in the form of lithium salts by dissolving each of the diastereoisomers in water and passing the solutions through a cation-exchange column in the Li^+ form. The eluates were evaporated under vacuum to volume of 2 ml and the enantiomers were crystallized after addition of the same volume of ethanol and cooling. $[\alpha]_D = \pm 13°$ or $[\alpha]_{436} = \pm 148°$ in 0.1% aqueous solution. *Anal.* Calcd for $(-)_D$-Li [Rh(EDDDA)] · $5H_2O$=$LiRhC_{12}H_{26}N_2O_{13}$ (FW = 516.18): C, 27.92; H, 5.07; N, 5.43. Found: C, 28.14; H, 4.89; N, 6.02.

Resolution of the Trans(O_5O_6) Geometrical Isomer of Sodium Ethylenediamine-N,N'-diacetato-N,N'-di-3-propionatorhodate(III) Trihydrate, Na[Rh(EDDDA)] ·$3H_2O$. – Na[Rh-(EDDDA)] · $3H_2O$ (0.99 g, 2 mmol was dissolved in water and converted to the Ag^+ form using the column technique. An equivalent amount of $(-)_D$-$[Co(en)_2(ox)]$Br · H_2O was added to the eluate and mixture was then stirred at 40°C for 30 min. The AgBr was removed and washed with 2 ml of warm water. The combined filtrate and wash was evaporated at room temperature to a volume of 6 ml and the solution was left to stand overnight at room temperature. The less soluble diastereoisomer,

$(-)_D$-[Co(en)$_2$-(ox)]-$(+)_D$-[Rh(EDDDA)] $\cdot$ x H_2O, was removed by filtration, washed with ethanol, then ether and air-dried (0.47 g). The remaining filtrate was then evaporated under vacuum at 30°C to a volume of 3 ml and left in a refrigerator to stand overnight to crystallize more of the less soluble diastereoisomer. The precipitate was removed by filtration (0.2 g). Total yield: 0.67 g. The more soluble diastereoisomer, $(-)_D$-[Co(en)$_2$(ox)]-$(-)_D$-[Rh(EDDDA)] $\cdot$ x H_2O, crystallized from the remaining filtrate after addition of three volumes of ethanol and cooling. Yield: 0.4 g.

The diastereoisomers were recrystallized from water at 40°C to constant values of optical rotation. Aqueous solutions (0.1%) gave $[\alpha]_D = -365°$ and $[\alpha]_D = -480°$ for the less and more soluble diastereoisomers, respectively.

The optical isomers in the form of the lithium salts were obtained using the ion-exchange column technique. The eluates were evaporated to dryness at room temperature. $[\alpha]_D = \pm 83°$ or $[\alpha]_{436} = \pm 455°$ in 0.1% aqueous solution. *Anal.* Calcd for $(+)_D$-Li[Rh(EDDDA)] $\cdot 2H_2O$ = $LiRhC_{12}H_{20}N_2O_{10}$ (FW = 462.14): C, 31.19; H, 4.36; N, 6.06. Found: C, 31.47; H, 4.81; N, 7.11.

Preparation of the Trans(O_5) Geometrical Isomer of Sodium (S,S)-Ethylenediamine-N,N'-disuccinatorhodate(III) Monohydrate, Na[Rh(S,S-EDDS)] $\cdot$ H_2O. – This complex was prepared using the procedure given by Neal and Rose[8]. The pure complex was obtained by ion-exchange chromatography and Gel filtration. $[\alpha]_D = +164°$ or $[\alpha]_{546} = +194°$ in 0.1% aqueous solution.

Physical Measurements

The $[\alpha]_\lambda$ values were measured in a 1 dm tube at 20° on a Perkin-Elmer SP Polarimeter.

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

The circular dichroism curves were recorded at room temperature with a Jobin-Yvon Dichrographe III using a Xenon Arc Source.

Analyses

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

RESULTS AND DISCUSSION

The reaction of the S,S-EDDS ligand with Co(III)[10,11], Cr(III)[15], and Rh(III)[8] ions are reported to be stereospecific with only the *trans*(O_5) geometrical isomers of known (Λ) configuration[8,10,15,16] obtained (Figure 1a, isomer I). The optically active ligand results from the preparation of the S,S-EDDS ligand by joining two S-aspartic acid molecules by an ethylene linkage. On sexidentate coordination it could form theoretically two geometric isomers (I and II, Figure 1a) having opposite absolute configuration.

The EDDDA ligand, on sexidentate coordination, forms three five- and two six-membered chelate rings. Three geometrical isomers which differ in the number (0, 1, or 2) of six-membered rings in the girdle plane are possible: *trans*(O_5) (I), *trans*(O_5O_6) (II), and *trans*(O_6) (III) (Figure 1b). Two isomers, *trans*(O_5) and *trans*(O_5O_6), of the EDDDA-Co(III)[13,16] and EDDDA-Rh(III)[7] have been prepared and characterized. The isomers II were isolated in smaller amounts than the isomers I. In the case of the corresponding EDDDA-Cr(III) complex[15], only one, the *trans*(O_5), has been isolated. No *trans*(O_6) geometrical isomers (isomer III Figure 1b) of sexidentate

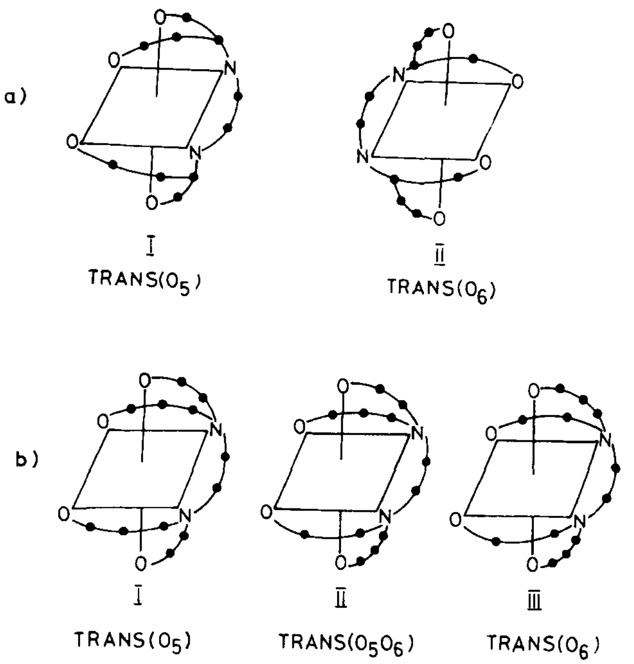

FIGURE 1 Possible Geometrical Isomers of Sexidentate Complexes:

(a) M(S,S-EDDS)$^-$
(b) M(EDDDA)$^-$

EDDDA-M(III) complexes have been isolated. The predominance of the *trans*(O_5)-M(III)-EDDDA$^-$ isomers bears out the preference for isomers in which the more flexible β-alaninate rings are in the diamine (G) plane.

Electronic Absorption Spectra

The electronic absorption and CD spectra of the Rh(III) complexes containing EDDDA and *S,S*-EDDS are shown in Figure 2a. Spectral data are summarized in Table 1. For comparison, the corresponding values of the recently investigated EDDDA and *S,S*-EDDS sexidentate complexes of Co(III)[10,13,16] and Cr(III)[15] are also given.

The two spin-allowed ligand field transitions in a low-spin d^6 system in an octahedral field are $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ in order of increasing energy. In a tetragonal field, the two transitions split into two components each, *i.e.*, $^1T_{1g} = {}^1A_{2g} + {}^1E_g^a$ and $^1T_{2g} = {}^1B_{2g} + {}^1E_g^b$. All the complexes considered here could be considered to have holohedrized D_{4h} symmetry. If we define the metal-ethylenediamine backbone plane as the *xy* plane then the donor atoms along the *x*-axis and *y*-axis are in each case N and O. If we hypothetically replaced each of these in-plane N's and O's with X atoms, having ligand field strengths intermediate between N and O the complex would be of the type *trans*-$[MX_4O_2]^-$ in which the equatorial donor atoms (X's) are higher in the spectrochemical series than the axial atoms (O's). In this case, according to Wentworth and Piper[17] the $^1E_g^a(D_{4h})$ state from the $^1T_{1g}(O_h)$ should be lower in energy than the $^1A_{2g}$ from the same O_h state. Also the $^1B_{2g}$ should be lower in energy than the $^1E_g^b$ state (both derived from the $^1T_{2g}(O_h)$). This, of course, should apply for both Co(III) and Rh(III) complexes of this type.

Similar complexes of Cr(III), a d^3 case, should have two spin-allowed transitions in O_h: $^4A_{2g} \rightarrow {}^4T_{2g}$ (at low energy) and $^4A_{2g} \rightarrow {}^4T_{1g}$. In D_{4h} they become $^4B_{1g} \rightarrow {}^4B_{2g}$ and $^4E_g^a$ in the $^4T_{2g}(O_h)$ region and $^4B_{1g} \rightarrow {}^4E_g^b$ and $^4A_{2g}$ in the higher energy, $^4T_{1g}(O_h)$, region. Further, since d^3 is a three-electron case, the order of energies of the D_{4h} components of each particular kind of O_h state should be inverted

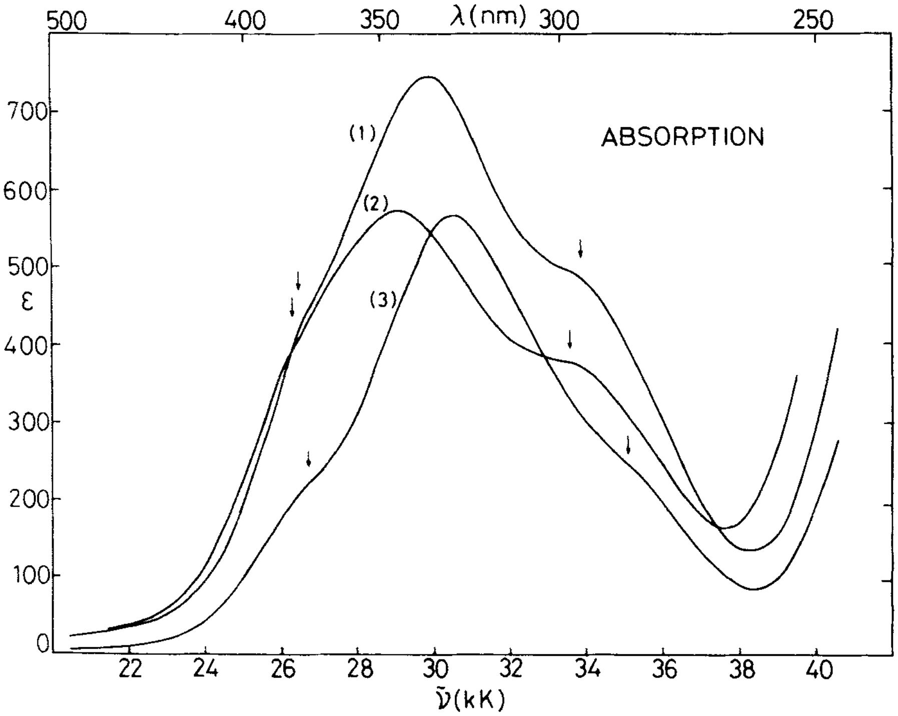

FIGURE 2a The Electronic Absorption Spectra of:

(1) *trans*(O_5)-Na[Rh(EDDDA)] · $2H_2O$
(2) *trans*(O_5O_6)-Na[Rh(EDDDA)] · $3H_2O$
(3) *trans*(O_5)-Na[Rh(*S,S*-EDDS)] · H_2O

TABLE I

Absorption and CD data for sexidentate metal(III) complexes containing EDDDA and *S,S*-EDDS ligands

	Absorption				Circular	Dichroism
Complex ion[x]	Peak Position (kK)	ϵ	Assignment: Parent O_h or D_{4h} state	Peak Position (kK)	$\Delta\epsilon$	Assignment: in D_{4h}
trans(O_5)-Co(EDDDA)$^-$	18.50	342	$^{1}T_{1g}(O_h)$	16.20	+0.40	E_g^a
$(-)_D$				18.30	−2.78	E_g^a
	25.70	186	$^{1}T_{2g}(O_h)$	24.20	+0.29	B_{2g}
				26.30	+0.36	E_g^b
trans(O_5O_6)-Co(EDDDA)$^-$	18.60	253	$^{1}T_{1g}(O_h)$	16.50	+2.25	E_g^a
$(-)_D$				18.40	−3.12	E_g^a
	25.80	142	$^{1}T_{2g}(O_h)$	24.40	+0.31	B_{2g}
				26.60	+0.56	E_g^b
trans(O_5)-Co(*S,S*-EDDS)$^-$	19.40	~290[y]	$^{1}T_{1g}(O_h)$	~16.5[y]	+[y]	E_g^a
$(-)_D$				~18.5[y]	−strong[y]	E_g^a
				~21[y]	+[y]	A_{2g}
	26.25	~190[y]	$^{1}T_{2g}(O_h)$	~25[y]	+[y]	B_{2g}
				~27[y]	+[y]	E_g^b
trans(O_5)-Cr(EDDDA)$^-$	18.90	214	$^{4}T_{2g}(O_h)$	16.50	+0.20	E_g^a
$(-)_D$				18.70	−0.78	E_g^a
				20.60(sh)	−0.20	B_{2g}
	25.30	107	$^{4}T_{1g}(O_h)$	24.30	−0.08	
				26.70	+0.22	
trans(O_5)-Cr(*S,S*-EDDS)$^-$	19.60	175	$^{4}T_{2g}(O_h)$	17.50	+0.40	E_g^a
$(+)_D$				19.30	−0.39	E_g^a
				21.70	+0.44	B_{2g}
	26.00	57	$^{4}T_{1g}(O_h)$	23.50(sh)	+0.34	
				26.90	+0.37	
trans(O_5)-Rh(EDDDA)$^-$	~26.45(sh)	405	$^{1}E_g^a(D_{4h})$	29.41	−2.10	E_g^a
$(-)_D$	29.85	745	$^{1}A_{2g}(D_{4h})$			A_{2g}
	~33.89(sh)	480	$^{1}B_{2g}$, $^{1}E_g^b(D_{4h})$	34.96	+0.36	B_{2g}, E_g^b
trans(O_5O_6)-Rh(EDDDA)$^-$	~26.31(sh)	390	$^{1}E_g^a(D_{4h})$	25.44	−1.80	E_g^a
$(-)_D$	29.07	565	$^{1}A_{2g}(D_{4h})$	28.98	+2.84	A_{2g}
	~33.55(sh)	380		35.71	−0.55	B_{2g}, E_g^b
trans(O_5)-Rh(*S,S*-EDDS)$^-$	~26.66(sh)	215	$^{1}E_g(D_{4h})$	27.54	−2.29	E_g^a
$(+)_D$	30.48	565	$^{1}A_{2g}(D_{4h})$	31.54	+2.74	A_{2g}
	~35.08(sh)	245				B_{2g}, E_g^b

[x] The numerical data for Co(III) and Cr(III) complexes are taken from references 10, 15 and 16.

[y] Estimated from figures in references 10 and 11; ΔA values only listed for CD.

for Cr(III) relative to the same state of Co(III) and Rh(III). Thus, for Cr(III), the $^4E_g^a$ should be lower in energy than the $^4B_{2g}$ state (both from $^4T_{2g}$). The ordering of the states for the $^4T_{1g}$ band depend on the signs and the relative values of two parameters, Ds and Dt.

These arguments are used as a basis for assigning the spectra reported here (Table I). They have been borne out by spectral investigations of other similar Co(III) complexes with holohedrized D_{4h} symmetry[18–21] as well as by polarized electronic absorption spectra of single crystals of *trans*-$[Cr(en)_2F_2]ClO_4$[22].

The shapes of the absorption bands of EDTA-type complexes of Co(III)[8,10,13,16] and Cr(III)[15] suggest pseudo-octahedral symmetry, but according to Neal and Rose[10] the interpretation of the electronic absorption spectra of these complexes based on a holohedrized tetragonal D_{4h} field would be more justified. Using pseudo-D_{4h} symmetry and Wentworth and Piper's treatment[17], they concluded that the *S,S*-EDDS ligand is a stronger donor toward Co(III) than is EDTA[10]. In accordance with that, D_q values of the *S,S*-EDDS complexes of Co(III)[8,16] and Cr(III)[15] are slightly greater than those of the corresponding EDDDA complexes[15,16].

The electronic absorption spectra of the presently investigated Rh(III) complexes (Figure 2a, Table I) are very similar to each other in shape. The bands are considerably more intense than those of the corresponding Co(III) and Cr(III) complexes (Table I). The absorption spectra of these Rh(III) complexes also show more evidence of broadening and splitting in the lower energy spin-allowed region than those of the corresponding Co(III) and Cr(III) complexes. For inert Rh(III) complexes of the type considered here, the lowering of symmetry (relative to O_h) has been observed usually to give rise only to absorption band broadening and intensification rather than distinct splitting[5,18,23,24]. The bands are so broad that both spin-allowed regions are included in the same band manifold. These factors, along with the fact that Rh(III) is larger than Co(III) and Cr(III) support the idea that the Rh(III) complexes are more distorted and of lower actual symmetry than the others. It should be pointed out, though, that the relatively high intensities could be at least partially accounted for by the closer proximity of the d–d absorption bands to charge transfer bands, from which they could borrow absorption intensity. It is also possible that the greater splitting of the lower energy spin-allowed bands could be attributed to greater spin-orbit coupling effects associated with the Rh(III) complexes.

The *trans*(O_5) isomers of Rh(*S,S*-EDDS)$^-$ and Rh(EDDDA)$^-$ (Figure 1, isomers I) have C_2 molecular symmetry, while the *trans*(O_5O_6) isomer of Rh(EDDDA)$^-$ possesses C_1 molecular symmetry. However, all isomers have pseudo-D_{4h} (holohedrized) symmetry with the quasi-C_4 axes being perpendicular to the equatorial planes. Since splitting under the first absorption bands is observed, the interpretation of these spectra is in accordance with the D_{4h} model. Because the equatorial donor atoms (2N and 2O) are higher in the spectrochemical series than are the axial (2O), the peaks at lower and higher energy are assigned to belong to the $E_g^a(D_{4h})$ and $A_{2g}(D_{4h})$ components relatively.

CD Spectra

The CD spectra, data, and tentative band assignments of the $(-)_D$ isomers of the Rh(EDDDA)$^-$ complexes and of $(+)_D$ *trans*(O_5)-[Rh(*S,S*)-EDDS]$^-$, are given in Figure 2b and Table I. As is true of their absorption spectra, the CD spectra of the Rh(III) complexes are also more intense than those of the corresponding Co(III) and Cr(III) complexes and similar explanations can be given. However, they are not as well resolved into low symmetry (C_2) components as are the Co(III) and Cr(III) CD spectra. The greater effects of spin-orbit coupling of Rh(III) could very well result in broadening of both CD and absorption bands. It is assumed implicitly that the Rh(*S,S*-EDDS)$^-$ complex is the *trans*(O_5) isomer which must have the Λ configuration[8]. It seems extremely unlikely that it could be the Δ, *trans*(O_5O_6), isomer for the following reasons:

a) Only the *trans*(O_5) isomer has been isolated for corresponding Co(III) and Cr(III) isomers.

b) The *trans*(O_5O_6) isomer would contain two in-plane five-membered rings, presumably causing greater strain than in the *trans*(O_5) isomer.

c) The Rh(III) ion is larger than either Co(III) or Cr(III), making strain an even more important factor than in the Co(III) and Cr(III) complexes.

The empirical rules for assigning the absolute configurations of d^3 and low-spin d^6 transition metal complexes are consistent with the results when D_{4h} symmetry is assumed if there are two CD peaks in the region of the low energy spin-allowed transition, one on each side of the absorption maximum, or assuming C_2 symmetry when there are three peaks or only two peaks in this region, both on the low-energy side of the absorption maximum. In a third case, when a single CD peak appears in the first absorption band region, the empirical rules also can be applied assuming the complete cancellation or masking of weak peaks[25] by a dominant peak.

Many Co(III)[13,16,26-29] and Cr(III)[15] complexes with EDTA-type ligands exhibiting similar CD splitting and sign patterns, have been treated in terms of C_2 symmetry. For complexes of this symmetry, Mason has shown[30] that the signs of the Cotton effects of components under the lowest energy (O_h) band are related to signs of Cotton effects of the parent levels in complexes with D_3 symmetry having the same configuration. The transition to the $A(C_2)$ state, derived from the $E_g^a(D_{4h})$ state is thought to be responsible for the low energy CD peak for Co(III)-EDTA-type complexes. For *cis*-$[Co(en)_2X_2]^{n+}$ (which are like the holohedrized *trans*-$[MX_4O_2]^-$ complexes of the type reported here, as described earlier) it is thought further that the $A(C_2)$ component retains the same sign as the $E_a(D_3)$ component of $[Co(en_3)]^{3+}$ of the same configuration[30]. The $A(C_2)$

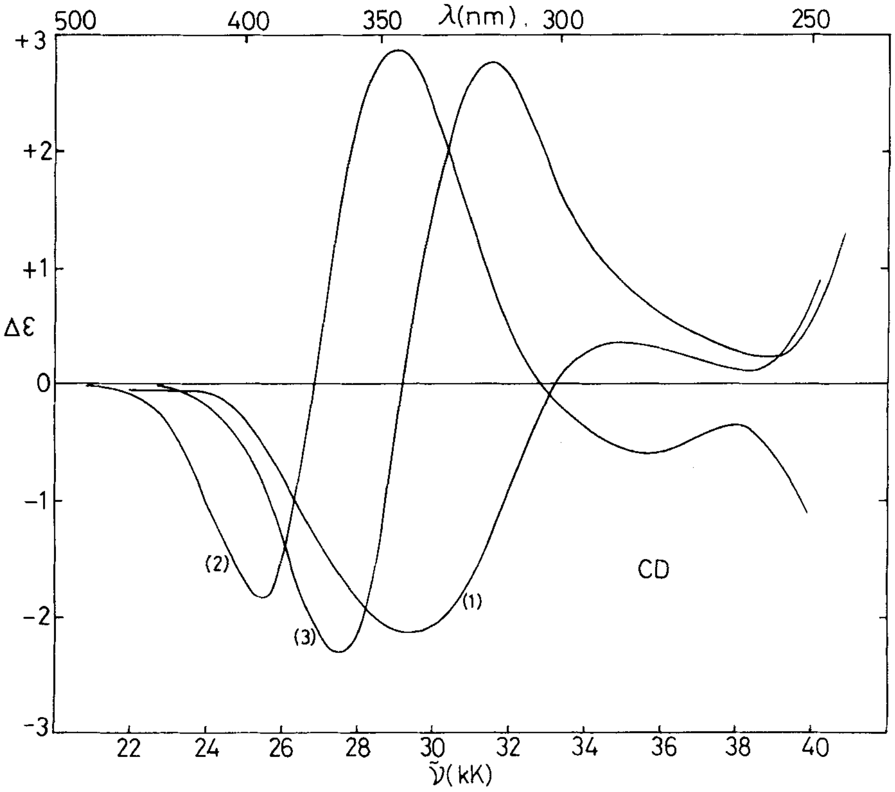

FIGURE 2b The CD spectra of:

(1) *trans*(O_5)-(−)$_D$-Li[Rh(EDDDA)]·$5H_2O$
(2) *trans*(O_5O_6)-(−)$_D$-Li[Rh(EDDDA)]·H_2O
(3) *trans*(O_5)-(+)$_D$-Na[Rh(*S*,*S*-EDDS)]·H_2O

components (at lowest energy) in the CD spectra of Λ-*cis*-$[Co(en)_2X_2]^{n+}$ complexes all have positive Cotton effects, the same sign as the $E_a(D_3)$ CD component of Λ-$[Co(en)_3]^{3+}$ [30]. The lowest energy, $A(C_2)$, component of the complexes reported here correlates with both the $E_g^a(D_{4h})$ and $E_a(D_3)$ states.

Although it seems that the CD spectra of all the M(III)-EDTA$^-$ type complexes are interpreted best in terms of symmetry lower than D_{4h}, *i.e.*, C_2, it is also apparent that the effects of centrosymmetric holohedrized D_{4h} symmetry have not vanished completely. Absorption spectra are strongly dependent upon only the electric dipole. The electric dipole operator, T_{1u} in O_h, transforms as A_{2u} and E_u in D_{4h} and thus retains its "ungerade" character. Since all ground and excited states in D_{4h} have "gerade" character, all transitions have "ungerade" character and are forbidden by the electric dipole mechanism. Rotational strength occurs via electric and magnetic dipole mechanisms. The magnetic dipole operator is T_{1g} in O_h and A_{2g} and E_g in D_{4h}. Thus magnetic dipole transitions all have "gerade" character and some are allowed. Transitions to the lowest energy spin-allowed states, $^1A_{2g}$ and $^1E_g^a(D_{4h})$, of Co(III) and Rh(III) are magnetically allowed, as are the transitions to $^4B_{2g}$ and $^4E_g^a(D_{4h})$ states in the lowest energy spin-allowed region for Cr(III). However, for the higher energy spin-allowed region, only the transitions to $^1E_g^b(D_{4h})$ for Co(III) and Rh(III) and to $^4E_g^b(D_{4h})$ for Cr(III) are magnetically allowed. Transitions to the $^1B_{2g}(D_{4h})$ state for Co(III) and Rh(III) and to the $^4A_{2g}(D_{4h})$ for Cr(III) in this region and forbidden by both magnetic and electric dipole mechanisms. This can account for the relatively low rotational strengths in the high energy spin-allowed regions for all the M(III) complexes. In non-centro-symmetric C_2 symmetry all possible transitions are electrically and magnetically allowed.

The optically active *S,S*-EDDS ligand, upon coordination, apparently forms only the *trans*(O$_5$) isomers which can have only the Λ absolute configuration shown in Figure 1a. The *trans*(O$_5$) isomers of Co(III)[9] and Cr(III)[15] *S,S*-EDDS complexes have three CD peaks of alternating sign in the lowest energy spin-allowed region, corresponding to the number of transitions expected for C$_2$ symmetry. The excited states in C$_2$ and their parent D$_{4h}$ states (parenthetical) are A(E_g^a), B(E_g^a) and B(A_{2g}) for Co(III) and A(E_g^a), B(E_g^a) and B(B_{2g}) for Cr(III). The positive lowest energy CD components, A(C$_2$), of these complexes have been correlated with the absolute configurations of EDTA type complexes[15,16]. The $(-)_D$ isomers of Co(III) and Cr(III) complexes with EDDDA (Table I) have two CD peaks in the low-energy region which occur at lower energy than the absorption maximum suggesting that they are components split from the E_g^a(D$_{4h}$) state. The positive lowest energy CD peaks of the EDDDA complexes are presumed to be the A(C$_2$) components and these $(-)_D$Co(III) and Cr(III) complexes have been assigned the Λ configuration[15,16]. This assignment has recently been confirmed crystallographically for Li$(-)_D$-[Cr(EDDDA)] · 5H$_2$O[31]. The positive sign and the known absolute configuration of the Cr complexes support the assignment of the lowest CD peak as A(C$_2$) of E_g^a(D$_{4h}$) parentage.

Since the absorption and CD spectra of the Rh(III) complexes show no clear indication of more than 2 components in the first band region, one must use effective symmetry (D$_{4h}$) which does not require more than 2 components. One might expect more distortion from effective D$_{4h}$ symmetry for the larger Rh(III), as compared to Co(III). It is possible that there is a third component masked by one of the others, but the band shapes do not give an indication of its location. For reasons cited above the $(+)_D$-*trans*-(O$_5$)-[Rh(*S,S*-EDDS)]$^-$ can be assigned the Λ configuration. The CD spectrum of $(-)_D$-*trans*-(O$_5$O$_6$)-[Rh(EDDDA)]$^-$ in the first absorption band region is almost the same as that of $(+)_D$-[Rh(*S,S*-EDDS)]$^-$ except for the shift of the CD peaks to lower energy for the EDDDA complex, as expected from the positions of the absorption bands. On this basis $(-)_D$-*trans*(O$_5$O$_6$)-[Rh(EDDDA)]$^-$ is assigned the Λ configuration. For each of these complexes the positive major CD peak is near the absorption maximum with the negative CD peak near the low energy shoulder on the absorption peak. For $(-)_D$-*trans*(O$_5$)-[Rh(EDDDA)]$^-$ there is only one CD peak in the region of the first absorption band. It occurs near the absorption band maximum and presumably is related to the same electronic transition as the positive CD peaks of the other two complexes. On the basis of opposite signs of related peaks, $(-)_D$-*trans*(O$_5$)-[Rh(EDDDA)]$^-$ would be assigned the Δ configuration. However, the CD band shows broadening on the low energy side suggesting the presence of a negative CD peak in the region of the low energy shoulder on the absorption band. One of these CD components is reversed in sign compared to the other complexes. The presence of a possible third component complicates the interpretation. It should be noted that the lowest energy CD peak for *trans*(O$_5$)-[Co(EDDDA)]$^-$ is very weak in comparison to that of the *trans*(O$_5$O$_6$)-isomer. The solubility rule[32,33] which relates absolute configurations of complexes which give the less soluble diastereomers with the same resolving agent is not infallible. However, it would indicate that $(-)_D$-*trans*(O$_5$)-[Rh(EDDDA)]$^-$ has the same (Λ) configuration as $(+)_D$-*trans*(O$_5$O$_6$)[Rh(EDDDA)]$^-$ in agreement with the assignment made on the basis of the dominant CD peak.

The assignments of absolute configurations are made on the basis of relating CD patterns to those of [Rh(EDDS)]$^-$. The assignments of the CD peaks to electronic transitions poses a problem. One expects the E(T$_{1g}$) component to be at lower energy than the A$_2$(T$_{1g}$) component for D$_{4h}$. If we relate these complexes to Co(EDTA)$^-$ type complexes, the assignments of absolute configurations here would be reversed. The peak assigned as E(D$_{4h}$) for Co(EDTA)$^-$ type complexes[13,16] is positive for the Λ (Λ Δ Λ) configuration. Alternatively one is forced to reverse the assignments of the E and A$_2$ peaks. There seems to be no reason to expect such reversal for these complexes. The empirical correlation using the stereospecificity of *S,S*-EDDS as a basis seems to be the better choice.

Contributions to the ligand field optical activity can be expected from the two asymmetric (*R,R*) nitrogens of $(-)_D$-*trans*(O$_5$)-Rh(EDDDA)$^-$. The effects of the *S,R* nitrogens of $(-)_D$-*trans*(O$_5$O$_6$)-Rh(EDDDA)$^-$ should cancel practically. The $(+)_D$-*trans*(O$_5$)-Rh(EDDDS)$^-$ has both asymmetric carbons (*S,S*) and asymmetric nitrogens (*S,S*). Because of the similarity of CD intensities of all three Rh(III) complexes it can be assumed that the optical activity in each case is due mainly to configurational effects. The situation is similar to that observed for corresponding Co(III) and Cr(III) complexes.

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