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

Part 4. Circular dichroism of the *trans*(O_5O_6) isomer of a cobalt(III) complex of 1,3-propanediamine-*N,N,N'*-triacetic-*N'*-3-propionic acid*

Dušan J. Radanović** and Srećko R. Trifunović

Department of Chemistry, Faculty of Science, University of Kragujevac, Kragujevac 34000 (Yugoslavia)

Chris Maricondi

Pennsylvania State University, McKeesport, PA 15132 (USA)

Bodie E. Douglas

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260 (USA)

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Abstract

One of two geometrical isomers of the hexadentate cobalt(III) complex with 1,3-propanediamine-*N,N,N'*-triacetate-*N'*-3-propionate ion (1,3-pd3ap) has been prepared and resolved. The NMR, electronic absorption and circular dichroism (CD) spectra were used to characterize the complex. The ^1H and ^{13}C NMR spectra of this geometrical isomer indicate that its six-membered propionate chelate ring is bound axially to the cobalt(III) ion, *trans*(O_5O_6)-[Co(1,3-pd3ap)]$^-$. The $(-)_{546}$-*trans*(O_5O_6)-[Co(1,3-pd3ap)]$^-$ complex, with a positive CD peak at lowest energy in the first spin-allowed absorption band region is tentatively assigned the Λ absolute configuration. Spectral data for this complex are discussed in relation to those of other [Co(edta-type)]$^-$ complexes which vary the size of carboxylate arms in the same way but maintain a six-membered diamine ring.

Key words: Cobalt complexes; Hexadentate ligand complexes; Chelate complexes

Introduction

Factors determining the structural types of M(III)–edta complexes (edta = ethylenediaminetetraacetate ion) include the d-electron configuration and the size of the central metal ion M. These influence differences in bond lengths (M–N and M–O), ring strain, and the ligand configuration [1–4].

Bonding parameters that greatly influence the coordination number (*CN*) of metal ions in edta and edta-type complexes have been discussed by Yamamoto *et al.* [1]. When the ionic radius of the metal ion, with other than d^0, d^5 or d^{10} configurations, exceeds that of Fe(III) (the 'critical' radius), a *CN* 6 is preferred because of ligand field stabilization. The edta ligand, however, cannot span the large ion as a hexadentate ligand, and these complexes are expected to contain pentadentate edta with water occupying the sixth position. When the ionic radius of M, with d^0, d^5 or d^{10} configurations, exceeds 0.79 Å (Fe(III) radius), octahedral coordination is not imposed and with edta the *CN* can be expected to increase to 7 or 8.

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 [5, 6]. This complex, having 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 [5, 6]. 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.

X-ray structural data have also been reported for closely related edta-type Co(III) complexes: [Co(1,3-pdta)]$^-$ (1,3-pdta = 1,3-propanediaminetetraacetate ion) [7], [Co(1,3-dhpta)]$^-$ (dhpta = 2-hydroxy-1,3-prop-

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*Parts 1, 2 and 3 are refs. 24, 25 and 30.

**Author to whom correspondence should be addressed.

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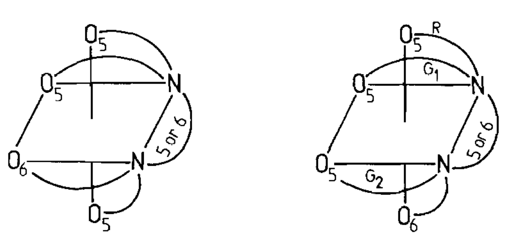
anediaminetetraacetate ion) [8], *trans*(O_5)-[Co(eddadp)]$^-$ (eddadp = ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate ion) [2], *trans*(O_6)-[Co(1,3-pddadp)]$^-$ (1,3-pddadp = 1,3-propanediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate ion) [3], [Co(edtp)]$^-$ (edtp = ethylenediaminetetra-3-propionate ion) [4]. Structural data indicate that all of these complexes are less strained than [Co(edta)]$^-$. Furthermore, X-ray studies show that the 1,3-pdta, eddadp, 1,3-pddadp and edtp ligands are hexadentate with larger metal ions such as iron(III) [1, 9], chromium(III) [4, 10–12] and rhodium(III) [10, 13].

Studies of [M(edta-type)]$^-$ complexes were undertaken to determine how various structural changes of the ligand affect the optical activity of the complexes [14, 15]. These complexes have been treated in terms of C_2 or effective D_{4h} symmetry and their CD spectra were discussed in relation to their absolute configurations and various theories of optical activity [14–32].

For the ligands having mixed five- and six-membered carboxylate arms, such as ed3ap (ed3ap = ethylenediamine-*N*,*N*,*N*′-triacetate-*N*′-3-propionate ion) [30], eddadp [1, 2, 11, 13, 20, 21, 31, 32], *SS*-edds (*SS*-edds = 2*S*,2*S*′-ethylenediamine-*N*,*N*′-disuccinate ion) [26, 31–33], *S*-eddams (*S*-eddams = *S*-ethylenediamine-*N*,*N*′-diacetate-*N*′-monosuccinate ion] [27], eda3p (eda3p = ethylenediamine-*N*-acetate-*N*,*N*′,*N*′-tri-3-propionate ion) [24] and 1,3-pddadp [3, 12, 25, 34, 35] geometrical isomers are possible that differ in the number (0, 1, 2) of six-membered rings lying in the equatorial plane. These ligands generally minimize strain by forming isomers that have a six-membered ring in the G 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 [14, 15, 27, 28].

The [Co(eda3p)]$^-$ complex ion [24] with three chelating propionate arms and one chelating acetate arm can form two possible geometrical isomers (*trans*(O_5O_6) and *trans*(O_6)), depending on whether the acetate arm is axially or equatorially coordinated. The [Co(ed3ap)]$^-$ complex [30] also has two possible geometrical isomers, differing in the position of the six-membered ring (*trans*(O_5) and *trans*(O_5O_6) isomers, Fig. 1). The isomers containing six-membered rings in the G plane (*trans*(O_5O_6) isomer in the case of eda3p complex and *trans*(O_5) isomer in the case of the ed3ap complex) form preferentially [24, 30], presumably, because G glycinate rings are more strained than R glycinate rings in the [Co(edta-type)]$^-$ complexes [5–7].

Two ligands (eddadp and 1,3-pddadp), differing in size of the diamine backbone ring, can form three geometrical isomers when coordinated: *trans*(O_5), *trans*(O_5O_6) and *trans*(O_6). The six-membered 3-propionate chelate with a five-membered diamine serves better for the formation of less-strained G rings, favoring *trans*(O_5)-[M(eddadp)]$^-$ complexes [1, 2, 11, 13, 20, 21, 31, 32]. However, in hexadentate [M(1,3-pddadp)]$^-$ complexes (M = Cr(III) [12] or Co(III) [3, 25, 34]), the dominant isomer was found to be the *trans*(O_6) isomer with the 3-propionate rings in axial positions. This is unexpected since the equatorial rings are generally more strained for the five-membered rings. The *trans*(O_6) geometry was verified by X-ray crystallography [3, 12].



I *trans*(O_5)

II *trans*(O_5O_6)

Fig. 1. Possible geometrical isomers of the [Co(ed3ap)]$^-$ and [Co(1,3-pd3ap)]$^-$ complexes (*Λ* configuration).

For the same configuration of the complex, changing from *trans*(O_5) to *trans*(O_6) for [M(eddadp)]$^-$ or [M(1,3-pddadp)]$^-$ involves inversion at chiral nitrogen centers. Either process, nitrogen inversion or inversion of configuration for the complex, requires an exchange of in-plane substituents for out-of-plane substituents [25, 36].

Recent studies on the formation of hexadentate [Rh(1,3-pddadp)]$^-$ complexes [35] showed that the *trans*(O_5) isomer is present. The size of the central metal ion (Co < Cr < Rh) in this case has a significant effect on the distribution of geometrical isomers.

A preliminary report of ^{1}H NMR [34] indicated the formation of the hexadentate [Co(1,3-pd3ap)]$^-$ complex. In continuation of this work we describe the syntheses of 1,3-propanediamine-*N*,*N*,*N*′-triacetic-*N*′-3-propionic acid and the preparation and resolution of the cobalt(III) complex. The ^{1}H and ^{13}C NMR, electronic absorption and CD spectra of the *trans*(O_5O_6) isomer of [Co(1,3-pd3ap)]$^-$ complex (Fig. 1, isomer II) are given here.

Experimental

All 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 wavelength λ ($(+)_\lambda$ or $(-)_\lambda$). The chirality is designated as Δ or *Λ* according to IUPAC rules [37].

Preparation of 1,3-propanediamine-N,N,N′-triacetic-N′-3-propionic acid ($H_4$1,3-pd3ap)

1,3-Propanediamine-*N*,*N*,*N*′-triacetic-*N*′-3-propionic acid was prepared by gradual condensation of 1,3-propanediamine (3.71 g, 0.0500 mol) with chloroacetic acid (4.725 g, 0.0500 mol), 3-chloropropionic acid (8.14 g, 0.0750 mol) and then chloroacetic acid (9.45 g, 0.100 mol) in aqueous NaOH solution as was recently described for $H_4$1,3-pddadp [25]. The obtained mixture of several 1,3-pdta-type acids was directly used for the preparation of the corresponding Co(III) complexes.

Preparation of the trans(O_5O_6) geometrical isomer of potassium (1,3-propanediamine-N,N,N′-triacetato-N′-3-propionato)cobaltate(III) dihydrate, trans(O_5O_6)-K[Co(1,3-pd3ap)]·2H_2O

Cobalt(II) chloride hexahydrate (11.89 g, 0.0500 mol) in 25 ml of water was added to the mixture containing the 1,3-pdta-type acids (pH ≃ 7). The mixture was heated at 40 °C with stirring for 0.5 h. The temperature of this solution was slowly increased to 70 °C with stirring for 2 h more. During this process *c*. 15 ml of 3% H_2O_2 was added gradually, causing the solution to turn blue–violet. The solution was evaporated to 40 ml and the deposited NaCl was separated by filtration. One half of the solution was desalted (Sephadex G-10 column) and the filtrate was poured into a 5×60 cm column containing Dowex 1-X4 (200–400 mesh) anion-exchange resin in the Cl^- form. The column was washed with H_2O and eluted with 0.1 M KCl (*c*. 0.5 ml/min). Three bands with 1- charge appeared on the column. The first eluate (probably a complex with two 3-propionate rings) was obtained in a small yield and has not been identified yet. The second band is the *trans*(O_5O_6) isomer of [Co(1,3-pd3ap)]$^-$ and the third band is K[Co(1,3-pdta)]·2H_2O of known structure. The second eluate was evaporated to 10 ml and desalted by passage through a G-10 Sephadex column with distilled water as eluent. The eluate was evaporated to *c*. 3 ml and *trans*(O_5O_6)-K[Co(1,3-pd3ap)]·2H_2O was crystallized after adding ethanol and cooling the solution in a refrigerator.

The crystals were collected, washed with ethanol, then ether, and air-dried. Yield 0.7 g of *trans*(O_5O_6)-K[Co(1,3-pd3ap)]·2H_2O (eluate II). In the same way K[Co(1,3-pdta)]·2H_2O (eluate III) yielded 1.0 g. *Anal.* Calc. for *trans*(O_5O_6)-K[Co(1,3-pd3ap)]·2H_2O = $KCoC_{12}H_{20}N_2O_{10}$ (M_r=450.33): C, 32.00; H, 4.47; N, 6.22. Found: C, 31.59; H, 4.62; N, 6.51%.

Resolution of the trans(O_5O_6) geometrical isomer of potassium (1,3-propanediamine-N,N,N′-triacetato-N′-3-propionato)cobaltate(III) dihydrate, trans(O_5O_6)-K[Co(1,3-pd3ap)]·2H_2O

The complex $(-)_{589}$-[Co(en)$_2$(ox)]Br·H_2O (0.730 g, 0.0020 mol) was mixed with 0.334 g (0.00200 mol) of silver acetate in 5 ml of water and stirred at 50 °C for 0.5 h. The precipitated 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 0.90 g (0.0020 mol) of the *trans*(O_5O_6)-K[Co(1,3-pd3ap)]·2H_2O in 10 ml of water. The resulting solution was stirred with heating (50 °C) until the solution was reduced to 5 ml. The same volume of ethanol was then added and the solution was left to stand in the refrigerator overnight. The precipitated less-soluble diastereoisomer, $(-)_{589}$-[Co(en)$_2$(ox)]–$(-)_{546}$-[Co(1,3-pd3ap)]·$x$$H_2O$, was separated by filtration, washed with ethanol, then ether, and air-dried (0.9 g). The diastereoisomer was crystallized from water–ethanol (1:1) to a constant value of optical rotation. A 0.1% aqueous solution gave $(\alpha)_{589} = -1430°$ and $[\alpha]_{546} = -725°$. To the filtrate after removing the less-soluble diastereoisomer, more ethanol (5 ml) was added and the solution was refrigerated overnight. The more soluble diastereoisomer, $(-)_{589}$-[Co(en)$_2$(ox)]–$(+)_{546}$-[Co(1,3-pd3ap)]·$x$$H_2O$, was separated by filtration, washed with ethanol, then ether, and air-dried (0.4 g). The diastereoisomer was crystallized from a mixture of water-ethanol (1:2) to a constant value of optical rotation. An aqueous solution (0.1%) gave $[\alpha]_{589} = +740°$ and $[\alpha]_{546} = -340°$. The potassium salts of the corresponding enantiomers were obtained using ion-exchange chromatography. The eluate was evaporated to a volume of 2 ml and then to dryness after standing in a desiccator over $CaCl_2$. Optical rotation: $[\alpha]_{589} = -1445°$ and $[\alpha]_{546} = -310°$ in 0.1% aqueous solution. *Anal.* Calc. for *trans*(O_5O_6)-$(-)_{546}$-K[Co(1,3-pd3ap)]·2H_20 = $KCoC_{12}H_{20}N_2O_{10}$ (M_r=450.33): C, 32.00; H, 4.47; N, 6.22. Found: C, 32.08; H, 4.44; N, 6.38%.

Physical measurements

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

The proton NMR spectrum was measured on a Varian Gemini-200 NMR spectrometer (200 MHz). 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 solution of the substance was used.

A ^{13}C NMR spectrum was obtained using a JEOL GSX270 spectrometer operated at *c*. 68 MHz in the noise decoupling mode. This spectrum was measured in D_2O relative to external TMS dissolved in benzene.

The electronic absorption spectrum was measured using a Varian SuperScan 3 spectrophotometer on an aqueous solution (*c*. 5×10^{-3} M).

The circular dichroism (CD) spectrum was recorded at room temperature with a JASCO model J-500A spectropolarimeter using a xenon arc source. The spectrum was measured in a 1 cm quartz cell in aqueous solution with a concentration of about 2×10^{-3} M.

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 *trans*(O_5) (I) and *trans*(O_5O_6) (II) isomers of the [Co(1,3-pd3ap)]$^-$ and [Co(ed3ap)]$^-$ [30] complexes (Fig. 1) differ in the position of the six-membered 3-alaninate ring. Only the favored less-strained *trans*(O_5) isomer of [Co(ed3ap)]$^-$ was isolated and characterized [30]. The in-plane strain may be eased when the five-membered diamine ring is enlarged to six-members by substituting 1,3-propanediamine for ethylenediamine in ed3ap to give the 1,3-pd3ap ligand. Although two geometrical isomers of the [Co(1,3-pd3ap)]$^-$ complex (Fig. 1) are possible, only one isomer [*trans*(O_5O_6)] of this complex was formed. This suggests that another important source of strain in edta-type complexes should be considered in this case. For the same configuration of the complex, changing from a *trans*(O_5) to a *trans*(O_5O_6) arrangement (without changing other chelate rings) for [Co(ed3ap)]$^-$ or [Co(1,3-pd3ap)]$^-$ inverts the chiral nitrogen centers. This change causes an exchange of in-plane substituents for out-of-plane substituents [25, 36] and can significantly affect the nature and extent of non-bonded interactions among the different chelate rings as was discussed for the *trans*(O_5)-[M(eddadp)]$^-$ and *trans*(O_6)-[M(1,3-pddadp)]$^-$ complexes [15, 25, 30, 36].

The isolated *trans*(O_5O_6)-[Co(1,3-pd3ap)]$^-$ complex (Fig. 1, isomer II) has a rhombic ligand field with C_1 molecular symmetry. Its geometry was assigned on the basis of the ^{1}H and ^{13}C NMR spectra, indicating an R (out-of-plane) and two G (G_1 and G_2 in-plane) glycinate rings.

^{1}H and ^{13}C NMR spectra and geometry of the complex

The ^{1}H NMR spectrum of the *trans*(O_5O_6)-[Co(1,3-pd3ap)]$^-$ complex is interpreted in light of the results obtained for other (aminopolycarboxylato)cobalt(III) complexes [38–40]. The magnitudes of geminal glycinate proton coupling constants, J, for these complexes are 16 Hz for in plane G rings and 18 Hz for out-of-plane R rings [38]. A relationship between the chemical shift differences for glycinate proton gemmates as well as the orientation of the coordinated glycinates was first shown by Legg and co-workers [39]. These arguments were used to distinguish between geometrical isomers of a hexadentate [Co(eddadp)]$^-$ [20, 21], [Co(eda3p)]$^-$ [24], [Co(ed3ap)]$^-$ [30] and a series of pentadentates based on the general formula, [Co(ed3a)(X)] (ed3a = ethylenediamine-*N,N,N′*-triacetate ion; X = monodentate ligand) [40].

Preliminary ^{1}H NMR data for *trans*(O_5O_6)-[Co(1,3-pd3ap)]$^-$ have been reported [34]. The proton NMR spectrum of this isomer is given in Fig. 2 and Table 1, and the assignments are given here. In the spectrum of this complex, having C_1 molecular symmetry, three AB patterns are expected for three non-equivalent glycinate rings (see Fig. 1). There are three well-resolved AB patterns: for two non-equivalent G rings (G_1 with $J_{AB} = 15.8$ Hz and AB pattern centered at 3.84 ppm, $\delta_A = 4.09$ ppm, $\delta_B = 3.57$ ppm; G_2 with $J_{AB} = 16.7$ Hz, and AB pattern centered at 3.64 ppm, $\delta_A = 3.90$ ppm, $\delta_B = 3.37$ ppm; and one R glycinate ring with $J_{AB} = 18.90$ Hz and AB pattern centered at 3.84 ppm, $\delta_A = 4.11$ ppm, $\delta_B = 3.57$ ppm).

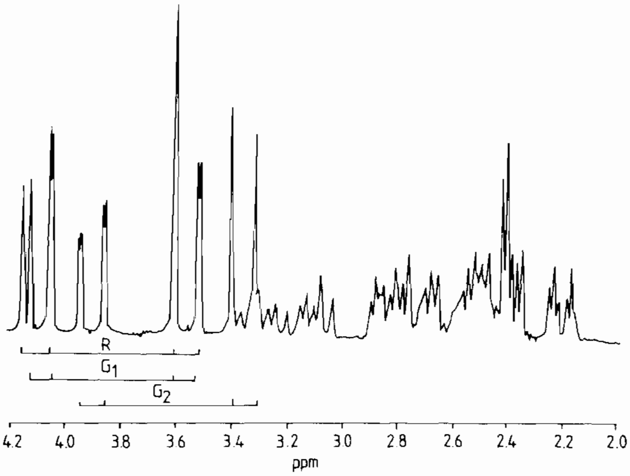


Fig. 2. ^{1}H NMR spectrum of the *trans*(O_5O_6)-[Co(1,3-pd3ap)]$^-$ complex.

TABLE 1. Coupling constants and chemical shifts[a] for methylene protons of the R and G glycinate rings and ^{13}C resonances[b] of the *trans*(O_5O_6)-[Co(1,3-pd3ap)]$^-$ complex

	R ring	G_1 ring	G_2 ring
δ_A (ppm)	4.11	4.09	3.90
δ_B (ppm)	3.57	3.57	3.37
J_{AB} (Hz)	18.9	15.8	16.7
$\delta_A - \delta_B$ (ppm)	0.54	0.52	0.53

^{13}C resonances positions

Carboxyl	Methylene
186.54, 186.21, 185.56, 184.76	72.84, 70.65, 65.56, 58.82, 55.05, 54.50, 35.26, 24.46

[a] Values are in ppm downfield from DSS as internal standard. [b] δ (ppm) relative to external TMS dissolved in benzene.

The ^{13}C NMR spectrum of this isomer shows four distinct carbonyl peaks between 184 and 187 ppm and eight distinct peaks due to the different methylene carbons between 24 and 73 ppm. These results given in Table 1, along with the ^1H NMR results show unambiguously that the complex should be assigned as the *trans*(O_5O_6) isomer.

Electronic absorption and circular dichroism spectra

Electronic absorption and CD spectra of the *trans*(O_5O_6)-[Co(1,3-pd3ap)]$^-$ complex compared to those of Λ-[Co(1,3-pdta)]$^-$ [7, 19] and those of two isomers of the Λ-[Co(1,3-pddadp)]$^-$ complexes [25] are shown in Fig. 3. The absorption and CD data for these complexes are summarized in Table 2.

Electronic spectra of the [Co(1,3-pdta-type)]$^-$ complexes (Table 2) which maintain the six-membered diamine ring and with 3-propionate arms substituted for acetate arms (series: 1,3-pdta to 1,3-pdtp) (1,3-pdtp = 1,3-propanediaminetetra-3-propionate ion) are more similar than the corresponding spectra of the [Co(edta-type)]$^-$ complexes which vary the size of carboxylate arms in the same way but maintain a five-membered diamine ring (series: edta to edtp) [15, 30].

In general, the spectra of the [Co(edta-type)]$^-$ complexes show two visible absorption bands that are usually symmetrical with no obvious splitting. Two symmetrical spin-allowed bands are expected for O_h complexes:

$$^1A_{1g} \longrightarrow {}^1T_{1g} \text{ and } {}^1A_{1g} \longrightarrow {}^1T_{2g}$$

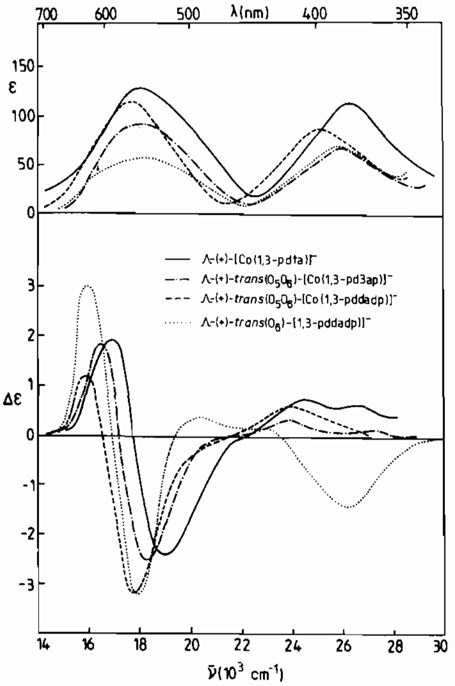


Fig. 3. Electronic absorption and CD spectra for: (——) Λ-(+)-[Co(1,3-pdta)]$^-$, (–·–·–) Λ-(+)-*trans*(O_5O_6)-[Co(1,3-pd3ap)]$^-$, (– – –) Λ-(+)-*trans*(O_5O_6)-[Co(1,3-pddadp)]$^-$ and (···) Λ-(+)-*trans*(O_6)-[Co(1,3-pddadp)]$^-$.

The molecular symmetry for the [Co(edta-type)]$^-$ complexes containing edta or edtp (1,3-pdta or 1,3-pdtp) is C_2, but it is usually C_1 for complexes involving acetate and 3-propionate arms. The holohedrized symmetry for these complexes is tetragonal (D_{4h}). Thus the axial ligand field (two O along z axis) is different from that in the equatorial plane which is the average of that of the N and O donors. If the axial ligand field strength is not much smaller than that of 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 [15]. The only exception for complexes of this type, *trans*(O_6)-[Co(1,3-pddadp)]$^-$ [25] (Table 2), shows an apparent shoulder on the lower energy absorption band.

The CD spectra for the [Co(edta-type)]$^-$ complexes [15, 30] 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 the CD spectra is not observed for absorption spectra because the absorption bands are very broad.

The absorption spectrum of *trans*(O_5O_6)-[Co(1,3-pd3ap)]$^-$ (Fig. 3, Table 2) shows two visible region bands without apparent shoulders. The intensities of these bands are lower than those of [Co(1,3-pdta)]$^-$ probably because of less strain in the [Co(1,3-pd3ap)]$^-$ system.

The energy of the absorption maximum for *trans*(O_5O_6)-[Co(1,3-pd3ap)]$^-$ is slightly lower (18 050 cm^{-1}) than that for [Co(1,3-pdta)]$^-$ (18 200 cm^{-1}). The energy of the second band is also lower for the 1,3-pd3ap complex (26 010 cm^{-1}) than that for [Co(1,3-pdta)]$^-$ (26 400 cm^{-1}). As expected, however, the energies of both bands of the [Co(1,3-pd3ap)]$^-$ complex lie between those of [Co(1,3-pdta)]$^-$ and those of the two isomers of the [Co(1,3-pddadp)]$^-$ complexes containing two 3-propionate arms.

The ratios of absorption intensity values (ϵ_1/ϵ_2) for edta-type complexes decrease in the order: edtp > eda3p > eddadp > u-eddadp > ed3ap > edta. Here the ϵ_1/ϵ_2 ratio increases with the number of propionate arms replacing the acetate arms [30]. This is not the case for the 1,3-pdta-type complexes given in Table 2. The ϵ_1/ϵ_2 ratio is 1.14 for [Co(1,3-pdta)]$^-$ and increases for the 1,3-pd3ap complex (1.33) containing one 3-propionate arm replacing an acetate arm. These values for the two isomers of the [Co(1,3-pddadp)]$^-$ complex which have two 3-propionate arms replacing the acetate arms are 1.29 for the *trans*(O_5O_6) and 0.81 for the *trans*(O_6) isomer showing an apparent shoulder on the lower energy absorption band (Table 2) [15, 25].

TABLE 2. Absorption (AB) and circular dichroism (CD) data for hexadentate [Co(1,3-pdta-type)]$^-$ complexes

Complex[a]	AB			CD		Reference
	ν (10^3 cm^{-1})	ϵ	ϵ_1/ϵ_2	ν (10^3 cm^{-1})	$\Delta\epsilon$	
Λ-(+)-(−)$_{546}$-Na[Co(1,3-pdta)]·3H$_2$O	18.20	131		17.00	+1.91	7, 19
				19.00	−2.41	
			1.14			
	26.40	115		24.60	+0.69	
				26.70[b]	+0.65[b]	
Λ-(+)-(−)$_{546}$-*trans*(O_5O_6)-K[Co(1,3-pd3ap)]·2H$_2$O	18.05	93		16.50	+1.76	this work
				18.26	−2.48	
			1.33			
	26.01	69		23.92	+0.36	
				27.31	+0.15	
Λ-(+)-(+)$_{546}$-*trans*(O_5O_6)-K[Co(1,3-pddadp)]·2H$_2$O	17.76	114		15.92	+1.20	25
				17.86	−3.20	
			1.29			
	25.19	88		24.10	+0.58	
Λ-(+)-(+)$_{546}$-*trans*(O_6)-K[Co(1,3-pddadp)]·3H$_2$O	16.34sh	~25		16.08	+3.02	25
	18.42	58		17.92	−3.21	
				20.41	+0.41	
			0.81			
	25.77	71		23.15	+0.19	
				26.18	−1.40	
				29.00sh	−0.12	

[a]Data are given for isomers having a positive rotatory strength associated with the lowest energy CD bands. [b]Values estimated from spectrum [19].

Absolute configurations have been verified by X-ray methods for Δ-(+)$_{546}$-[Co(edta)]$^-$ [6], Λ-(−)$_{546}$-[Co(1,3-pdta)]$^-$ [7], Δ-(+)$_{589}$-[Co(dhpta)]$^-$ (dhpta = 2-hydroxy-1,3-propanediaminetetraacetate ion) [8], and Δ-(+)$_{589}$-[Co(edtp)]$^-$ [4]. All of these complexes exhibit two well-defined CD peaks in the region of the first absorption band and optical isomers with the lowest energy CD peak positive and the next peak negative are assigned the Λ configuration. Complexes of optically active edta-type ligands: *S*-pdta [16], *SS*-cdta [17], *SS*-sdta [22], *SS*-edds [26] and *S*-eddams [27] are formed stereospecifically as Λ.

The empirical rules for assigning the absolute configurations of the [Co(edta-type)]$^-$ complexes are consistent if one assumes effective D_{4h} symmetry with two CD peaks in the region of the low-energy spin-allowed transition, one on each side of the absorption maximum. For C_2 symmetry, three peaks are expected, but usually only two peaks appear in this region, both on the low-energy side of or near the absorption maximum. In a third case, a single CD peak appears in the first absorption band region because of complete cancellation or masking of weak peaks by the dominant peak.

In general, there are three CD patterns for Λ-[Co(edta-type)]$^-$ complexes:

(1) There are three CD components (+,−,+) for the Λ-(+)-*trans*(O_5)-[Co(*SS*-edds)]$^-$ [26, 28] and Λ-(+)$_{546}$-*trans*(O_6)-[Co(1,3-pddadp)]$^-$ [25] complexes in the region of the lower-energy absorption band. The 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. Three components were observed also for Λ-(−)$_{546}$-[Co(en)(mal)$_2$]$^-$ (mal = malonate ion) prepared as a *cis*-[Co(N_2)(O_4)] strain-free model of [Co(edta)]$^-$, both having C_2 symmetry [16].

(2) There are two components with two peaks of opposite CD sign (+,−) in the lower absorption region for the Λ configuration. One CD peak has lower energy than that of the absorption maximum and the other peak has higher energy than that of ϵ_{max}. These spectra have been interpreted using D_{4h} symmetry. This is the case for all edta-type complexes having only acetate arms with five-membered diamine or six-membered diamine rings [15, 19, 30]. These spectra have been interpreted using the D_{4h} model [15, 25, 30].

(3) There are two components (+,−) with both components on the lower-energy side of the absorption band for complexes with acetate and/or propionate arms (Λ configuration). This case includes the following complexes: (+)-(+)$_{546}$-[Co(eda3p)]$^-$ [24], (+)-(−)$_{589}$-

trans(O_5)-[Co(eddadp)]$^-$ and (+)-(−)$_{589}$-*trans*(O_5O_6)-[Co(eddadp)]$^-$ [20, 21], (+)-(−)$_{546}$-*trans*(O_5)-[Co(ed3ap)]$^-$ and (+)-(+)$_{546}$-[Co(u-eddadp)]$^-$ [30], and (+)$_{546}$-[Co(edtp)]$^-$ [4, 19]. All of these complexes have the ethylenediamine chelate ring. These complexes have the same (+, −) CD sign pattern and such close similarity to one of the compounds of known configurations [4, 6–8] that these were assigned the Λ configurations. These assignments are consistent with absolute configurations from X-ray crystallography and for complexes formed stereospecifically from optically active ligands.

For *trans*(O_5O_6)-[Co(1,3-pddadp)]$^-$ reported earlier [25] the second CD peak (17.86×10^3 cm^{-1}) is at a slightly higher energy than that of ϵ_{max} (17.76×10^3 cm^{-1}). Also for *trans*(O_5O_6)-[Co(1,3-pd3ap)]$^-$ reported here the second CD peak (18.26×10^3 cm^{-1}) is at a slightly higher energy than that of ϵ_{max} (18.05×10^3 cm^{-1}). These values are close to the pattern of compounds (3) except they have the 1,3-pn chelate ring.

The CD spectra are shown (Fig. 3, Table 2) for (+)-*trans*(O_5O_6)-[Co(1,3-pd3ap)]·$2H_2O$ and closely related complexes. They all have the (+, −) sign pattern and are assigned the Λ configuration, using a D_{4h} model with $^1E_g^a$ lower in energy than that of $^1A_{2g}$.

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 [29]. The B states should mix, affecting the CD spectra in the higher-energy region of the first absorption band, and this could vary with structural changes.

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