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Synthesis and characterization of hexadentate cobalt(III) complexes with novel edta-type ligands
Part 2. Circular dichroism of the *trans*(O_5O_6) and *trans*(O_6) isomers of a cobalt(III) complex of 1,3-propanediamine-*N,N'*-diacetic-*N,N'*-di-3-propionic acid*

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Abstract

Cobalt(III) complexes with the hexadentate ligand, 1,3-propanediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate ion (1,3-pddadp) were prepared, chromatographically separated into two geometrical isomers with respect to the N–O chelate ring size [*trans*(O_5O_6) and *trans*(O_6)], and resolved. The ^{1}H NMR, electronic absorption and circular dichroism (CD) spectra were used to characterize the complexes. The splitting of the $T_{1g}(O_h)$ band of the *trans*(O_6)-[Co(1,3-pddadp)]$^-$ complex indicates that the tetragonal field is enhanced, relative to the fields in other [Co(edta)]$^-$-type complexes reported. The $(+)_{546}$-*trans*(O_5O_6)-[Co(1,3-pddadp)]$^-$ and $(+)_{546}$-*trans*(O_6)-[Co(1,3-pddadp)]$^-$ complexes with a positive CD peak at lowest energy in the first spin-allowed d–d absorption band region are tentatively assigned the *Λ* absolute configuration. Preliminary results of a crystallographic study of the K*trans*(O_6)-[Co(1,3-pddadp)]·$3H_2O$ confirm the assignments of geometrical isomers of the complexes.

Introduction

Many structural studies have been reported on transition metal complexes of the ethylenediaminetetraacetate ion (edta) [1], and the molecular structures of these complexes have been discussed in terms of the size of the central metal ion M and its d-electron configuration [2]. Apparently, when the ionic radius of the metal ion exceeds that of iron(III) ($\simeq 0.79$ Å), and the electron configuration is other than d^0, d^5 or d^{10}, the edta ligand can be expected to be pentadentate with water occupying the sixth position. When a transition metal ion has an electron configuration of d^0, d^5 or d^{10} with an ionic radius that exceeds 0.79 Å, then its coordination number with edta can be expected to increase from 6 to 7 or 8. The low-spin Co(III) ion with an ionic radius of 0.69 Å forms an octahedral hexadentate complex with edta [3, 4]. Bonding angles exhibited by edta complexes show significant deviations from ideal values suggesting that this chelate system is strained. Ring angle sums for [Co(edta)]$^-$ show that the two glycinate rings in an equatorial plane (G rings) are more strained than the two glycinate rings coordinated axially (R rings).

X-ray structural studies have also been reported for very closely related edta-type Co(III) complexes. These include [Co(1,3-pdta)]$^-$ (1,3-pdta = 1,3-propanediaminetetraacetate ion) [5], *trans*(O_5)-[Co(eddadp)]$^-$ (eddadp = ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate ion) [6] and [Co(edtp)]$^-$ (edtp = ethylenediaminetetra-3-propionate ion) [7]. Data indicate that all of these complexes are less strained than [Co(edta)]$^-$. Furthermore, X-ray studies show that the 1,3-pdta and eddadp ligands are hexadentate with larger metal ions such as iron(III) [2], chromium(III) [8, 9] and rhodium(III) [8, 10].

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Complexes of the [Co(edta)]$^-$-type are of interest in the study of factors contributing to their optical activity. Ligands that are similar to edta but have various structural changes in the diamine 'backbone' ring or the carboxylate arms have been studied, and CD spectra of their Co(III) complexes discussed [11–18]. For the ligands having mixed five- and six-membered carboxylate arms (the eddadp, *S*,*S*'-edds, *S*-eddams and eda3p ligands) (*S*,*S*'-edds = (2*S*,2*S*')-ethylenediamine-*N*,*N*'-disuccinate ion; *S*-eddams = (2*S*')-ethylenediamine-*N*,*N*'-diacetate-*N*'-succinate ion; eda3p = ethylenediamine-*N*-acetate-*N*,*N*',*N*'-tri-3-propionate ion) geometrical isomers are possible that differ in the number (0, 1 or 2) of six-membered rings lying in the girdling plane. As was found, these ligands apparently minimize strain by forming isomers that have six-membered rings in the G plane [13–18].

Because of only slight changes in the CD spectra among complexes related to [Co(*S*,*S*-edds)]$^-$, Jordan and Legg [17] concluded that there is only a very small contribution to rotational strength due to the asymmetric nitrogen atoms. The contribution of the chelate rings to optical activity for [Co(edta)]$^-$-type complexes, then, strongly depends on both their relative size [16] and their disposition to octahedral coordination. The relative contributions of the carboxylate chelate rings could be clarified if the CD spectra of a series related to edta-type complexes could be measured.

edta-type ligands, such as eddadp and 1,3-pddadp (1,3-pddadp = 1,3-propanediamine-*N*,*N*'-diacetate-*N*,*N*'-di-3-propionate), might be expected to yield a maximum of three geometrical isomers when coordination is hexadentate: *trans*(O_5), *trans*(O_5O_6) and *trans*(O_6), as shown in Fig. 1 (O_5 and O_6 refer to the five- and six-membered carboxylate rings). The ligand eddadp forms five-membered diamine rings and the 1,3-pddadp ligand forms six-membered diamine 'backbone' rings. Both *trans*(O_5) and *trans*(O_5O_6) isomers have been characterized for cobalt(III) and rhodium(III) of eddadp [13, 14, 19]. For the eddadp chromium(III) complex, however, only the *trans*(O_5) isomer was isolated and identified [9, 20]. The five-membered glycinate ring is strained as a G ring, and the strain is relieved when the ring is expanded. The six-membered 3-propionate chelate serves better for the formation of less-strained G rings, favoring the *trans*(O_5) isomers for the eddadp complexes [9, 10, 13, 14, 19, 20].

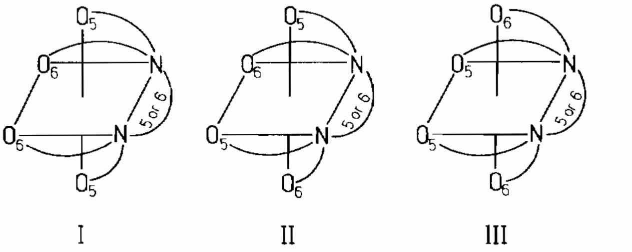

Fig. 1. Possible geometrical isomers of [Co(eddadp)]$^-$ and [Co(1,3-pddadp)]$^-$ complexes (*Λ* configuration).

The 1,3-pddadp ligand has recently been used in the preparation of the corresponding hexadentate complexes of chromium(III) [21] and cobalt(III) [22]. In both cases the dominant isomer was found to be the *trans*(O_6) with 3-propionate rings in an axial position, a coordination geometry which has been verified by X-ray analysis [21, 23].

Another important source of strain in edta-type complexes involves the coordinated nitrogens. The G ring strain in hexadentate edta-type complexes involves distortion of the ideal bonding geometry of the nitrogen atoms [7]. Sums of deviations of all angles are commonly compared because distortions do not correlate well with particular angles. For the same absolute configuration of the complex changing from *trans*(O_5) to *trans*(O_6) for [M(eddadp)]$^-$ or [M(1,3-pddadp)]$^-$ involves inversion at the chiral nitrogen centers. Either process, nitrogen inversion or inversion of configuration for the complex results in an exchange of in-plane substituents for out-of-plane substituents [24]. These changes can significantly affect the nature and extent of non-bonded interactions among the different chelate rings.

Preliminary reports of ^{1}H NMR [22], absorption and CD spectra [25] have been presented for two geometrical isomers (*trans*(O_5O_6) and *trans*(O_6), Fig. 1) of the [Co(1,3-pddadp)]$^-$ complex. In the continuation of this work, we describe the syntheses of 1,3-propanediamine-*N*,*N*'-diacetic-*N*,*N*'-di-3-propionic acid and the preparation and resolution of the corresponding hexadentate cobalt(III) complexes. Complete assignments of the electronic absorption and CD spectra of these two isomers of the [Co(1,3-pddadp)]$^-$ complex are given.

Experimental

The ligand 1,3-propanediamine-*N*,*N*'-diacetic acid dihydrochloride ($H_21,3$-pdda·2HCl), was prepared using a previously described procedure [26]. 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 wavelength $\lambda[(+)_\lambda$ or $(-)_\lambda]$. The chirality is designated as Δ or *Λ* according to IUPAC rules [27].

Preparation of 1,3-propanediamine-N,N'-diacetic-N,N'-di-3-propionic acid, $H_41,3$-pddadp

A 60.0 g quantity of 3-chloropropionic acid (0.5500 mol) was dissolved in 40 ml of water and cooled in an ice bath. A cooled solution of KOH (30.85 g, 0.5500 mol) in 40 ml of water was added dropwise, and the rate of addition was adjusted so that the temperature remained below 15 °C (solution I). Solution II was prepared by adding 40 ml of an aqueous solution of KOH (56.1 g, 1.0000 mol) to 40 ml of an aqueous solution of 1,3-propanedimine-*N*,*N'*-diacetic acid dihydrochloride ($H_2$1,3-pdda·2HCl; 65.8 g, 0.2500 mol). Solutions I and II were mixed, and the reaction mixture was refluxed at 60 °C with stirring for 8 h. During this time, an additional amount of KOH (28.1 g, 0.5000 mol) in 80 ml of water was added dropwise to keep the pH in the range 7–8. The volume of the resulting solution was reduced on a steam bath to 180 ml and allowed to stand in a refrigerator overnight. The deposited KCl was separated by filtration. To the filtrate, which was heated at 80 °C with vigorous stirring, a hot solution (80 °C) of $BaCl_2 \cdot 2H_2O$ (124.6 g, 0.5100 mol in 200 ml of water) was added. Stirring with the maintenance of the temperature at 80 °C was continued for 30 min. After the mixture stood in the refrigerator overnight, the white precipitate of $Ba_2$1,3-pddadp·$8H_2O$ was collected by filtration, washed with ethanol and then ether, and air-dried. Yield 150 g (80.1% based on the 1,3-pdda ligand). This product was recrystallized from boiling water (105 g).

$Ba_2$1,3-pddadp·$8H_2O$ (105 g) was dissolved in hot water, and an equivalent amount of 2 M H_2SO_4 was added dropwise to this solution until the precipitation of $BaSO_4$ was complete. The $BaSO_4$ was removed by filtration and the volume of the filtrate was reduced on a steam bath to 70 ml and left to stand at room temperature overnight. The white precipitate that formed was collected by filtration, washed with ethanol and then ether, and air-dried (30 g). The remaining filtrate was evaporated to a volume of 35 ml and allowed to stand at room temperature to collect a second crop (10 g). Total yield 40 g of $H_4$1,3-pddadp. This product was recrystallized from water to obtain a pure acid. *Anal.* Calc. for $Ba_2$1,3-pddadp·$8H_2O = Ba_2C_{13}H_{34}N_2O_{16}$ ($M_r = 749.09$): C, 20.85; H, 4.57; N, 3.74; H_2O, 19.23. Found: C, 21.25; H, 4.87; N, 4.45; H_2O, 19.99%. Calc. for $H_4$1,3-pddadp $= C_{13}H_{22}N_2O_8$ ($M_r = 334.32$): C, 46.70; H, 6.63; N, 8.38. Found: C, 46.36; H, 6.55; N, 8.63%.

Preparation of the trans(O_5O_6) and trans(O_6) isomers of potassium (1,3-propanediamine-N,N'-diacetato-N,N'-di-3-propionato)cobaltate(III), K[Co(1,3-pddadp)]

Cobalt(III) hydroxide [28], freshly prepared from 5.82 g (0.0200 mol) of $Co(NO_3)_2 \cdot 6H_2O$, was filtered, washed, and added to the solution obtained by dissolving 6.69 g (0.0200 mol) of $H_4$1,3-pddadp and 1.12 g (0.0200 mol) of KOH in 80 ml of water. The temperature of this solution was increased to 80 °C and heated with stirring at the same temperature for 2 h. The resulting blue–violet solution was poured into a 5 × 60 cm column containing Dowex 1-X8 (200–400 mesh) anion-exchange resin in the Cl^- form. The column was then washed with water and eluted with 0.1 M KCl (*c.* 0.5 ml/min). Two bands were obtained (*c.* 1:3). The first band (blue) and the second band (blue–violet) eluates were evaporated to 10 ml and desalted by passage through a G-10 Sephadex column, with distilled water as the eluant. Each eluate was concentrated to a volume of 3 ml and stored in a desiccator over methanol for several days. The blue and blue–violet crystals were collected, washed with methanol and then ether, and air-dried. Yield: 1.5 g of K*trans*(O_5O_6)-[Co(1,3-pddadp)]·$2H_2O$ (the first band, blue) and 3.5 g of K*trans*(O_6)-[Co(1,3-pddadp)]·$3H_2O$ (the second band, blue–violet). The compounds were dried in a desiccator over anhydrous calcium chloride. *Anal.* Calc. for K*trans*(O_5O_6)-[Co(1,3-pddadp)]·$2H_2O = KCoC_{13}H_{22}N_2O_{10}$ ($M_r = 464.48$): C, 33.62; H, 4.77; N, 6.05; H_2O, 7.75. Found: C, 32.85; H, 4.83; N, 6.00; H_2O, 7.74%. Calc. for K*trans*(O_6)-[Co(1,3-pddadp)]·$3H_2O = KCoC_{13}H_{24}N_2O_{11}$ ($M_r = 482.50$): C, 32.36; H, 5.01; N, 5.83. Found: C, 31.82; H, 4.81; N, 6.21%.

Resolution of the trans(O_5O_6) isomer of potassium (1,3-propanediamine-N,N'-diacetato-N,N'-di-3-propionato)cobaltate(III), Ktrans(O_5O_6)-[Co(1,3-pddadp)]·$2H_2O$

Silver acetate (0.167 g, 0.0010 mol) and $(-)_{589}$-$[Co(en)_2(ox)]Br \cdot H_2O$ (0.365 g, 0.0010 mol) were stirred at 60 °C for 30 min in 5 ml of water. The precipitated AgBr was removed by filtration and washed with 2 ml of hot water. To the filtrate combined with washing, 0.464 g (0.0010 mol of K*trans*(O_5O_6)-[Co(1,3-pddadp)]·$2H_2O$) was then added, and stirring of the mixture was continued for 15 min more. After adding 6 ml of ethanol, the solution was left to stand in the refrigerator overnight. The less soluble diastereoisomer, $(-)_{589}$-$[Co(en)_2(ox)]$-$(+)_{546}$-[Co(1,3-pddadp)]·$4H_2O$, was separated by filtration, washed with ethanol, then ether, and air-dried (0.35 g). The diastereoisomer was crystallized from a 1:1 water–ethanol solution to constant optical rotation. An aqueous solution (0.1%) gave $[\alpha]_{589} = -1390°$ and $[\alpha]_{546} = -96°$. 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 K^+ form. The eluate was evaporated to a small amount in air and then to dryness in a desiccator over anhydrous $CaCl_2$. Optical rotation: $[\alpha]_{589} = -1590°$, $[\alpha]_{546} = +673°$ in 0.1% aqueous solution. The opposite enantiomer was obtained by the same procedure using $(+)_{589}$-$[Co(en)_2(ox)]I$ as the resolving agent. *Anal.* Calc. for $(-)_{589}$-$[Co(en)_2(ox)]$-$(+)_{546}$-[Co(1,3-pddadp)]·$4H_2O = Co_2C_{19}H_{42}N_6O_{16}$ ($M_r = 728.44$): C, 31.32; H, 5.81; N, 11.53. Found: C, 31.21; H, 6.04; N, 11.97%. Calc.

for K-$(+)_{546}$-*trans*(O_5O_6)-[Co(1,3-pddadp)]$\cdot 2H_2O$ = $KCoC_{13}H_{22}N_2O_{10}$ (M_r=464.48): C, 33.62; H, 4.77; N, 6.05. Found: C, 32.93; H, 5.36; N, 6.16%.

Resolution of the trans(O_6) isomer of potassium (1,3-propanediamine-N,N′-diacetato-N,N′-di-3-propionato)cobaltate(III) trihydrate, Ktrans(O_6)-[Co(1,3-pddadp)]$\cdot 3H_2O$

This complex (0.482 g, 0.0010 mol) was dissolved in 5 ml of water and converted from the K^+ to the Ag^+ form by passing the solution through a cation-exchange column in the Ag^+ form. To the eluate heated to 60 °C, an equivalent amount of $(-)_{589}$-$[Co(en)_2(ox)]Br\cdot H_2O$ (0.365 g, 0.0010 mol) was added. The mixture was stirred and maintained at 60 °C for 30 min. The AgBr was removed by filtration and washed with 2 ml of warm water. The volume of the resulting filtrate was reduced to 5 ml and then 3 ml of ethanol was added to this solution. The mixture was left to stand overnight at room temperature. The less soluble diastereoisomer, $(-)_{589}$-$[Co(en)_2(ox)]$-$(+)_{546}$-[Co(1,3-pddadp)]$\cdot 3H_2O$, was removed by filtration, washed with ethanol, then ether and air-dried (0.35 g). The diastereoisomer was crystallized from a water–ethanol solution to a constant optical rotation. An aqueous solution (0.1%) gave $[\alpha]_{589} = -1767°$ and $[\alpha]_{546} = -155°$.

A 7 ml volume of ethanol was added to the remaining solution which was then allowed to stand overnight in a refrigerator to crystallize the more soluble diastereoisomer. The precipitate of $(-)_{589}$-$[Co(en)_2(ox)]$-$(-)_{546}$-[Co(1,3-pddadp)]$\cdot 5H_2O$ was collected, washed with ethanol and ether (0.3 g), and finally recrystallized from a water–ethanol solution (1:2) to a constant optical rotation for an aqueous solution (0.1%) $[\alpha]_{589} = +896°$ and $[\alpha]_{546} = -820°$.

The optical isomers in the form of the potassium salts were obtained using the ion-exchange column technique. The eluates were evaporated to dryness at room temperature. Aqueous solutions (0.1%) gave: $[\alpha]_{589} = \mp 2330°$; $[\alpha]_{546} = \pm 560°$. *Anal.* Calc. for $(-)_{589}$-$[Co(en)_2(ox)]$-$(+)_{546}$-[Co(1,3-pddadp)]$\cdot 3H_2O$ $= Co_2C_{19}H_{40}N_6O_{15}$ (M_r=710.42): C, 32.12; H, 5.67; N, 11.83. Found: C, 32.18; H, 6.48; N, 11.27%. Calc. for $(-)_{589}$-$[Co(en)_2(ox)]$-$(-)_{546}$-[Co(1,3-pddadp)]$\cdot 5H_2O$ $= Co_2C_{19}H_{44}N_6O_{17}$ (M_r=746.45): C, 30.57; H, 5.94; N, 11.25. Found: C, 30.01; H, 6.43; N, 11.42%. Calc. for K-$(+)_{546}$-*trans*(O_6)-[Co(1,3-pddadp)]$\cdot 3H_2O$ = KCo-$C_{13}H_{24}N_2O_{11}$ (M_r=482.50): C, 32.36; H, 5.01; N, 5.83. Found: C, 32.58; H, 5.01; N, 6.27%.

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 using a Bruker/IBM AF-300 NMR spectrometer on D_2O solutions containing <0.1% 4,4-dimethyl-4-sila-1-pentanesulfonate (DSS) as an internal reference.

The electronic absorption spectra were obtained with a Varian SuperScan 3 spectrophotometer. For these measurements, aqueous solutions (*c*. 0.005–0.01 M) were used.

The circular dichroism spectra were recorded at room temperature with a Jobin-Yvon Dichrographe III using a Xenon Arc Source. Spectra were measured in 1-cm quartz cells in aqueous solutions with concentration of about 2×10^{-3} M.

Elemental 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 geometrical isomers of the $[Co(1,3\text{-pddadp})]^-$ and $[Co(eddadp)]^-$ complexes shown in Fig. 1 differ in the way that the two glycinate rings and the two 3-propionate rings coordinate octahedrally. The in-plane strain may be eased when the five-membered diamine ring is enlarged to six-membered by substituting 1,3-propanediamine for ethylenediamine in eddadp to give the 1,3-pddadp ligand. This might make it possible to form all geometrical isomers shown in Fig. 1. The *trans*(O_5) and *trans*(O_6) isomers have a tetragonal ligand field with C_2 molecular symmetry neglecting any conformational differences. The *trans*(O_5O_6) isomer has a rhombic field with C_1 molecular symmetry. All the isomers have pseudo-D_{4h} (holohedrized) symmetry with the quasi-C_4 axis being perpendicular to the plane containing the diamine ring.

The eddadp ligand encircles M(III) and M(II) ions more favorably if the resulting complex is a *trans*(O_5) isomer. In these complexes the six-membered 3-propionate chelate arm prefers to form the less strained G rings [2, 6], as evidenced by the formation of the *trans*(O_5)-$[M^{III}(eddadp)]^-$ complexes [9, 10, 13, 14, 19, 20]. In the case of the $[M^{III}(1,3\text{-pddadp})]^-$ complexes, all three isomers, *trans*(O_5), *trans*(O_5O_6) and *trans*(O_6) with Cr(III) [21] have been isolated and characterized, but only the *trans*(O_6) and *trans*(O_5O_6) have been isolated and characterized with Co(III) [22]. In both cases, the *trans*(O_6) isomer dominates [21–23].

It was surprising that the *trans*(O_6)-$[M(1,3\text{-pddadp})]^-$ was the dominant isomer since the glycinate ligands form strained G rings. Dreiding models show, however, that there are significantly unfavorable non-bonding interactions between methylene hydrogen atoms of the R glycinate rings and those of the equatorial diamine ring for the *trans*(O_5) isomers. A glycinate arm as an R ring is required to be very nearly planar and does not allow for any flexibility of movement by the methylene hydrogens to minimize repulsions.

Two isomers of the [Co(1,3-pddadp)]$^-$ complex (*trans*(O_5O_6) and *trans*(O_6)) are described here. The geometry of these complexes has been verified crystallographically in the case of K*trans*(O_6)-[Co(1,3-pddadp)]·$3H_2O$ [23]. The conformations of the chelate rings are found to be envelope for the acetates and skew boat for the 3-propionates and 1,3-propanediamine rings in both Cr(III) [21] and Co(III) [23] complexes having *trans*(O_6) geometry.

NMR spectra. Distinguishing between the two geometrical isomers of K[Co(1,3-pddadp)]

Proton NMR spectra of these complexes were interpreted in light of the results obtained for other (aminopolycarboxylato)cobalt(III) complexes comparing the G and R glycinate rings [29, 30]. The magnitudes of geminal glycinate proton coupling constants, *J*, for (aminocarboxylate)cobalt(III) complexes are 16 Hz for in-plane G rings and 18 Hz for out-of-plane R rings [29]. A relationship between the chemical shift differences for glycinate proton gemmates as well as the orientation of the coordinated glycinates was first elucidated by Legg and co-workers [30]. These arguments were used to distinguish between geometrical isomers of a hexadentate [Co(eddadp)]$^-$ [14] and [Co(eda3p)]$^-$ [18] complexes (eda3p = ethylenediamine-*N*-acetate-*N*,*N'*,*N'*-tri-3-propionate ion) and a series of pentadentates based on the general formula, [Co(ed3a)(X)] (ed3a = ethylenediamine-*N*,*N*,*N'*-triacetate ion; X = monodentate ligand) [31].

Preliminary ^1H NMR spectra data for the *trans*(O_6) and *trans*(O_5O_6) isomers of the [Co(1,3-pddadp)]$^-$ complex have been reported [22]. Proton NMR spectra of these isomers are given, and the assignments are completed here. The spectrum of the *trans*(O_6) complex is simple in that only one well resolved AB pattern is evident and centered at 3.73 ppm with $\delta_A = 4.11$ ppm, $\delta_B = 3.33$ ppm and $J_{AB} = 16.6$ Hz (Table 1, Fig. 2(a)). These results are consistent with the expected C_2 symmetry of the *trans*(O_6) isomer having two equivalent glycinate G rings and two equivalent 3-propionate rings in the axial positions.

In the same region, the *trans*(O_5O_6) isomer, with lower molecular symmetry (C_1), shows signals of two well resolved AB patterns suggesting two non-equivalent R and G rings. The AB pattern of the R ring is centered at 3.77 ppm, has $\delta_A = 3.82$ ppm and $\delta_B = 3.72$ ppm with a J_{AB} coupling constant of 18.8 Hz. The other AB pattern, caused by the G ring methylene hydrogen atoms, is centered at 3.57 ppm, with $\delta_A = 3.89$ ppm and $\delta_B = 3.24$ ppm and a J_{AB} coupling constant of 16.7 Hz (Table 1, Fig. 2(b)). The $\delta_A - \delta_B$ values obtained for the G rings of both isomers are consistent with the possibility that these systems represent less strained model complexes relative to [Co(edta)]$^-$ [30].

TABLE 1. Coupling constants and chemical shifts[a] for methylene protons of R and G glycinate rings of the [Co(1,3-pddadp)]$^-$ complex

	Geometrical isomers		
	trans(O_6)	*trans*(O_5O_6)	
	G rings	R rings	G rings
δ_A (ppm)	4.11	3.82	3.89
δ_B (ppm)	3.33	3.72	3.24
J_{AB} (Hz)	16.6	18.8	16.7
$\delta_A - \delta_B$ (ppm)	0.78	0.10	0.65

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

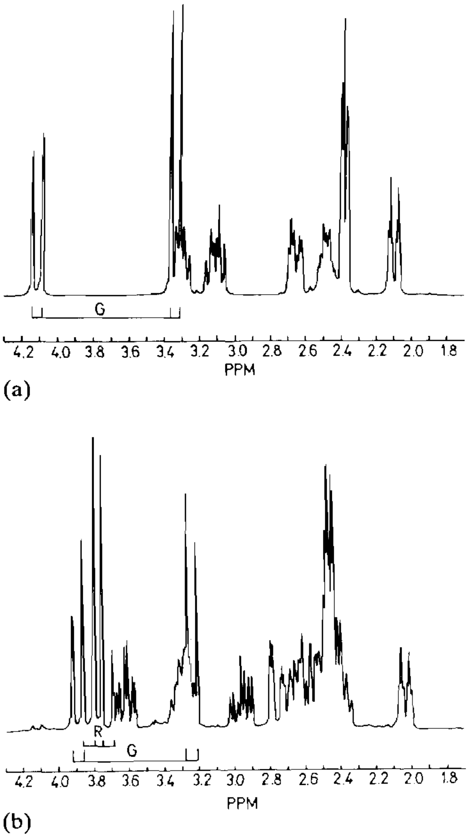

Fig. 2. ^1H NMR spectra: (a) *trans*(O_6)-[Co(1,3-pddadp)]$^-$; (b) *trans*(O_5O_6)-[Co(1,3-pddadp)]$^-$.

Electronic absorption and circular dichroism

The electronic absorption and CD spectra of the *trans*(O_6)-[Co(1,3-pddadp)]$^-$ and *trans*(O_5O_6)-[Co(1,3-

pddadp)]$^-$ complexes compared to that of the Λ-[Co(1,3-pdta)]$^-$ [5, 11, 12] are shown in Fig. 3. The corresponding numerical data of absorption and CD maxima for these complexes and those of Λ-[Co(edta)]$^-$ [4, 11, 32] and other edta-type complexes of known Λ configuration are summarized in Table 2. The complexes shown in Fig. 3 contain the 1,3-propanediamine 'backbone' ring but differ in the number of five-membered glycinate and six-membered 3-propionate rings. For the complexes investigated so far, the preferred conformation of the diamine ring is the skew boat and is apparently symmetry driven in the sense that a boat conformation without much flexibility vitiates C_2 symmetry [5, 23].

As expected, the absorption energies of the two isomers of the [Co(1,3-pddadp)]$^-$ complex (the bands I and II) are shifted slightly to lower energy relative to the corresponding bands of the [Co(1,3-pdta)]$^-$ complex [11]. Also, the values of molar absorptivity, ϵ, of the less-strained [Co(1,3-pddadp)]$^-$ complexes are significantly lower than those of [Co(1,3-pdta)]$^-$ (Table 2, Fig. 3).

The absorption spectra of the *trans*(O_6)-[Co(1,3-pddadp)]$^-$ complex differs from the spectra shown in Fig. 3 and the other [Co(edta)]$^-$-type complexes reported [11–18, 32] in two respects: the higher energy band at 25 773 cm^{-1} ($\epsilon = 71$) is more intense than the lower energy band, and the lower energy band at 18 426 cm^{-1} ($\epsilon_1 = 58$) shows a pronounced shoulder on the lower energy side ($\sim$16 340 cm^{-1}, $\epsilon \cong 25$). This splitting of the $T_{1g}(O_h)$ band suggests that the tetragonal field is enhanced relative to the same fields in other [Co(edta-type)]$^-$ complexes [11–18, 32]. Apparently, the equatorial N_2O_2 ligand field due to the glycinate arms and the diamine ring is considerably larger than the one imposed by the axially coordinated 3-propionate donor oxygen atoms.

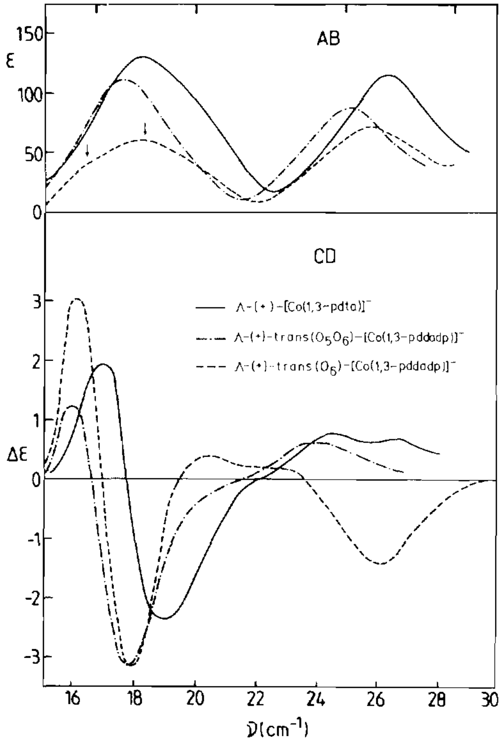

Fig. 3. Electronic absorption and CD spectra for: Λ-(+)-[Co(1,3-pdta)]$^-$, Λ-(+)-*trans*(O_5O_6)-[Co(1,3-pddadp)]$^-$, and Λ-(+)-*trans*(O_6)-[Co(1,3-pddadp)]$^-$.

The absorption spectra of the two complexes, *trans*(O_5O_6)-[Co(1,3-pddadp)]$^-$ and [Co(1,3-pdta)]$^-$ (Fig. 3), are similar in shape with two bands corresponding to transitions from the ground state to the $T_{1g}(O_h)$ and $T_{2g}(O_h)$ states. The bands I and II show no obvious splitting, as would be expected for *cis*-[Co(N)$_2$(O)$_4$]-type complexes. The absence of apparent splitting of the T_{1g} and T_{2g} absorption bands suggests pseudooctahedral symmetry, but the interpretation of the electronic absorption spectra for these complexes based on a tetragonal field is preferred [15].

The two spin-allowed transitions in a low-spin d^6 system in an octahedral crystal field are $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ in order of increasing energy. In a tetragonal field, the degeneracies of the excited states are removed, i.e. $^1T_{1g} = {}^1A_{2g} + {}^1E_g{}^a$ and $^1T_{2g} = {}^1B_{2g} + {}^1E_g{}^b$. If the complexes presented here can be considered to have holohedrized D_{4h} symmetry, then the $^1E_g{}^a(D_{4h})$ state should be lower in energy than the $^1A_{2g}$ state, both of which are derived from the same $^1T_{1g}$ (O_h) state. Also, the $^1B_{2g}$ should be lower in energy than the $^1E_g{}^b$ state (both derived from the same $^1T_{2g}(O_h)$ state) [33].

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 (A(C_2) or E(D_{4h})) for hexadentate [Co(edta)]$^-$-type complexes. The lowest energy CD components of these complexes have a positive sign for the Λ ($\Lambda\Delta\Lambda$) configuration [11–16, 32–38] corresponding to the chirality [27] of the isomers shown in Fig. 1. This assignment is consistent with the empirical observation [39] that the sign of the A→A(C_2) component can be correlated with the absolute configuration, and this statement has been verified crystallographically in the case of Λ-[Co(edta)]$^-$ [4], Λ-[Co(1,3-pdta)]$^-$ [5], Λ-[Co(edtp)]$^-$ [7] and Λ-[Co(S,S-edds)]$^-$ [40].

Complexes of this type with C_2 symmetry can be related to [Co(en)(mal)$_2$]$^-$, ethylenediamine-bis-malonatocobaltate(III), which can be correlated with *cis*-[Co(en)$_2$(X)$_2$]$^{n+}$ complexes [39] to retain the sign of the $E_a(D_3)$ component for [Co(en)$_3$]$^{3+}$. The empirical correlation is tenuous because the *cis*-[Co(N)$_2$(O)$_4$]-type complex has the weak- and strong-field ligands reversed compared to the case for *cis*-[Co(N)$_4$(X)$_2$].

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

Complex[a]	AB		CD		Reference
	ν (10^3 cm^{-1})	ϵ	ν (10^3 cm^{-1})	$\Delta\epsilon$	
KΛ-(+)-(−)$_{546}$-[Co(edta)]$\cdot$2H$_2$O	18.63	347	17.10	+1.50	4, 11, 32
			19.80	−0.69	
	26.04	246	23.80	+0.28	
			25.60	−0.09	
			27.60	+0.29	
AgΛ-(+)-(−)$_{589}$-*trans*(O$_5$)-[Co(eddadp)]$\cdot$2H$_2$O	18.50	342	16.20	+0.40	13, 14
			18.30	−2.78	
	25.70	186	24.20	+0.29	
			26.30	+0.36	
AgΛ-(+)-(−)$_{589}$-*trans*(O$_5$O$_6$)-[Co(eddadp)]$\cdot$3H$_2$O	18.60	253	16.50	+2.25	13, 14
			18.40	−3.12	
	25.80	142	24.40	+0.31	
			26.60	+0.56	
KΛ-(+)-(+)$_{546}$-*trans*(O$_5$O$_6$)-[Co(eda3p)]$\cdot$3H$_2$O	18.25	318	16.05	+0.90	18
			18.08	−3.18	
	25.19	147	23.81	+0.43	
			26.04	+0.58	
LiΛ-(+)-(+)$_{546}$-[Co(cdtp)]$\cdot$3H$_2$O	18.00	253	15.77	+1.05	7, 11
			17.57	−3.68	
	24.80	110	23.30	+0.10	
			26.30	+0.20	
NaΛ-(+)-(−)$_{546}$-[Co(1,3-pdta)]$\cdot$3H$_2$O	18.20	131	17.0	+1.91	5, 11, 12
			19.0	−2.41	
	26.40	115	24.6	+0.69	
KΛ-(+)-(+)$_{546}$-*trans*(O$_6$)-[Co(1,3-pddadp)]$\cdot$3H$_2$O	16.34sh	~25	16.08	+3.02	this work
	18.42	58	17.92	−3.21	
			20.41	+0.41	
	25.77	71	23.15	+0.19	
			26.18	−1.40	
			29.00sh	−0.12	
KΛ-(+)-(+)$_{546}$-*trans*(O$_5$O$_6$)-[Co(1,3-pddadp)]$\cdot$2H$_2$O	17.76	114	15.92	+1.20	this work
			17.86	−3.20	
	25.19	88	24.10	+0.58	

[a] Data are given for isomers having a positive rotatory strength associated with the lowest energy CD bands.

The empirical correlations for [Co(edta)]$^-$-type complexes are consistent with results using a D_{4h} model when two CD peaks appear, one on each side of the absorption maximum, or from C_2 symmetry when there are three CD peaks or only two peaks, both on the lower energy side of the absorption maximum.

Two complexes of known configuration, (cf. Table 2) Λ-[Co(edta)]$^-$ [4, 32] and Λ-[Co(1,3-pdta)]$^-$ [5, 11] show two lower energy peaks of opposite sign (+, −), one on either side of the first absorption band. The D_{4h} model is consistent with this CD pattern, the lower energy peak being E$_g$(D_{4h}) and the higher energy peak being A$_{2g}$(D_{4h}). The sign of the lower energy component, E$_g$(D_{4h}), is retained by the A(C_2) component of E$_g$ parentage.

The CD spectra are very similar for the complexes involving 3-propionate arms: Λ-(+)-[Co(edtp)]$^-$ [7, 11], Λ-(+)-*trans*(O$_5$O$_6$)-[Co(eda3p)]$^-$ [18], and the *trans*(O$_5$) and *trans*(O$_5$O$_6$) isomers of Λ-(+)-[Co(eddadp)]$^-$ (Table 2) [13, 14]. The CD spectra of these complexes differ from those of Λ-(+)-[Co(edta)]$^-$ [4, 32] and Λ-(+)-[Co(1,3-pdta)]$^-$ [5, 11, 12], and show two CD peaks in the low-energy region, occurring at lower energy than the absorption maximum. In accordance with the D_{4h} model, these components are split from the E$_g$(D_{4h}) state because of lower symmetry.

The third transition, expected for complexes of C_2 symmetry, should be on the higher energy side of the absorption maximum, but presumably it is obscured by the dominant peak. The CD spectra of these complexes were compared to a complex of known Λ configuration, and the Λ configuration is assigned to isomers that exhibit two CD peaks in the region of the first absorption band with the lower energy CD peak positive and the next peak negative.

For [Co(edta)]$^-$-type complexes [11–14, 18, 32], the usual CD pattern has two peaks (+, −) for the lowest energy absorption band, but Λ-(+)-*trans*(O_5)-[Co(*S,S*-edds)]$^-$ [15, 40] shows three peaks of alternating sign, corresponding to the number of transitions expected for a complex with C_2 symmetry.

In general, the spectral data obtained for the [Co(1,3-pddadp)]$^-$ isomers are closer to those of the Λ-[Co(1,3-pdta)]$^-$ species [5, 11] than to those of the Λ-[Co(edta)]$^-$ complex [4, 32]. The CD spectra of two isomers of [Co(1,3-pddadp)]$^-$ are compared to those of the [Co(edta)]$^-$-type of known Λ configuration (Table 2). The CD spectrum of (+)-*trans*(O_5O_6)-[Co(1,3-pddadp)]$^-$, in accordance with the D_{4h} model, shows two well defined low energy peaks of opposite sign, one either side of the first absorption band as do the Λ-[Co(edta)]$^-$ and Λ-[Co(1,3-pdta)]$^-$ complexes. In the case of the (+)-*trans*(O_6)-[Co(1,3-pddadp)]$^-$ complex, three peaks of alternating sign, (+, −, +), appear as part of what can be considered to be the T_{1g} absorption band region and correspond to the number of electronic transitions expected for a complex with C_2 symmetry. The positive lowest energy CD peaks of these complexes are presumed to be the A(C_2) component of $E_g(D_{4h})$ parentage and isomers presented are assigned the Λ configuration.

In the case of the [Co(1,3-pddadp)]$^-$ complexes, there are possible contributions to the CD intensities from the two coordinated asymmetric nitrogen atoms, as well as from the configurational effect which was found to be dominant [14–18]. The configurations of the two asymmetric nitrogens of the Λ-[Co(1,3-pddadp)]$^-$ complexes (Fig. 3) are *S,S* for *trans*(O_6) and *S,R* for *trans*(O_5O_6) isomers, respectively. The contributions of the *SR* nitrogen atoms in the latter should cancel. The similarity in shapes of CD curves of the Λ-[Co(1,3-pdta)]$^-$ complex [11], in which there is no contribution due to asymmetric nitrogens, and those of the Λ-*trans*(O_6)-[Co(1,3-pddadp)]$^-$ complex and the relative intensities of their CD component in the T_{1g} region support the idea that the contribution due to the asymmetric nitrogens is small in this system. Thus, the difference in CD spectra of these complexes is due mostly to the differences of the relative contributions of chelate rings and the dependence on their size and position about the coordination octahedron.

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