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Synthesis and characterization of hexadentate cobalt(III) complexes with new edta-type ligands

Part 3. Circular dichroism of cobalt(III) complexes of ethylenediamine-*N,N,N'*-triacetic-*N'*-3-propionic acid and ethylenediamine-*N,N*-diacetic-*N',N'*-di-3-propionic acid*

Dušan J. Radanović**, Miloš I. Djuran
Faculty of Science, University of Kragujevac, Kragujevac YU-34000 (Serbia)

Tomislav S. Kostić
Faculty of Science, University of Priština, Priština YU-38000 (Serbia)

Chris Maricondi
The Pennsylvania State University, McKeesport, PA 15132 (USA)

and Bodie E. Douglas
University of Pittsburgh, Pittsburgh, PA 15260 (USA)

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Abstract

Cobalt(III) complexes with the hexadentate ligands, ethylenediamine-*N,N,N'*-triacetate-*N'*-3-propionate ion (ed3ap) and ethylenediamine-*N,N*-diacetate-*N',N'*-di-3-propionate ion (u-eddadp), have been prepared, chromatographically separated and resolved. Only one of two geometrical isomers of the $[Co(ed3ap)]^-$ complex was isolated. A ^1H NMR spectrum of this isomer, *trans*(O_5)-$[Co(ed3ap)]^-$, indicates that its six-membered propionate chelate ring is bound equatorially to the cobalt(III) ion. There is no similar structural variation possible for the hexadentate u-eddadp ligand. $(-)_{546}$-*trans*(O_5)-$[Co(ed3ap)]^-$ and $(+)_{546}$-$[Co(u\text{-}eddadp)]^-$ complexes with a positive CD peak at lowest energy in the first spin-allowed absorption band region are tentatively assigned the Λ absolute configuration. Spectral data of these complexes are discussed in relation to those of other $[Co(edta\text{-}type)]^-$ complexes of known structure.

Introduction

Factors determining structural types of edta (ethylenediaminetetraacetate ion) and related complexes have been discussed in detail in terms of the d-electron configuration and the size of the central metal ion M, and the difference in bond lengths between the M–N and M–O bonds involved [1]. The Co(III) ion with an ionic radius of 0.69 Å forms an octahedral hexadentate complex with edta and its structural parameters are known [2, 3]. The $[Co(edta)]^-$ ion, with two different pairs of glycinate rings (G rings in equatorial positions and R rings in axial positions), is strained. The G rings of this complex are more strained than the R glycinate rings [2, 3]. Larger ions can show higher coordination numbers and for ions with high octahedral ligand field stabilization energy, one H_2O can replace a carboxylate arm.

Aminopolycarboxylate complexes less strained but similar to $[M(edta)]^-$ usually contain ligands that have a longer diamine backbone and/or carboxylate chains. These complexes of Co(III) and Cr(III) have been reviewed recently [4]. X-ray studies show that 1,3-pdta (1,3-propanediaminetetraacetate ion) and eddadp (symmetrical ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate ion) ligands are hexadentate with larger metal ions such as iron(III) [1a], chromium(III) [5, 6] and rhodium(III) [5, 7].

Studies of these complexes were undertaken to determine how various structural changes of the ligand affect the optical activity of thc complexes [4, 8]. The edta-type complexes were treated in terms of C_2 or

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*Parts 1 and 2 are refs. 14 and 15.

**Author to whom correspondence should be addressed.

effective D_{4h} symmetry and their CD spectra discussed in relation to their absolute configurations and various theories of optical activity [8, 9–19].

For the ligands having mixed (five- and six-membered) carboxylate arms, such as eddadp [10, 11], eda3p (ethylenediamine-*N*-acetate-*N*,*N'*,*N'*-tri-3-propionate ion) [14], 1,3-pddadp (1,3-propanediamine-*N*,*N'*-diacetate-*N*,*N'*-di-3-propionate ion) [15], geometrical isomers are possible that differ in the number (0, 1 or 2) of six-membered rings lying in the girdling plane. The configurational effect (the contribution to optical activity due to the relative size and distribution of the chelate rings) appears to be responsible for the variation of the rotational strengths of the CD bands for these complexes [8, 17, 18].

The $[Co(eda3p)]^-$ complex ion [14] with three chelating propionate arms and one chelating acetate arm has two possible geometrical isomers depending on whether the acetate arm is axially or equatorially coordinated. These isomers are named either *trans*(O_5O_6) or *trans*(O_6), respectively. The former forms preferentially [14], presumably, because G glycinate rings are more strained than R glycinate rings in $[Co(edta)]^-$-type complexes [2, 3, 20].

The symmetrical ligands, eddadp and 1,3-pddadp, differing only in the diamine ring, can form a maximum of three geometrical isomers when coordinated: *trans*(O_5), *trans*(O_5O_6) and *trans*(O_6). Both isomers, *trans*(O_5) and *trans*(O_5O_6), of cobalt(III) [10, 11] and rhodium(III) [21] with eddadp ligand have been characterized, however, only the *trans*(O_5) isomer of the corresponding chromium(III) complex was identified [6, 22]. The eddadp ligand apparently minimizes chelate strain by forming *trans*(O_5) isomers that have six-membered rings in the G plane [6, 7, 10, 11, 21, 22]. Curiously, in hexadentate $[M(1,3\text{-pddadp})]^-$ complexes (M = Cr(III) [23] or Co(III) [15, 24, 25]) the dominant isomer was found to be *trans*(O_6) with 3-propionate arms in axial positions, a coordination geometry which has been verified by X-ray analysis [23, 24].

For the same configuration of the complex, changing from a *trans*(O_5) to a *trans*(O_6) arrangement for $[M(eddadp)]^-$ or $[M(1,3\text{-pddadp})]^-$ inverts the chiral nitrogen centers or the configuration of the complex. This change causes an exchange of in-plane substituents for out-of-plane substituents [15, 26] and can significantly affect the nature and extent of non-bonded interactions among the different chelate rings.

Recent studies on the formation of hexadentate $[Rh(1,3\text{-pddadp})]^-$ complexes [27] showed that the *trans*(O_5) isomer is present. As expected, the size of the metal ion [Co < Cr < Rh] in this case has a profound effect on the distribution of geometrical isomers.

Experimental

Ethylenediamine-*N*-acetic acid dihydrochloride dihydrate ($Hedma \cdot 2HCl \cdot 2H_2O$) was prepared by using a previously described procedure [28]. Other commercially obtained reagent-grade chemicals were used without further purification.

Optical isomers are identified by (+) or (−), corresponding to the sign of the lowest energy CD band, or by the sign of the optical rotation at a wavelength λ [$(+)_\lambda$ or $(-)_\lambda$]. The chirality is designated as Δ or Λ according to IUPAC rules [29].

Preparation of ethylenediamine-N,N,N'-triacetic-N'-3-propionic acid (H_4ed3ap) and ethylenediamine-N,N-diacetic-N',N'-di-3-propionic acid (H_4u-eddadp)

Ethylenediamine-*N*-acetic acid dihydrochloride dihydrate, $Hedma \cdot 2HCl \cdot 2H_2O$, (22.70 g, 0.1000 mol) was dissolved in 35 ml of water, and NaOH (12.00 g, 0.3000 mol in 40 ml of water) was added (solution I). 3-Chloropropionic acid (21.70 g, 0.2000 mol) was dissolved in 50 ml of water and cooled in an ice bath. A cooled solution of NaOH (8.00 g, 0.200 mol in 40 ml of water) was added dropwise, the rate of addition being adjusted so that the temperature remained below 15 °C (solution II). Solutions I and II were mixed, and the reaction mixture was stirred at room temperature for 5 days. During this process, the necessary amount of NaOH was added dropwise to keep the pH in the range 8–9 (solution III). Chloroacetic acid (18.90 g, 0.2000 mol) was dissolved in 50 ml of water and cooled in an ice bath. A cooled solution of NaOH (8.00 g, 0.200 mol in 40 ml of water) was added dropwise (solution IV). Solutions III and IV were mixed, and the mixture was left with stirring at room temperature for 3 days. During that time the pH of the solution was kept to *c.* 7–8 by the addition of NaOH solution (8.00 g, 0.200 mol in 40 ml of water). The volume of the resulting solution was reduced at room temperature to 80 ml, and the deposited NaCl was separated by filtration. The obtained filtrate is a mixture of several H_4edta-type acids involving zero to three propionate arms. Because of the difficulty in the separation of these products, the mixture was used directly for the preparation of the complexes that are more easily separated.

Preparation and separation of complexes: trans(O_5) geometrical isomer of potassium (ethylenediamine-N,N,N'-triacetato-N'-3-propionato)cobaltate(III)-dihydrate, K[Co(ed3ap)]·$2H_2O$, and potassium (ethylenediamine-N,N-diacetato-N',N'-di-3-propionato)-cobaltate(III) dihydrate, K[Co(u-eddadp)]·$2H_2O$

Cobalt(III) chloride hexahydrate (23.79 g, 0.1000 mol in 50 ml of water) was added to the mixture containing the edta-type acids. The temperature of this solution was slowly increased to 65 °C with stirring for 2 h. During this process, ≈30 ml of 3% $\mathrm{H_2O_2}$ was added gradually, causing the solution to turn blue–violet. The solution was evaporated to 60 ml, and the deposited NaCl was separated by filtration. A quarter of this solution was poured into a 5×60 cm column containing Dowex 1-X8 (200–400 mesh) anion-exchange resin in the $\mathrm{Cl^-}$ form. The column was then washed with $\mathrm{H_2O}$ and eluted with 0.1 M KCl (*c.* 0.5 ml/min). Five bands with 1− charge appeared on the column. Three of these are complexes of known structure: *trans*($\mathrm{O_5O_6}$)-$[\mathrm{Co(eda3p)}]^-$ (first eluate), *trans*($\mathrm{O_5}$)-$[(\mathrm{Co(eddadp)}]^-$ (second eluate) and $[\mathrm{Co(edta)}]^-$ (last eluate). The third and fourth eluates were evaporated to 10 ml and desalted by passage through a G-10 Sephadex column, with distilled water as the eluent. The third eluate was evaporated to a small amount and then to dryness after standing in a desiccator over $\mathrm{CaCl_2}$. The complex was crystallized after dissolving in 20 ml of methanol with addition of *c.* 10 ml of acetone and standing at 0 °C for 12 h. The blue–violet crystals were collected and air-dried; yield 0.9 g of $\mathrm{K[Co(u\text{-}eddadp)]\cdot 2H_2O}$. The fourth eluate was concentrated to a volume of 5 ml and stored in a desiccator over methanol for several days. Violet crystals were collected, washed with methanol and then ether, and air-dried; yield 1.5 g of *trans*($\mathrm{O_5}$)-$\mathrm{K[Co(ed3ap)]\cdot 2H_2O}$. *Anal.* Calc. for *trans*($\mathrm{O_5}$)-$\mathrm{K[Co(ed3ap)]\cdot 2H_2O = KCoC_{11}H_{18}N_2O_{10}}$ (M_r=436.30): C, 30.28; H, 4.16; N, 6.42. Found: C, 29.36; H, 4.04; N, 6.28%. Calc. for $\mathrm{K[Co(u\text{-}eddadp)]\cdot 2H_2O = KCoC_{12}H_{20}N_2O_{10}}$ (M_r=450.33): C, 32.00; H, 4.47; N, 6.22. Found: C, 32.41; H, 4.27; N, 6.45%.

Resolution of the trans(O_5) geometrical isomer of potassium (ethylenediamine-N,N,N′-triacetato-N′-3-propionato)cobaltate(III) dihydrate, K[Co(ed3ap)]·2H_2O

Silver acetate (0.42 g, 0.0025 mol) and $(-)_{589}$-$\mathrm{[Co(en)_2(ox)]Br\cdot H_2O}$ (0.91 g, 0.0025 mol) were stirred together at 50 °C for 20 min in 15 ml of water. AgBr was removed by filtration and washed with 2 ml of water. The combined filtrate and washing were added to the solution obtained by dissolving 2.18 g (0.0050 mol) of *trans*($\mathrm{O_5}$)-$\mathrm{K[Co(ed3ap)]\cdot 2H_2O}$ in 10 ml of water. The resulting solution was stirred with heating (50 °C) for 15 min and then allowed to stand at room temperature overnight. The precipitated less-soluble diastereoisomer, $(-)_{589}$-$\mathrm{[Co(en)_2(ox)]}$-$(-)_{546}$-$\mathrm{[Co(ed3ap)]}\cdot x\mathrm{H_2O}$, was removed by filtration, washed with ethanol and then ether, and air-dried (1.22 g). This diastereoisomer was crystallized from water to a constant value of optical rotation. Aqueous solution (0.05%) gave: $[\alpha]_{589} = -980°$; $[\alpha]_{546} = -960°$. The corresponding enantiomer in the form of the potassium salt was obtained by dissolving the diastereoisomer in water and passing the solution through a cation-exchange column in the $\mathrm{K^+}$ form. The eluate was evaporated to a volume of 5 ml, and this enantiomer was crystallized after addition of *c.* 10 ml of ethanol and cooling in a refrigerator for two days. The violet crystals were collected, washed with ethanol and then ether, and air-dried. The opposite enantiomer was obtained by the same procedure using $(+)_{589}$-$\mathrm{[Co(en)_2(ox)]I}$ as the resolving agent. Aqueous solutions (0.05%) gave: $[\alpha]_{589} = \pm 920°$; $[\alpha]_{546} = \pm 780°$. *Anal.* Calc. for *trans*($\mathrm{O_5}$)-$(-)_{546}$-$\mathrm{K[Co(ed3ap)]\cdot 2H_2O = KCoC_{11}H_{18}N_2O_{10}}$ (M_r= 436.30): C, 30.28; H, 4.16, N, 6.42. Found: C, 30.08; H, 4.32; N, 6.33%.

Resolution of potassium (ethylenediamine-N,N-diacetato-N′,N′-di-3-propionato)cobaltate(III) dihydrate, K[Co(u-eddadp)]·2H_2O

Silver acetate (0.17 g, 0.0010 mol) and $(-)_{589}$-$\mathrm{[Co(en)_2(ox)]Br\cdot H_2O}$ (0.37 g, 0.0010 mol) were stirred together at 45 °C for 30 min in 10 ml of water. The AgBr was removed by filtration and washed with 2 ml of water. The wash was added to the filtrate, to which solid $\mathrm{K[Co(u\text{-}eddadp)]\cdot 2H_2O}$ (0.90 g, 0.0020 mol) was then added, and the temperature of this mixture was increased to 50 °C with stirring for 15 min. To the resulting solution, 20 ml of methanol was added and the solution was allowed to stand at room temperature overnight. The less-soluble diastereoisomer, $(-)_{589}$-$\mathrm{[Co(en)_2(ox)]}$-$(+)_{546}$-$\mathrm{[Co(u\text{-}eddadp)]}\cdot x\mathrm{H_2O}$, was removed by filtration, washed with a small amount of methanol and then ether, and air-dried; yield 0.62 g. This diastereoisomer was fractionally recrystallized to a constant value of optical rotation by dissolving in a small amount of water and adding methanol followed by cooling in a refrigerator overnight. Aqueous solution (0.05%) gave: $[\alpha]_{589} = -1480°$; $[\alpha]_{546} = -485°$. The corresponding enantiomer in the form of the potassium salt was obtained by passing the aqueous solution of the diastereoisomer through a cation-exchange column in the $\mathrm{K^+}$ form. The eluate was evaporated over $\mathrm{CaCl_2}$ in a vacuum desiccator to dryness. The opposite enantiomer was obtained by the same procedure using $(+)_{589}$-$\mathrm{[Co(en)_2(ox)]I}$ as the resolving agent. Aqueous solutions (0.05%) gave: $[\alpha]_{589} = \pm 1770°$; $[\alpha]_{546} = \pm 78°$. *Anal.* Calc. for $(+)_{546}$-$\mathrm{K[Co(u\text{-}eddadp)]\cdot 2H_2O = KCoC_{12}H_{20}N_2O_{10}}$ (M_r=450.33); C, 32.00; H, 4.47; N, 6.22. Found: C, 31.77; H, 4.75; N, 6.40%.

Physical measurements

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

Proton NMR spectra were measured on a Varian Gemini-200 NMR spectrometer (200 MHz). $\mathrm{D_2O}$, containing 0.1% sodium 4,4-dimethyl-4-sila-1-pentanesulfonate (DSS) as an internal reference, was used as a solvent, and ≃1.5% D_2O solutions of the substances were used.

The electronic absorption spectra were obtained with a Varian SuperScan 3 spectrophotometer. For these measurements aqueous solutions (*c.* 2×10^{-3} M) were used.

The circular dichroism (CD) spectra were recorded at room temperature on a JASCO Model J-500A spectropolarimeter 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

Two complexes, each, with a new unsymmetrical edta-type ligand, $[Co(ed3ap)]^-$ and $[Co(u\text{-}eddadp)]^-$, are characterized here. The ed3ap ligand with hexadentate coordination can yield two geometrical isomers differing in the position of the six-membered ring: *trans*(O_5) (**I**) and *trans*(O_5O_6) (**II**), (Fig. 1(a)). Only one, the favored less-strained *trans*(O_5) isomer of the $[Co(ed3ap)]^-$ was isolated. The unsymmetrical u-eddadp ligand, has N-geminal 3-alaninate and N-geminal glycinate rings and forms only one geometrical isomer (Fig. 1(b)). Both complexes presented here possess a rhombic field and have C_1 molecular symmetry. ^1H NMR, electronic absorption and CD spectra were used to characterize the complexes. The spectral data of these complexes are discussed in relation to those of other $[Co(edta\text{-}type)]^-$ complexes of known structures.

^1H NMR spectra and geometry of complexes

The ^1H NMR spectra of *trans*(O_5)-$[Co(ed3ap)]^-$ and $[Co(u\text{-}eddadp)]^-$ are shown in Fig. 2 (Table 1). These spectra are interpreted in light of the results obtained for other (aminopolycarboxylato)cobalt(III) complexes containing the various type glycinate rings [30–32]. In the spectrum of the *trans*(O_5)-$[Co(ed3ap)]^-$ complex (Fig. 2(a)) having C_1 molecular symmetry, three AB patterns can be expected for three non-equivalent glycinate rings. The spectrum of this complex shows a glycinate singlet at 3.97 ppm for the R_2 ring (Fig. 1) and two well-resolved AB patterns belonging to two non-equivalent (R_1 and G) glycinate rings. Similar results were found in the case of [Co(ed3a)(X)] com-

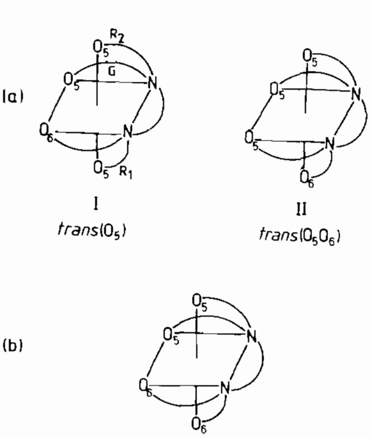

Fig. 1. (a) Two possible geometrical isomers of the Λ-$[Co(ed3ap)]^-$ complex; (b) structure of Λ-$[Co(u\text{-}eddadp)]^-$.

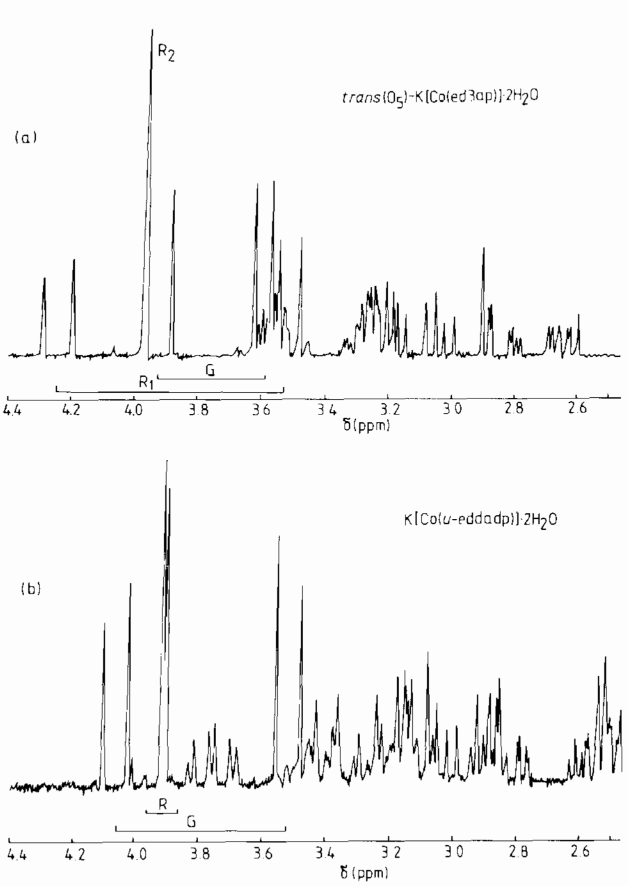

Fig. 2. ^1H NMR spectra: (a) *trans*(O_5)-$[Co(ed3ap)]^-$; (b) $[Co(u\text{-}eddadp)]^-$.

TABLE 1. ^1H NMR parameters for the complexes studied[a]

	trans(O_5)-K[Co(ed3ap)]·$2H_2O$			K[Co(u-eddadp)]·$2H_2O$	
	R_2 ring	R_1 ring	G ring	R ring	G ring
δ_A (ppm)	3.97 (singlet)	4.25	3.93	3.96	4.06
δ_B (ppm)		3.53	3.58	3.86	3.52
J_{AB} (Hz)		18.3	15.9	18.4	15.6
$\delta_A-\delta_B$ (ppm)	0	0.72	0.35	0.10	0.54

[a] Values are in ppm downfield from DSS as internal standard.

plexes ($X = NO_2^-$ or H_2O) where the R_2 protons also appeared as singlets and other glycinate protons for R_1 and G rings have been found to produce AB patterns with good resolutions [32].

The AB pattern for the R_1 ring of the *trans*(O_5)-[Co(ed3ap)]$^-$ complex (centered at 3.89 ppm) has $\delta_A = 4.25$ ppm, $\delta_B = 3.53$ ppm and $J_{AB} = 18.3$ Hz. The other AB pattern, caused by the G ring methylene hydrogen atoms, is centered at 3.74 ppm, with $\delta_A = 3.93$ ppm and $\delta_B = 3.58$ ppm and a J_{AB} coupling constant of 15.9 Hz (Table 1).

In the same region, the [Co(u-eddadp)]$^-$ complex (Fig. 2(b)) shows signals of two well-resolved AB patterns for two non-equivalent glycinate rings (R and G) that emanate from the same nitrogen. The AB pattern of the R ring is centered at 3.91 ppm, has $\delta_A = 3.96$ ppm and $\delta_B = 3.86$ ppm, with a J_{AB} coupling constant of 18.4 Hz. The other AB pattern for the G ring (centered at 3.79 ppm) has $\delta_A = 4.06$ ppm, and $\delta_B = 3.52$ ppm with $J_{AB} = 15.6$ Hz. The $\delta_A - \delta_B$ values obtained for the G rings (Table 1) for both complexes are consistent with the fact that these systems represent less strained model complexes relative to [Co(edta)]$^-$ [30].

Electronic absorption and circular dichroism spectra

Absorption spectra

Electronic absorption and CD spectra of the *trans*(O_5)-[Co(ed3ap)]$^-$ and [Co(u-eddadp)]$^-$ complexes are shown in Fig. 3 (and Table 2) for comparison with those of Λ-[Co(edta)]$^-$ [3, 33] and two isomers of Λ-[Co(eddadp)]$^-$ [10, 11]. Data are included in Table 2 for Λ-[Co(eda3p)]$^-$ [14] and Λ-[Co(edtp)]$^-$ (ethylenediaminetetra-3-propionate ion) [9, 34].

Electronic spectra of [Co(edta-type)]$^-$ complexes (Table 2) which maintain the five-membered diamine ring and with 3-propionate arms substituted for acetate arms (edta to edtp) are more similar than the corresponding spectra of the [Co(1,3-pdta-type)]$^-$ complexes which vary the size of carboxylate arms in the same way but maintain a six-membered diamine ring (1,3-pdta to 1,3-pdtp) [15].

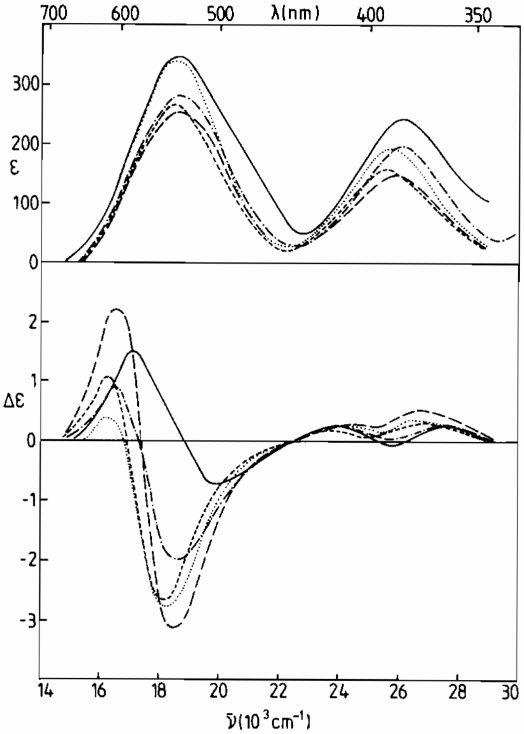

Fig. 3. Electronic absorption and CD spectra of hexadentate [Co(edta-type)]$^-$ complexes: (——) Λ-(+)-(−)$_{546}$-[Co(edta)]$^-$, (–·–) Λ-(+)-(−)$_{546}$-[Co(ed3ap)]$^-$ (**A**), (-----) Λ-(+)-(+)$_{546}$-[Co(u-eddadp)]$^-$ (**B**), (·····) Λ-(+)-(−)$_{589}$-*trans*(O_5)-[Co(eddadp)]$^-$, (– – –) Λ-(+)-(−)$_{589}$-*trans*(O_5O_6)-[Co(eddadp)]$^-$.

The absorption spectra of [Co(edta-type)]$^-$ complex ions generally show two visible (ligand field or d → d) absorption bands that are usually symmetrical and show no obvious splitting. Two symmetrical spin-allowed bands are expected for O_h complexes (${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$). The intensities are low as expected for LaPorte-forbidden (but vibronically allowed) transitions. The symmetry of [Co(edta)]$^-$ and [Co(edtp)]$^-$ is C_2, but it is usually C_1 for complexes involving acetate and propionate arms. The d orbitals are centrosymmetric and the absorption spectra of octahedral complexes often show symmetry higher than actual because *trans* ligands interact with lobes of the same d orbital. The [Co(edta)]$^-$ ion with *cis*-[Co(N)$_2$(O)$_4$] microsymmetry was studied [35]. The holohedrized symmetry is tetragonal (D_{4h}) for this case. Thus the axial ligand field (two O donors along the *z* axis) is different from that in the equatorial plane. The field along *x*, the same as along *y*, is the average of that of the N and O donors. If the axial ligand field intensity is not much smaller than the equatorial field, the D_{4h} splitting [${}^1E_g^a + {}^1A_{2g}({}^1T_{1g})$] and [${}^1E_g^b + {}^1B_{2g}({}^1T_{2g})$] is small, and two symmetrical absorption bands appear. This is generally the case for [Co(edta-type)]$^-$ complexes suggesting pseudo-octahedral complexes. Only two of these complexes of this type, *trans*(O_6)-[Co(eda3p)]$^-$ [36] and *trans*(O_6)-[Co(1,3-pddadp)]$^-$ [15], show an apparent shoulder on the lower energy absorption band. The CD spectra for [Co(edta-type)]$^-$ complexes generally show two peaks in the region of the lower energy absorption band. This pattern is expected for D_{4h} symmetry. The small splitting indicated from CD spectra is not observed for absorption spectra because the absorption bands are very broad.

The absorption spectra of the new *trans*(O_5)-[Co(ed3ap)]$^-$ (**A**) and [Co(u-eddadp)]$^-$ (**B**) complexes are very similar in shape, each showing two visible region bands without apparent shoulders (Fig. 3, Table 2). The intensities of their bands are lower than those

TABLE 2. Absorption (AB) and circular dichroism (CD) data for hexadentate [Co(edta-type)]$^-$ complexes

Complex	AB			CD		Reference
	ν (10^3 cm^{-1})	ϵ	ϵ_1/ϵ_2	ν (10^3 cm^{-1})	$\Delta\epsilon$	
Λ-(−)$_{546}$-[Co(edta)]$^-$	18.63	347	1.41	17.10	+1.50	3, 33
				19.80	−0.69	
	26.04	246		23.80	+0.28	
				25.60	−0.09	
				27.60	+0.29	
Λ-(−)$_{546}$-*trans*(O_5)-[Co(ed3ap)]$^-$ (**A**)	18.63	286	1.46	16.53	+0.91	this work
				18.62	−1.98	
	26.04	196		24.09	+0.33	
				27.55	+0.30	
Λ-(+)$_{546}$-[Co(u-eddadp)]$^-$ (**B**)	18.45	279	1.68	16.31	+1.11	this work
				18.25	−2.66	
	25.57	166		23.81	+0.26	
				26.95	+0.36	
Λ-(−)$_{589}$-*trans*(O_5O_6)-[Co(eddadp)]$^-$	18.60	253	1.78	16.50	+2.25	11
				18.40	−3.12	
	25.80	142		24.40	+0.31	
				26.60	+0.56	
Λ-(−)$_{589}$-*trans*(O_5)-[Co(eddadp)]$^-$	18.50	342	1.84	16.20	+0.40	10, 11
				18.30	−2.78	
	25.70	186		24.20	+0.29	
				26.30	+0.36	
Λ(+)$_{546}$-*trans*(O_5O_6)-[Co(eda3p)]$^-$	18.25	318	2.16	16.05	+0.90	14
				18.08	−3.18	
	25.19	147		23.81sh	+0.43	
				26.04	+0.58	
Λ-(+)$_{546}$-[Co(edtp)]$^-$	18.00	253	2.30	15.77	+1.05	9, 14, 34
				17.57	−3.68	
	24.80	110		23.30	+0.10	
				26.30	+0.20	

of [Co(edta)]$^-$ probably because these complexes have less strain. The absorption intensities for [Co(edta)]$^-$ ($\epsilon_1 = 347$) are higher than usual for O_h complexes ($\epsilon \leq 100$). The ring strain, distorting the octahedral arrangement around Co in [Co(edta)]$^-$, is expected to raise the intensities. The first absorption band has about the same intensities for **A** and **B**. The low energy sides of these bands coincide but the band for **A** is broader, suggesting that the tetragonal splitting, although obscured for both, is greater for **A**.

The energy of the maximum for **A** is the same (18 630 cm^{-1}) as that for [Co(edta)]$^-$ indicating that the *Dq* values of these two ligands are nearly identical. The energy of the maximum for **B** is slightly lower (18 450 cm^{-1}), but the lack of broadening on the higher energy side of the band could account for this small apparent shift. The energy of the second d → d absorption band is also the same (26 040 cm^{-1}) for **A** and [Co(edta)]$^-$. The energy of the corresponding band (25 570 cm^{-1}) for **B** is slightly lower as is its first band. The energy separations between the two bands are very nearly the same (7100–7400 cm^{-1}) for the three complexes supporting the close similarities of the *Dq* values.

The ratios of absorption intensity values (ϵ_1/ϵ_2 in Table 2) decrease in the order: edtp (2.30) > eda3p (2.16) > eddadp (1.84, 1.78) > u-eddadp (1.66) > ed3ap (1.46) > edta (1.41). Here the ϵ_1/ϵ_2 ratio is greater the number of propionate arms replacing acetate arms. The ratios differ slightly for *trans*(O_5O_6)-[Co(eddadp)]$^-$ (1.78) and [Co(u-eddadp)]$^-$ (1.68), both having one axial and one equatorial propionate arm. The value is higher (1.84) for *trans*(O_5)-[Co(eddadp)]$^-$ which has both propionate arms equatorial and is close to that of *trans*(O_5O_6)-[Co(eda3p)]$^-$ with two equatorial arms.

Circular dichroism spectra and absolute configurations

Absolute configurations were determined by X-ray methods for Δ-(+)$_{546}$-[Co(edta)]$^-$ [3], Λ-(−)$_{546}$-[Co(1,3-pdta)]$^-$ [20], Λ-(−)$_{589}$-[Co(dhpta)]$^-$ (2-hydroxy-1,3-propanediaminetetraacetate ion) [37] and Δ-(+)$_{589}$-[Co(edtp)]$^-$ [34]. The Λ configuration is assigned to the isomers of these complexes that exhibit two well-defined CD peaks in the region of the first absorption band with the lowest energy CD peak positive and the next peak negative. The complexes (+)-(+)$_{546}$-[Co(eda3p)]$^-$ [14], (+)-(−)$_{589}$-*trans*(O_5)-[Co(eddadp)]$^-$ and (+)-(−)$_{589}$-*trans*(O_5O_6)-[Co(eddadp)]$^-$ [10, 11] and complexes reported here, (+)-(−)$_{546}$-*trans*(O_5)-[Co(ed3ap)]$^-$ and (+)-(+)$_{546}$-[Co(u-eddadp)]$^-$, have the same (+,−) CD sign pattern and such close similarity to one of the compounds of known configurations that these can be assigned Λ configurations with confidence. Complexes of optically active edta-type ligands give the Λ configuration stereospecifically [12, 38, 39]. Other related complexes with 1,3-propanediamine backbones and other structural variations, reviewed recently [4], with the same (+,−) CD patterns have the Λ configuration.

The CD spectra of *all* [Co(edta-type)]$^-$ complexes having only acetate arms, for ethanediamine or 1,3-propanediamine backbones, have two peaks of opposite sign (+,−) for Λ in the lower-energy absorption region [4]. One CD peak has lower energy than that of the absorption maximum and the other peak has higher energy than that of $\epsilon_{\max}$. These spectra have been interpreted using D_{4h} symmetry.

Two complexes, Λ-(+)-*trans*(O_5)-[Co(*S*,*S*-edds)]$^-$ (2*S*,2*S*′-ethylenediamine-*N*,*N*′-disuccinate ion) [16, 18] and Λ-(+)-(+)$_{546}$-*trans*(O_6)-[Co(1,3-pddadp)]$^-$ [15], show three CD peaks (+,−,+) in the region of the lower-energy absorption band. This absorption band shows an obvious shoulder for each of these complexes indicating greater splitting than typical complexes of the series. For these two complexes the splitting is great enough to reveal three CD peaks, the pattern expected for C_2 symmetry. This is probably the actual splitting pattern for the entire series. For [Co(edta-type)]$^-$ complexes with acetate arms only the lowest-energy and a combination of the higher-energy components are resolved. Three components were observed also for Λ-(−)$_{546}$-[Co(en)(mal)$_2$]$^-$ (mal = malonate ion) [33] which was prepared as a simple strain-free model of [Co(edta)]$^-$, both having C_2 symmetry.

For complexes of ed3ap, eddadp (2 isomers) u-eddadp, eda3p and edtp, there are two CD peaks (+,− for Λ) in the region of the lower-energy absorption. One peak is at lower energy than that of $\epsilon_{\max}$, but the other CD peak is also at lower energy than that of $\epsilon_{\max}$, or, in some cases, very near to $\epsilon_{\max}$. The higher-energy CD peak must not be the same component as that observed for the complexes with only acetate arms.

In summary, there are three CD patterns for the Λ configuration: (a) three components (+,−,+) for [Co(edds)]$^-$ and *trans*(O_6)-[Co(1,3-pddadp)]$^-$, (b) two components (+,−) with one component at higher energy and one at lower energy relative to the absorption band maximum for complexes with only acetate arms, and (c) two components (+,−) with both components on the lower-energy side of the absorption band for complexes with acetate and/or propionate arms. Empirical rules for assigning absolute configurations have relied on the sign of the lowest-energy CD peak which appears in all three patterns. These assignments are consistent with absolute configurations from X-ray crystallography and for complexes formed stereospecifically from optically active ligands. If the symmetry is lowered to C_2, the sign of the lower-energy component $E_g(D_{4h})$, is expected to be retained by the $A(C_2)$ component of E_g parentage. The B component from E_g should have the same sign as A and the other $B[A_{2g}(D_{4h})]$ should have the opposite sign [19]. The B states should mix, affecting the CD spectra in the higher-energy region of the first absorption band. The extend of mixing could vary with structural changes.

The CD pattern (c) (+,−) is the one expected for a positive first component and an intense negative second component that cancels the third component. Cancellation on the higher-energy side of the second component shifts its maximum to lower energy so both CD peaks appear at energies lower than $\epsilon_{\max}$. Pattern (b) with well separated positive and negative peaks, one on each side of the absorption band maximum, requires greater separation of components 1 and 2 and smaller separation of components 2 and 3. Component 2 is more intense so component 3 is cancelled.

One complex, Λ-(−)-*trans*(O_5)-[Co(eddams)]$^-$ (2*S*′-ethylenediamine-*N*,*N*-diacetate-*N*′-succinate ion) [17] shows one intense negative CD peak (18 400 cm^{-1}) in the region of the lower-energy absorption band (19 360 cm^{-1}). The complex is formed stereospecifically and the Λ configuration is consistent with the only negative CD peak corresponding to the second component of the general (+,−,+) pattern. For most of the complexes, this negative CD peak is dominant, but not for [Co(edta)]$^-$.

The Cahn-Prelog-Ingold priority rule assigns the *R* absolute configuration to the chiral nitrogen in Λ-*trans*(O_5)-[Co(ed3ap)]$^-$. Jordan and Legg [18] noted that N-vicinal, C-vicinal and ring-conformational effects were small for $[Co(edds)]^-$ compared to $[Co(edta)]^-$ and complexes of substituted edds ligands. The shapes of CD curves of the Λ-$[Co(edtp)]^-$ and Λ-$[Co(u\text{-}eddadp)]^-$ (with no asymmetric nitrogens) and those of the Λ-$[Co(ed3ap)]^-$, Λ-$[Co(eda3p)]^-$ and two isomers of Λ-$[Co(eddadp)]^-$ (Fig. 3 and Table 2) are very similar, as are the relative intensities of their CD components. These similarities support the idea that the difference in CD spectra of these complexes is mostly due to configurational effects associated with the distribution of the five-membered and six-membered chelate rings. The contributions of the asymmetric N is small.

Differences between the CD curves for closely related complexes might reveal the contributions of structural changes. The difference CD curve for (CD of Λ-$[Co(ed3ap)]^-$ − CD of Λ-$[Co(edta)]^-$) gives one broad negative peak between poorly defined weak positive peaks. This might be expected to reflect the effect for one 3-alaninate ring replacing a glycinate ring in an equatorial position. However, the resolved CD peaks for these two complexes represent the lowest-energy component and combinations of the other two components. The CD peaks for Λ-(+)-$[Co(edtp)]^-$ and Λ(+)-$[Co(eda3p)]^-$ correspond to the same lower-energy components. The difference CD curve in Fig. 4 (CD of Λ-$[Co(edtp)]^-$ − CD of Λ-$[Co(ed3ap)]^-$) shows three well-defined peaks (+, −, +) in the lower-energy absorption band region. The difference between the two complexes results from the replacement in an axial position of a glycinate ring by a 3-alaninate ring. This difference curve is similar to the CD curves for Λ-(+)-$[Co(edds)]^-$, Λ-(+)-*trans*(O_6)-$[Co(1,3\text{-}pddadp)]^-$ and Λ-(+)-$[Co(en)(mal)_2]^-$. These peaks presumably identify the three C_2 components.

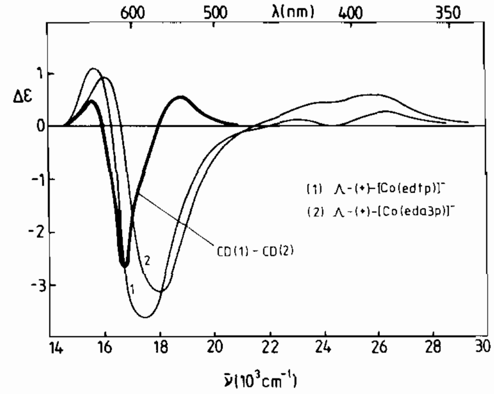

Fig. 4. Difference CD curve (——): CD of Λ-$[Co(edtp)]^-$ (1) − CD of Λ-$[Co(eda3p)]^-$ (2).

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