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Synthesis and Characterization of Hexadentate Cobalt(III) Complexes with New edta-Type Ligands Part 5.# Structure and Absolute Configuration of the *trans*(O_5)($-$)$_{546}$-Isomer of Lithium (Ethylenediamine-*N*,*N*,*N*′-triacetato-*N*′-3-propionato)cobaltate (III) Monohydrate, ($-$)$_{546}$-*trans*(O_5)-Li[Co(ed3ap)]·H_2O. Strain Analysis of [Co(edta-Type)]$^-$ Chelates in Relation to Their Octahedral Distortion

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The preparation and resolution of the two hexadentate Co(III) complexes containing unsymmetrical edta-type ligands, [Co(ed3ap)]$^-$ (**A**) and [Co(*u*-eddadp)]$^-$ (**B**) (ed3ap = ethylenediamine-*N*,*N*,*N*′-triacetate-*N*′-3-propionate ion; *u*-eddadp = ethylenediamine-*N*-diacetate-*N*′-di-3-propionate ion) have been reexamined. The X-ray data are reported for the Λ-($-$)$_{546}$-*trans*(O_5)-Li[Co(ed3ap)]·H_2O for which the same (Λ) absolute configuration was predicted from the CD sign pattern of the lowest energy band. The complex crystallizes in the space group $P2_1$ (#4) of the monoclinic crystal system with $a = 6.523(4)$, $b = 15.025(7)$, $c = 7.464(3)$ Å, $\beta = 105.40(4)°$, and $Z = 2$. The conformations of the chelate rings are found to be envelope for the glycinates and *skew-boat* (*half-chair*) for the β-alaninate ring. Structural parameters and strain analysis of [Co(edta-type)]$^-$ chelates are discussed in relation to the structure of the ligand and octahedral distortion of complexes. The CD and IR (carboxylate region) spectra of complexes **A** and **B** are also discussed.

The spectral data and structural parameters of the [Co(edta)]$^-$ complex (edta = ethylenediaminetetraacetate ion) are available.[1,2] This complex, containing five-membered rings only, shows notable departures from regular octahedral coordination and was found to be strained.[2] The ethylenediamine backbone ring (E ring) and two glycinate rings in equatorial positions (G rings) are more strained than the two glycinate rings in axial positions (R rings). Aminopolycarboxylate complexes less-strained but similar to [M(edta)]$^{n-}$ usually contain ligands that have longer (diamine or carboxylate) chains. These complexes of Co(III) and Cr(III) have been reviewed recently.[3]

Structural data for closely related edta-type Co(III) complexes are also known: [Co(1,3-pdta)]$^-$[4] (1,3-pdta = 1,3-propanediaminetetraacetate ion), [Co(1,3-dhpta)]$^-$[5] (1,3-dhpta = 2-hydroxy-1,3-propanediaminetetraacetate ion), *trans*(O_5)-[Co(eddadp)]$^-$[6] (eddadp=ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate ion), *trans*(O_6)-[Co(1,3-pddadp)]$^-$[7] (1,3-pddadp = 1,3-propanediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate ion), [Co(edtp)]$^-$[8] (edtp = ethylenediaminetetra-3-propionate ion), and [Co(*S*,*S*-edds)]$^-$ complex forming stereospecifically[9] (*S*,*S*-edds = 2*S*,2*S*′-ethylenediamine-*N*,*N*′-disuccinate ion). Structural data indicate that all of these complexes are less strained than [Co(edta)]$^-$. Also, X-ray studies show that these ligands with larger chelate rings form six-coordinate complexes with larger metal ions such as Fe(III),[10,11] Cr(III),[12—14] Rh(III),[13,15] Ni(II),[16] and Cu(II).[17,18]

Factors governing the structural types of M-edta-type complexes include the *d*-electron configuration of 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.[3,6—8,10] Larger ions containing edta ligands usually show higher coordination numbers (C.N.) than 6 and for ions with high ligand field stabilization energy, one H_2O can replace a carboxylate arm.[3]

For the ligands having mixed five- and six-membered carboxylate arms such as ed3ap (ed3ap = ethylenediamine-*N*,*N*,*N*′-triacetate-*N*′-3-propionate ion), 1,3-pd3ap (1,3-pd3ap = 1,3-propanediamine-*N*,*N*,*N*′-triacetate-*N*′-3-propionate ion), eda3p (eda3p = ethylenediamine-*N*-acetate-*N*,*N*′,*N*′-tri-3-propionate ion), eddadp, 1,3-pddadp, and *S*,*S*-edds geometrical isomers are possible that differ in the number (0, 1, or 2) of six-membered rings lying in the equatorial plane.

For the [Co(eda3p)]$^-$ complex[19] with three chelating propionate arms and one chelating acetate arm, two possible geometrical isomers can be expected (*trans*(O_5O_6) and

Parts 1, 2, 3, and 4 are Refs. 19, 25, 20, and 21.

trans(O_6)). O_5 and O_6 refer to the five- and six-membered carboxylate rings. The [Co(ed3ap)]$^-$[20] and [Co(1,3-pd3ap)]$^-$[21] complexes also have two possible geometrical isomers, differing in the position of the six-membered ring: *trans*(O_5) (I) and *trans*(O_5O_6) (II) (Fig. 1). Because of the strain in the G plane the isomers (*trans*(O_5O_6) isomer in the case of the eda3p complex and *trans*(O_5) isomer in the case of the ed3ap complex) form preferentially.[19,20] However, in the case of the [Co(1,3-pd3ap)]$^-$ complex,[21] the *trans*(O_5O_6) isomer was found to be favored.

Two symmetrical 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 chelates serve better for the formation of less-strained G rings, favoring *trans*(O_5)-[M(eddadp)]$^{n-}$ complexes, (M = Co(III),[3,6,22] Cr(III),[12,23] Fe(III),[10] Rh(III),[15,24] or Ni(II).[16a] A similar situation was found for the optically active *S,S*-edds complexes forming stereospecifically. Only one (*trans*(O_5)) of two geometrical isomers was found to dominate, in this case favoring Λ-[M(*S,S*-edds)]$^{n-}$ complexes (M=Co(III),[3,9] Cr(III),[23] Rh(III),[24] Fe(III),[11] Ni(II),[16b] or Cu(II)[18]). However, in hexadentate [M(1,3-pddadp)]$^{n-}$ complexes (M = Cr(III),[14] Co(III),[7,25] or Cu(II)[17]) the dominant isomer was found to be *trans*(O_6) with the β-alaninate rings in axial positions. On the other hand, in [M(1,3-pddadp)]$^{n-}$ complexes (M = Ni(II)[26] or Rh(III)[27]) the dominant isomer was found to be the *trans*(O_5). Based on the size of the central metal ion M (Co(III) < Cr(III) < Fe(III) < Rh(III) < Ni(II) < Cu(II)) and the presence of strain in the G plane, the formation of the *trans*(O_5) isomers can be expected to even more strongly favor Ni(II) and Rh(III) over Co(III) and Cr(III). The Ni(II) and Cu(II) ions are nearly of the same size but the favored *trans*(O_6) coordination in complexes of Cu(II) was expected and was found.[17] Due to the *d*-electron configuration of Cu(II) ion, the ligand field stabilization was found to be the dominant factor in governing geometry in this case (the tetragonal octahedral complexes with β-alaninate rings in axial positions).[17]

The complexes of [M(edta-type)]$^-$ 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.[1,3,19–25,28–35] For the [Co(edta-type)]$^-$ complexes, the general sign pattern in the region of the lower energy absorption band was found to be a lowest energy-positive CD peak followed by a negative peak for the Λ configuration. We found that this statement should be checked for hexadentate complexes containing unsymmetrical edta-type ligands.

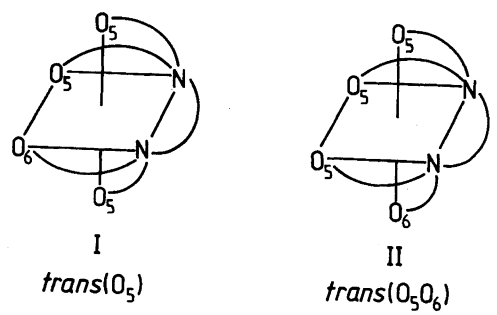

Fig. 1. Two possible geometrical isomers of the [Co(ed3ap)]$^-$ complex.

The complexes *trans*(O_5)-[Co(ed3ap)]$^-$ (**A**) and [Co(*u*-eddadp)]$^-$ (**B**) (*u*-eddadp = ethylenediamine-*N*-diacetate-*N'*-di-3-propionate ion) have recently been prepared and resolved.[20] The lowest energy CD component of these complexes was found to be positive for the Λ ($\Lambda\Delta\Lambda$) configuration. In this work the preparation and resolution of complexes **A** and **B** have been repeated. The X-ray data are given for the $(-)_{546}$-*trans*(O_5)-Li[Co(ed3ap)]·H_2O. The absolute configuration (Λ) of this enantiomer was found to be the same as that proposed on the basic of CD data. Structural parameters and strain analysis data of this complex are discussed in relation to those of the other [Co(edta-type)]$^-$ complexes of known structures. Spectral characteristics of complexes **A** and **B** are also reported 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.[36]

The unsymmetrical edta-type ligands, ethylenediamine-*N,N,N'*-triacetic-*N'*-3-propionic acid (H_4ed3ap) and ethylenediamine-*N*-diacetic-*N'*-di-3-propionic acid (H_4*u*-eddadp) (condensation mixture) were prepared by gradual condensation of ethylenediamine-*N*-acetic acid dihydrochloride dihydrate (Hedma·2HCl·$2H_2O$, 22.70 g, 0.1000 mol) with 3-chloropropionic acid (21.70 g, 0.2000 mol) and then chloroacetic acid (18.90 g, 0.2000 mol) in aqueous NaOH solution as was recently described.[20]

Preparation and Resolution of Complexes. Both complexes, the *trans*(O_5)-[Co(ed3ap)]$^-$ (**A**) and [Co(*u*-eddadp)]$^-$ (**B**) were prepared, separated, and resolved in the way described earlier.[20] The complexes were resolved using the same resolving agent, $(-)_{589}$-[Co(en)$_2$(ox)]Br·H_2O. The precipitated less soluble diastereoisomer, $(-)_{589}$-[Co(en)$_2$(ox)]-$(-)_{546}$-[Co(ed3ap)]·$2H_2O$ (1.3 g) was crystallized from water to a constant value of optical rotation: $[\alpha]_{589} = -990°$; $[\alpha]_{546} = -970°$. Found: C, 30.58; H, 4.75; N, 12.72%. Calcd for $(-)_{589}$-[Co(en)$_2$(ox)]-$(-)_{546}$-[Co(ed3ap)]·$2H_2O$ = $Co_2C_{17}H_{34}N_6O_{14}$ (FW = 664.35): C, 30.73; H, 5.16; N, 12.65%. The corresponding enantiomer in the form of the lithium salt was obtained by dissolving the diastereoisomer in water and passing the solution through a cation-exchange column in the Li^+ form. The eluate was evaporated to a volume of 4 ml and blue-violet crystals were formed after addition of 10 ml of ethanol and cooling in a refrigerator. The crystals of $(-)_{546}$-*trans*(O_5)-Li[Co(ed3ap)]·H_2O were collected by filtration, washed with ethanol, and then ether and air-dried. Aqueous solution (0.05%) gave: $[\alpha]_{589} = -1160°$; $[\alpha]_{546} = -970°$. Found: C, 34.95; H, 4.06; N, 7.45%. Calcd for $(-)_{546}$-*trans*(O_5)-Li[Co(ed3ap)]·H_2O = $LiCoC_{11}H_{16}N_2O_9$ (FW = 386.13): C, 34.22; H, 4.17; N, 7.25%.

The enantiomer of the complex **B** in the form of the potassium salt was obtained from less-soluble diastereoisomer, $(-)_{589}$-[Co(en)$_2$(ox)]-$(+)_{546}$-[Co(*u*-eddadp)]·xH_2O on the same way as was earlier described.[20] Aqueous solution (0.05%) of $(+)_{546}$-K[Co(*u*-

eddadp)]·2H_2O gave: $[\alpha]_{589} = -1780°$; $[\alpha]_{546} = +80°$.

Physical Measurements. (+)$_{646}$-Λ-(−)$_{546}$-*trans*(O_5)-Li[Co(ed3ap)]·H_2O: A blue-violet crystal having approximate dimensions of 0.20×0.20×0.15 mm, obtained from aqueous ethanol solution, was used. Intensity measurements were made on a Rigaku AFC7S diffractometer using graphite monochromated Mo $K\alpha$ radiation at 23 °C.

Crystal data: $LiCoC_{11}H_{16}N_2O_9$, FW=386.13, monoclinic, space group $P2_1$ (#4), $a = 6.523(4)$, $b = 15.025(7)$, $c = 7.464(3)$ Å, $\beta = 105.40(4)°$, $V = 705.3(6)$ Å^3, $Z = 2$, $D_c = 1.82$ g cm^{-3}, $F_{000} = 396$, μ(Mo $K\alpha$) = 12.71 cm^{-1}.

The structure was solved by the Patterson heavy-atom method,[37] expanded using Fourier techniques,[38] and refined by least-squares techniques to $R = 0.065$ and $R_w = 0.047$ for 2648 reflections ($I > 3.00\sigma(I)$) of 3534 collected in the range of $2\theta < 55.0°$. The non-hydrogen atoms were refined anisotropically and hydrogen atoms, excluding those of O(9) water molecules, were included but not refined.

The absolute configuration was identified based on the Bijvoet method using the intensity data measured with Mo $K\alpha$ radiation (Table 1). The positional parameters are presented in Table 2.

Selected bond distances and angles are summarized in Table 3. Neutral atom scattering factors were taken from Crommer and Waber.[39] All calculations were done using the teXsan crystallographic software package.[40] Lists of the structure factors, anisotropic thermal parameters for non-hydrogen atoms, and positional parameters for the hydrogen atoms have been deposited as Document No. 71035 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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

Electronic absorption spectra were recorded on a JSCO UVIDEC-670 spectrophotometer. For these measurements about 2×10^{-3} M aqueous solutions were used.

CD spectra were recorded at room temperature on a JSCO Model J-720 spectropolarimeter using a xenon arc source.

IR spectra in the solid state were recorded on a JSCO FT/IR-5300 spectrophotometer using KBr discis.

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

Results and Discussion

Two complexes containing unsymmetrical edta-type ligands, [Co(ed3ap)]$^-$ (**A**) and [Co(*u*-eddadp)]$^-$ (**B**) have recently been prepared and characterized.[20] The ed3ap ligand with hexadentate coordination can yield two geometrical isomers: *trans*(O_5) (I) and *trans*(O_5O_6) (II), (Fig. 1). Only one (*trans*(O_5)) of two geometrical isomers was found to be favored. There is no similar structural variation possible for the hexadentate [Co(*u*-eddadp)]$^-$ complex **B** containing the ligand with N-geminal 3-alaninate and N-geminal glycinate rings. Both complexes **A** and **B** have a rhombic field and C_1 molecular symmetry. The Λ ($\Lambda\Delta\Lambda$) configuration was assigned to the isomers of these complexes that have 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. Many other Co(III)-edta-type complexes with the same (+, −) CD patterns were also assigned the Λ configuration.[3] It was of interest to check the spectral assignments by X-ray crystallography for representative Co(III) complexes containing unsymmetrical edta-type ligands. In this paper, the preparation and resolution of two complexes, [Co(ed3ap)]$^-$ (**A**) and [Co(*u*-eddadp)]$^-$ (**B**) have been reexamined. The X-ray data are reported for the (−)$_{546}$-*trans*(O_5)-[Co(ed3ap)]$^-$ for which the Λ absolute configuration was found to be the same as that assigned from the CD sign pattern.[20] Structural parameters and strain analysis data of Λ-(−)$_{546}$-*trans*(O_5)-[Co(ed3ap)]$^-$ and other [Co(edta-type)]$^-$ chelates of known structures are discussed in relation to their octahedral distortion. The CD and IR (carboxylate region) data for complexes **A** and **B** are also given and discussed.

Table 1. Determination of the Absolute Configuration of Λ-(−)$_{546}$-*trans*(O_5)-Li[Co(ed3ap)]·H_2O (The Bijvoet Inequality Relationship by the Mo $K\alpha$ Radiation)

Significant difference[a]	Correct trend	Incorrect trend
> 4.0	13	1
3.0—4.0	18	1
2.0—3.0	51	14
1.0—2.0	169	52
< 1.0	488	356

a) Significant difference $= ||F_c(+)| - |F_c(-)||/\mathrm{sqrt}(\sigma[F_o(+)]^2+\sigma[F_o(-)]^2)$.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters with esds in Parentheses

Atom	x	y	z	B_{eq} (Å^2)
Co	−0.20313(10)	−0.0065(9)	−0.16119(8)	2.08(1)
O(1)	−0.3826(6)	−0.0961(9)	−0.2958(5)	2.91(8)
O(2)	−0.7185(5)	−0.1187(9)	−0.4647(5)	3.38(9)
O(3)	−0.1785(5)	0.0443(9)	−0.3896(4)	2.45(7)
O(4)	−0.2374(6)	0.1705(9)	−0.5442(5)	3.61(9)
O(5)	−0.0141(5)	0.0817(9)	−0.0355(4)	2.40(7)
O(6)	0.1893(6)	0.1181(9)	0.2485(5)	3.61(9)
O(7)	0.0288(5)	−0.0843(9)	−0.1445(4)	2.61(8)
O(8)	0.2015(6)	−0.2111(9)	−0.0907(4)	3.22(8)
O(9)	−0.1629(6)	−0.2286(9)	−0.4492(4)	3.17(8)
N(1)	−0.4451(6)	0.0708(9)	−0.2001(5)	2.31(8)
N(2)	−0.2395(7)	−0.0419(9)	0.0768(5)	2.52(7)
C(1)	−0.4793(8)	0.0863(10)	−0.0130(7)	2.9(1)
C(2)	−0.4514(6)	−0.005(1)	0.0855(6)	3.02(9)
C(3)	−0.6338(8)	0.0246(10)	−0.3291(6)	2.6(1)
C(4)	−0.5785(9)	−0.0703(9)	−0.3645(7)	2.56(9)
C(5)	−0.3855(8)	0.1536(9)	−0.2940(7)	2.7(1)
C(6)	−0.2593(8)	0.1226(9)	−0.4222(7)	2.8(1)
C(7)	−0.0621(7)	0.002(1)	0.2234(6)	2.72(10)
C(8)	0.0471(8)	0.0723(9)	0.1456(6)	2.69(9)
C(9)	−0.2396(8)	−0.139(1)	0.1037(7)	3.2(1)
C(10)	−0.0357(8)	−0.1850(9)	0.0915(7)	3.1(1)
C(11)	0.0669(8)	−0.1583(9)	−0.0602(6)	2.40(10)
Li	−0.843(2)	−0.218(1)	−0.371(1)	3.2(2)

Description of Molecular Structure. The molecular structure (ORTEP) of the complex anion (−)$_{546}$-*trans*(O_5)-[Co(ed3ap)]$^-$ (Λ configuration) is depicted in Fig. 2, where the numbering schemes adopted for the respective atoms are

Table 3. Bond Distances (Å) and Bond Angles (°) of Λ-(−)$_{546}$-*trans*(O$_5$)-Li[Co(ed3ap)]·H$_2$O

Co–O(1)	1.894(7)	O(8)–C(11)	1.25(1)	C(3)–H(5)	0.95
Co–O(3)	1.914(7)	O(8)–Li	2.02(2)	C(3)–H(6)	0.95
Co–O(5)	1.878(7)	O(9)–Li	2.03(2)	C(5)–C(6)	1.50(2)
Co–O(7)	1.898(7)	N(1)–C(1)	1.48(1)	C(5)–H(7)	0.95
Co–N(1)	1.920(8)	N(1)–C(3)	1.52(1)	C(5)–H(8)	0.95
Co–N(2)	1.933(8)	N(1)–C(5)	1.53(1)	C(7)–C(8)	1.48(1)
O(1)–C(4)	1.32(1)	N(2)–C(2)	1.50(1)	C(7)–H(9)	0.95
O(2)–C(4)	1.23(1)	N(2)–C(7)	1.50(1)	C(7)–H(10)	0.95
O(2)–Li	1.95(2)	N(2)–C(9)	1.47(1)	C(9)–C(10)	1.55(1)
O(3)–C(6)	1.29(1)	C(1)–C(2)	1.50(2)	C(9)–H(11)	0.95
O(4)–C(6)	1.19(1)	C(1)–H(1)	0.95	C(9)–H(12)	0.95
O(4)–Li	1.92(2)	C(1)–H(2)	0.95	C(10)–C(11)	1.50(1)
O(5)–C(8)	1.30(1)	C(2)–H(3)	0.95	C(10)–H(13)	0.95
O(6)–C(8)	1.25(1)	C(2)–H(4)	0.95	C(10)–H(14)	0.95
O(7)–C(11)	1.27(1)	C(3)–C(4)	1.51(1)		
O(1)–Co–O(3)	90.3(3)	O(7)–Co–N(1)	176.1(4)	Co–N(1)–C(5)	105.8(6)
O(1)–Co–O(5)	177.0(3)	O(7)–Co–N(2)	93.5(3)	C(1)–N(1)–C(3)	112.3(8)
O(1)–Co–O(7)	88.1(3)	N(1)–Co–N(2)	89.7(4)	C(1)–N(1)–C(5)	115.5(8)
O(1)–Co–N(1)	89.4(3)	Co–O(1)–C(4)	113.4(7)	C(3)–N(1)–C(5)	109.1(8)
O(1)–Co–N(2)	94.9(3)	C(4)–O(2)–Li	122.2(9)	Co–N(2)–C(2)	106.1(6)
O(3)–Co–O(5)	87.6(3)	Co–O(3)–C(6)	114.4(7)	Co–N(2)–C(7)	106.8(6)
O(3)–Co–O(7)	93.6(3)	C(6)–O(4)–Li	151.0(10)	Co–N(2)–C(9)	113.1(7)
O(3)–Co–N(1)	83.4(3)	Co–O(5)–C(8)	114.5(7)	C(2)–N(2)–C(7)	109.5(8)
O(3)–Co–N(2)	171.3(3)	Co–O(7)–C(11)	128.8(7)	C(2)–N(2)–C(9)	110.5(9)
O(5)–Co–O(7)	89.8(3)	C(11)–O(8)–Li	108.5(9)	C(7)–N(2)–C(9)	110.7(8)
O(5)–Co–N(1)	92.5(3)	Co–N(1)–C(1)	105.9(7)	N(1)–C(1)–C(2)	107.5(9)
O(5)–Co–N(2)	87.5(3)	Co–N(1)–C(3)	107.9(6)	N(1)–C(1)–H(1)	110.0
N(1)–C(1)–H(2)	110.0	N(1)–C(5)–H(7)	110.1	C(10)–C(9)–H(11)	108.0
C(2)–C(1)–H(1)	110.0	N(1)–C(5)–H(8)	110.1	C(10)–C(9)–H(12)	108.0
C(2)–C(1)–H(2)	110.0	C(6)–C(5)–H(7)	110.1	H(11)–C(9)–H(12)	109.5
H(1)–C(1)–H(2)	109.3	C(6)–C(5)–H(8)	110.1	C(9)–C(10)–C(11)	118.3(9)
N(2)–C(2)–C(1)	108.0(8)	H(7)–C(5)–H(8)	109.3	C(9)–C(10)–H(13)	107.2
N(2)–C(2)–H(3)	109.9	O(3)–C(6)–O(4)	123(1)	C(9)–C(10)–H(14)	107.2
N(2)–C(2)–H(4)	109.9	O(3)–C(6)–C(5)	115.3(10)	C(11)–C(10)–H(13)	107.2
C(1)–C(2)–H(3)	109.8	O(4)–C(6)–C(5)	121.1(10)	C(11)–C(10)–H(14)	107.2
C(1)–C(2)–H(4)	109.8	N(2)–C(7)–C(8)	112.2(8)	H(13)–C(10)–H(14)	109.5
H(3)–C(2)–H(4)	109.5	N(2)–C(7)–H(9)	108.8	O(7)–C(11)–O(8)	120.5(10)
N(1)–C(3)–C(4)	111.7(9)	N(2)–C(7)–H(10)	108.8	O(7)–C(11)–C(10)	123.3(9)
N(1)–C(3)–H(5)	108.9	C(8)–C(7)–H(9)	108.7	O(8)–C(11)–C(10)	116.2(9)
N(1)–C(3)–H(6)	108.9	C(8)–C(7)–H(10)	108.7	O(2)–Li–O(4)	111.8(10)
C(4)–C(3)–H(5)	109.0	H(9)–C(7)–H(10)	109.5	O(2)–Li–O(8)	112(1)
C(4)–C(3)–H(6)	109.0	O(5)–C(8)–O(6)	123.6(10)	O(2)–Li–O(9)	115(1)
H(5)–C(3)–H(6)	109.4	O(5)–C(8)–C(7)	116.4(9)	O(4)–Li–O(8)	114(1)
O(1)–C(4)–O(2)	122.7(10)	O(6)–C(8)–C(7)	120.0(10)	O(4)–Li–O(9)	100.5(10)
O(1)–C(4)–C(3)	117.1(10)	N(2)–C(9)–C(10)	115.3(9)	O(8)–Li–O(9)	100.3(9)
O(2)–C(4)–C(3)	120(1)	N(2)–C(9)–H(11)	107.9		
N(1)–C(5)–C(6)	107.0(8)	N(2)–C(9)–H(12)	107.9		

also given. One can see from the ORTEP diagram (Fig. 2) that the Co(III) ion is encircled by all of the six ligand atoms (2N and 4O) of ed3ap to form an octahedral complex. The complex anion represents a *trans*(O$_5$) isomer (Fig. 1, isomer I) with the two glycinate (R) rings in *trans* positions and the two (one glycinate and one β-alaninate) G rings coordinated in the equatorial plane. The absolute configuration of the complex anion (Fig. 2) is the Λ ($\Lambda\Delta\Lambda$) according to IUPAC rules.[36] The configuration of one asymmetric nitrogen atom (N2 atom) of the Λ-(−)$_{546}$-*trans*(O$_5$)-[Co(ed3ap)]$^-$ complex is R.[41] The puckered diamine ring (E ring), as expected, has a δ conformation. The two glycinate rings lying out of G plane (R1 and R2 rings) are relatively flat. The glycinate G1 ring shows a significant deviation from planarity with a λ conformation. The equatorially coordinated β-alaninate ring (G2 ring) (Fig. 2) shows a significant deviation from an ideal *twist-boat* conformation. The conformation of the G2 ring is close to *half-chair* (δ). The carbonyl oxygen atoms of the carboxylate rings are involved with either, H-bonding to water molecules or to the lithium ion. The distorted tetrahedron about the Li$^+$ ion is linked to three carbonyl oxygen atoms belonging to three neighboring complex units and one water oxygen atom (O(W9)) making four bonds (Li–O(2), 1.95(2); Li–O(4), 1.92(2); Li–O(8), 2.02(2); Li–O(W9), 2.03(2) Å)

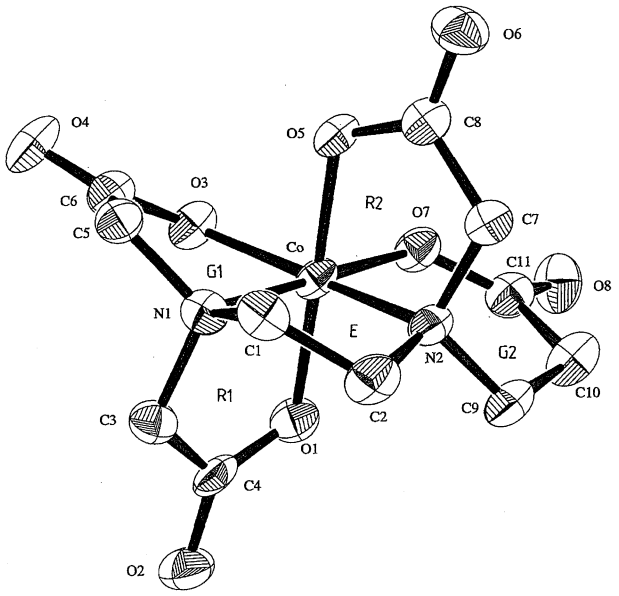

Fig. 2. Molecular Structure (ORTEP) of the Λ-(−)$_{546}$-*trans*(O$_5$)-[Co(ed3ap)]$^-$ in Λ-(−)$_{546}$-*trans*(O$_5$)-Li[Co(ed3ap)]·H$_2$O.

and six bond angles (O(2)–Li–O(4), 111.8(10)°; O(2)–Li–O(8), 112(1)°; O(2)–Li–O(W9), 115(1)°; O(4)–Li–O(W9), 100.5(10)°; O(4)–Li–O(8), 114(1)°, and O(8)–Li–O(W9), 100.3(9)°). The effects of non-bonded contacts (up to 3.60 Å) on the conformations of the rings are uncertain.

Structural Parameters and Strain Analysis of [Co(edta-type)]$^-$ Chelates in Relation to the Structure of the Ligand and Octahedral Distortion of Complexes. Selected bond distances and bond angles within the complex anion (Fig. 2) are listed in Table 3. The Co–L bond distances for this complex are given in Table 4. The mean Co–L bond distances in *trans*(O$_5$)-[Co(ed3ap)]$^-$ (**2**) for Co–N and Co–O are 1.93 and 1.90 Å, respectively, and these values are comparable to corresponding bond lengths in related Co(III) complexes (Co–N range, 1.92—1.96 Å and Co–O range, 1.88—1.92 Å) (Table 4).[2,4—8] In Co(III) edta-type chelates where glycinates coordinated axially, the axial Co–O(R) distances are slightly shorter than (or nearly equal to) the Co–O(G) distances (Table 4). Apparently, *trans*(O$_6$) coordination[7,8] (complexes **4** and **7**) allows the equatorial Co–O(G) and axial Co–O(R) distances to be practically equal. Mean Co–N bond distances for the complexes listed are larger than mean Co–O distances except for [Co(edta)]$^-$[2] (**1**) for which the same mean Co–L distances were found (Co–N = Co–O = 1.92 Å) (Table 4).

For complexes forming five-membered diamine rings, the mean Co–N bond distances increase exactly on going from **1** to **4** with increasing number of the β-alaninate rings (mean Co–N range 1.92—1.96 Å). On the other hand, the mean Co–N distances are nearly the same for complexes **5**, **6**, and **7** forming six-membered diamine rings (mean Co–N = 1.96 Å). On the same order, going from **1** to **7** (Table 4), the mean Co–O(G) bond distances slightly decrease (1.94—1.90 Å), while the mean Co–O(R) distances slightly increase (1.89—1.91 Å). Moreover, the Co–N bond distances are more sensitive to the structure of the ligand than are Co–O bond distances.

The main Cartesian axes (O(R1)–Co–O(R2), O(G1)–Co–N, and O(G2)–Co–N) would be nearly the same lengths if the mean Co–N distances were equal to the mean Co–O distances. Of these three axes given above, the O(R1)–Co–O(R2) angle of the complex studied (complex **2**) deviates least ($\Delta_1 = -3.0°$) from the ideal 180°. This was the case for all complexes listed (Table 4) having *trans*(O$_5$) coordination. However, of the three Cartesian axes, the O(R1)–Co–O(R2)

Table 4. Comparison of Bond Distances in Hexadentate Co(III)-edta-Type Complexes

Complex		Co–N (Å)	(Mean)	Co–O(G) (Å)	(Mean)	Co–O(R) (Å)	(Mean)	Co–O (Å) (Mean)	Ref.
[Co(edta)]$^-$	(**1**)	1.921(8)		1.945(7)		1.897(7)			2)
			1.92		1.94		1.89	1.92	
		1.929(8)		1.946(7)		1.887(7)			
trans(O$_5$)-[Co(ed3ap)]$^-$ (**A**)	(**2**)	1.920(8)		1.914(7)		1.878(7)			This work
			1.93		1.91		1.89	1.90	
		1.933(8)		1.898(7)		1.894(7)			
trans(O$_5$)-[Co(eddadp)]$^-$	(**3**)	1.946(4)		1.930(3)		1.888(3)			6)
			1.95		1.92		1.89	1.90	
		1.961(4)		1.905(3)		1.885(3)			
[Co(edtp)]$^-$	(**4**)	1.973(4)		1.917(4)		1.892(4)			8)
			1.96		1.92		1.90	1.91	
		1.956(5)		1.917(4)		1.903(4)			
[Co(1,3-pdta)]$^-$	(**5**)	1.966(9)	1.96	1.904(9)	1.90	1.861(8)	1.86	1.88	4)
[Co(dhpta)]$^-$	(**6**)	1.933(6)		1.923(6)		1.906(5)			5)
			1.95		1.92		1.90	1.91	
		1.969(7)		1.917(6)		1.889(5)			
trans(O$_6$)-[Co(1,3-pddadp)]$^-$	(**7**)	1.962(1)		1.901(1)		1.906(1)			7)
			1.96		1.90		1.91	1.91	
		1.967(1)		1.906(1)		1.908(1)			

angle shows the greatest deviation for complexes having *trans*(O_6) coordination ($\Delta_1 = -7.3°$ for **4** and $\Delta_1 = -6.2°$ for the complex **7**). In general, for complexes listed, the main Cartesian axes deviate only minimally from the ideal bond angle of 180° (Δ vary from −0.5 to −8.7°).

The results of a comparative study of the strain characteristics of related series of Co(III) edta-type chelates are given in Table 5. The strain characteristics data are reported for complexes **2** and **6**. For comparison, data are given in Table 5 for complexes **1**,[2] **3**,[6] **4**,[8] **5**,[4] and **7**[7] of known strain characteristics.[8] The major contributions to strain were considered to be: (i) the octahedral angles around the Co(III) ion, (ii) the ring angle sums of the various kinds of rings, (iii) the Co–O–C bond angles, and (iv) the bond angles that the chelating nitrogen atom makes with its connectors.

In Co(III)-edta-type chelates considered (Table 5) the six-membered rings (1,3-propanediamine rings (T rings) and β-alaninate rings (R and G rings)) are in distorted *boat* conformations. The ethylenediamine rings (E rings) and the G glycinate rings are usually observed to be puckered, while the R glycinate rings are observed to be more planar than the G's and are referred to as having an "envelope" conformation.

The octahedral bond angles in [Co(edta-type)]⁻ chelates vary from 83.47 to 103.21° for **1**,[2] 83.4 to 94.9° for **2** (Table 3), 83.9 to 94.6° for **3**,[6] 86.4 to 93.9° for **4**,[8] 84.3 to 99.0° for **5**,[4] 84.0 to 98.5° for **6**,[5] and 84.50 to 97.96° for the complex **7**[7]. The complex **1**, as expected, shows the greatest distortion among the Co(III)-edta-type complexes in Table 5. The greatest deviation in [Co(edta)]⁻ (**1**) complex was realized by the O(G1)–Co–O(G2) bond angle (103.21°). In general, the O(G1)–Co–O(G2) *cis* angles show greatest deviation for complexes forming five-membered diamine rings (complexes **1** to **4**, Table 5). However, in complexes forming six-membered diamine rings, the greatest deviation was realized by the N(1)–Co–N(2) bond angles (99.0° for **5**, 98.5° for **6**, and 97.96° for **7**).

From the Table 5 we can see that expanding the E ring and/or the glycinate ring lowers the octahedral strain. Angular octahedral deviations are significant only when they approach a 4°/angle. The total deviation of the octahedral angles sums 48 for the [Co(edta)]⁻ (**1**) complex (the mean angular deviation is 4°/angle) indicating a greater octahedral distortion than among the other complexes listed. Other complexes considered show less angular deviation which varies from ca. 2.5°/angle for a group of complexes forming five-membered rings (complexes **2**, **3**, and **4**) to ca. 3°/angle for a group of complexes forming six-membered diamine rings (complexes **5**, **6**, and **7**).

The bond angle chelate-ring sums for the R glycinate rings are close to the ideal value (538.5°) (total deviations vary from −1 to +1°). The bond angle chelating ring sums for the G glycinate and E rings are less (deviations are negative) than the corresponding ideal values. They show a negative total deviation of ca. 12° (for the G rings) and of ca. 13° (for the E rings) (Table 5). The larger deviations are positive for all six-membered rings (T rings and β-alaninate rings) for listed complexes (Table 5). The T rings in complexes **5**, **6**, and **7** show a positive total deviation of ca. 37° for **5** and **6** and of 28° for the complex **7**. The mean angular deviation in the T ring made by the chelating nitrogen is larger than was found for the E ring (ca. 4.5—6°/angle versus ca. 2.6°/angle).

The bond angles of the M–O–C fragment is expected to be between 109.5 and 120° depending on the degree of covalency of the M–O bond.[8] These bond angles in the β-alaninate rings are as high as 130°. The values are larger for the G β-alaninate rings (*trans*(O_5) coordination) than for the R β-alaninate rings (*trans*(O_6) coordination) as is the case for complexes of Co(III) listed in Table 5. What was unexpected was that the Cu–O–C(R) bond angles in [Cu(1,3-pddadp)]$^{2-}$[17b] complex do not show any deviation from the ideal value (Cu–O–C(R) = 109.0°) indicating that the deviation of these angles in Cu-edta-type complexes strongly depends on the length of the axial (Cu–O–C(R)) bond distances.[17b]

As was discussed,[8] the main causes of strain in the β-alaninate rings are due to the M–O–C (except for Cu(II)[17b]),

Table 5. Strain Analysis of edta-Type Chelates of Co(III)

Complex		$\Sigma\Delta$[a]	$\Delta\Sigma$[b]			$\Delta\{$Co–O–C$\}$[c]		$\Sigma\Delta$[d]	Ref.
		O_h	E(T)	R	G	R	G	N	
[Co(edta)]⁻	(**1**)	48	−12	−1	−9	+5	+3	18	2,8)
trans(O_5)-[Co(ed3ap)]⁻ (**A**)	(**2**)	29	−11	±1	−13(+44)[e]	+4, +5	+5(+19)[e]	18(12)	This work
trans(O_5)-[Co(eddadp)]⁻	(**3**)	31	−11	−1	+38	+6	+18	13	6,8)
[Co(edtp)]⁻	(**4**)	29	−14	+42	+41	+21	+21	18	8)
[Co(1,3-pdta)]⁻	(**5**)	34	+36	+1	−12	+7	+5	15	4,8)
[Co(dhpta)]⁻	(**6**)	34	+38	+1	−12	+6	+4	16	5)
trans(O_6)-[Co(1,3-pddadp)]⁻	(**7**)	38	+28	+33	−11	+17	+4	16	7,8)

a) $\Sigma\Delta(O_h)$ is the sum of the absolute values of the deviation from 90° of the L–Co–L′ bite angles. All values rounded off to the nearest degree. b) $\Delta\Sigma$(ring) is the deviation from the ideal of the corresponding chelate rings' bond angle sum. A mean value for the two rings (R or G)* is reported because the molecule is expected to have (in approximation) C_2 symmetry. c) $\Delta\{$Co–O–C$\}$(ring) is the mean value of the deviation of the corresponding rings' Co–O–C band angle from 109.5°. d) $\Sigma\Delta$(N) is the sum of the absolute values of the six band angles made by the chelate nitrogen atoms. A mean value for the two nitrogens is reported. For the complex **2** the two values for the two nitrogens are reported. The value in parenthesis is given for nitrogen atom incorporated in six-membered ring. e) For the complex **2** having C_1 molecular symmetry the two values are reported. The values in parentheses are given for six-membered rings.

C–C–C, N–C–C, and M–N–C bond angles. These bond angles (except M–N–C) deviate more for the G β-alaninate rings (*trans*(O_5) complexes) than the R β-alaninate rings (the *trans*(O_6) complexes) as was also the case for complexes of Co(III) (Table 5).[8] In the *trans*(O_5)-[Co(ed3ap)]$^-$ (**2**) these bond angles for the G2 ring (Fig. 2, Table 3) and their corresponding deviations are: Co–O–C(G2), 128.8° (+19.3°), C–C–C(G2) 118.3° (ca. +9°), and N(2)–C–C(G2), 115.3° (ca. +6°). The Co–N(2)–C(G2) bond angles of complexes **2** and **3** deviate minimally. For the G β-alaninate rings of the complex **3** (*trans*(O_5) coordination) the total deviation is positive and of 38° (the mean angular deviation is ca. 6.3°/angle). For the G2 β-alaninate ring of the complex **2** (*trans*(O_5) coordination) the total deviation is also positive and of 44°. The mean angular deviation is 7.3°/angle (the greatest deviation among the complexes in Table 5).

The β-alaninate R rings of the complex **7** (the *trans*(O_6) coordination) also show a positive total deviation and of 33° (the mean angular deviation is 5.5°/angle).[8] The Co–N–C-(R) bond angles of this complex deviate more (ca. +6.0°) than the N–C–C(R) and C–C–C(R) bond angles, and were opposite those in complexes **2** and **3** having the G β-alaninate rings (the *trans*(O_5) coordination).

The two β-alaninate rings (R and G) of complex **4**, having two N-geminal 3-alaninate rings, as was found,[8] show the same positive total deviation of ca. 41°. The Co–O–C(R,G) bond angles in the β-alaninate rings are as high as 130°, and the value is of the same order of magnitude for both kinds of rings, with the same deviation of these bond angles (+21°).

The effects of chelation of edta-type complexes can distort the tetrahedral geometry of the nitrogen atoms.[42] Each coordinated N-atom of this system makes four bonds, with six bond angles. When each of the deviations is summed for the six angles the total deviation (the absolute values) about the N-atoms was obtained (Table 5). For the complexes considered, a mean value for the two nitrogens is given except for the complex **2** for which the two values (about the N(1) and N(2) atoms) are reported. The greatest deviation about the N(1) atom is found for the C(E)–N(1)–C(G1), Co–N(1)–C-(G1), and Co–N(1)–C(E) fragments. These angles with their corresponding deviations are: 115.5° (+6°), 105.8° (−3.7°) and 105.9° (−3.6°). The total deviation about the chelating N(1) atom in this complex adds up to roughly 18° (Table 5). The greatest deviation about the N(2) atom is realized for bond angles, Co–N(2)–C(E), 106.1° (−3.4°), Co–N(2)–C-(G2), 113.1° (+3.6°), and Co–N(2)–C(R2), 106.8° (−2.7°). The total deviation about the chelating N(2) atom in the complex **2** adds up to roughly 12° (the value given in parenthesis, Table 5). Among the complexes in Table 5, the greatest deviation (18°) was found for group of complexes forming E rings and having N-geminal glycinate rings or N-geminal 3-alaninate rings (complexes **1**, **4**, and the N(1) nitrogen atom of the complex **2**). Other complexes of this group (*trans*(O_5) coordination) contain N atoms with less strained bonds (complexes **3** and the N(2) nitrogen atom of the complex **2**). The total deviation about chelating N atoms in these complexes adds up to roughly 12° (the least deviation among the complexes considered). For the remained complexes **5**, **6**, and **7** forming T rings the total deviation about the N atoms sums to ca. 16° (Table 5). These complexes, compared to those of **1**, **2**, and **4** listed in Table 5 contain N atoms with less strained bonds.

CD Spectra and Contributions of Structural Changes. Electronic absorption and CD data for complexes, Λ-$(-)_{546}$-*trans*(O_5)-[Co(ed3ap)]$^-$ (**A**) and Λ-$(+)_{546}$-[Co(*u*-eddadp)]$^-$ (**B**) are given in Table 6. The data given in parentheses are those earlier reported.[20] The CD spectra of complexes **A** and **B** and Λ-$(-)_{546}$-[Co(edta)]$^-$ complex[1b] are given in Fig. 3.

Electronic absorption and CD spectra of complexes **A** and **B** have been discussed in a series of related complexes forming five-membered diamine rings.[20] The Λ configuration was assigned to the isomers of these complexes that have two well-defined CD peaks in the region of the first absorption band, with the lowest energy CD peak positive and next peak negative. In this work this assignment was found to be correct by X-ray analysis of the complex **A** containing the unsymmetrical ed3ap ligand.

The absolute configuration of the chiral nitrogen in Λ-$(-)_{546}$-*trans*(O_5)-[Co(ed3ap)]$^-$ was assigned to be R.[41] The N-vicinal, C-vicinal, and ring conformational effects were found to be small for Λ-[Co(*SS*-edds)]$^-$[34] compared to Λ-

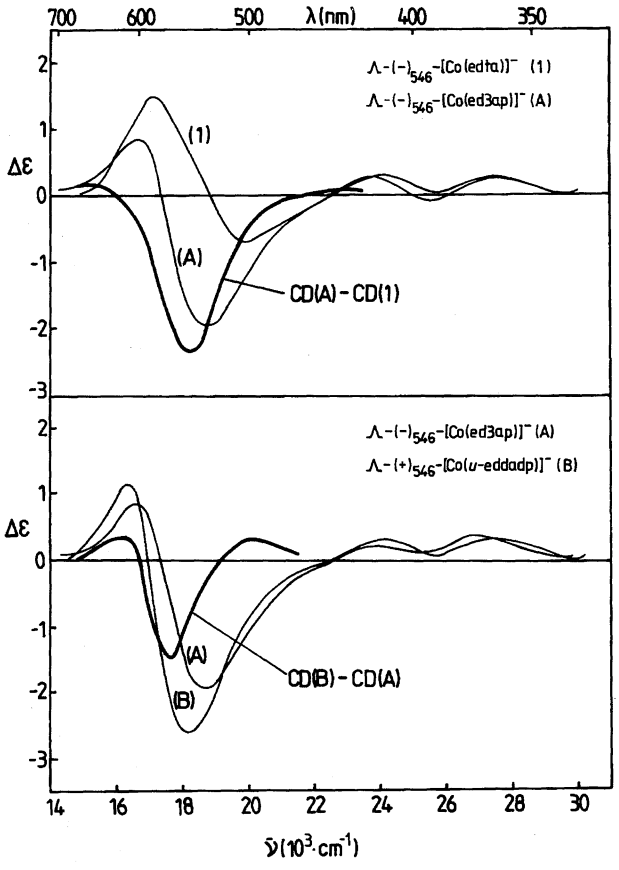

Fig. 3. Differences CD curves (—):
CD of Λ-[Co(ed3ap)]$^-$ (**A**) −CD of Λ-[Co(edta)]$^-$ (**1**) (above) and CD of Λ-[Co(*u*-eddadp)]$^-$ (**B**) −CD of Λ-[Co(ed3ap)]$^-$ (**A**) below.

Table 6. Absorption (AB) and Circular Dichroism (CD) data for Λ-(−)$_{546}$-*trans*(O$_5$)-[Co(ed3ap)]$^-$ (**A**) Λ-(+)$_{546}$-[Co(*u*-eddadp)]$^-$ (**B**) Complexes[a)]

Complex	AB				CD			
	ν (10^3 cm^{-1})		ε		ν (10^3 cm^{-1})		$\Delta\varepsilon$	
Λ-(−)$_{546}$-R-[Co(ed3ap)]$^-$ [b)] (**A**)	18.70	(18.63)	309	(286)	16.65	(16.53)	+0.86	(+0.91)
					18.72	(18.62)	−1.96	(−1.98)
	26.00	(26.04)	209	(196)	24.11	(24.09)	+0.26	(+0.33)
					27.41	(27.55)	+0.25	(+0.30)
Λ-(+)$_{546}$-[Co(*u*-eddadp)]$^-$ (**B**)	18.46	(18.45)	309	(279)	16.29	(16.31)	+1.11	
					18.14	(18.25)	−2.66	
	25.50	(25.57)	182	(166)	23.81		+0.26	
					26.72	(26.95)	+0.36	

a) The values in parentheses are those earlier reported.[20)] b) The *trans*(O$_5$) isomer.

Table 7. Asymmetric Stretching Carboxylate Frequencies in [Co(edta-type)]$^-$ Complexes (cm^{-1})

Complex	ν_{asym}	Chelate ring size	Ref.
Na[Co(edta)]·2H$_2$O	1638	5	43, 45
[Co(edta-type)]$^{n-}$ (C_2-general)	ca. 1680—1600	5	16a, 17b, 23a, 32, 44
	ca. 1600—1560	6	
trans(O$_5$)-Li[Co(ed3ap)]·H$_2$O (**A**)	1651	5	This work
	1635	5	
	1579	6	
K[Co(*u*-eddadp)]·2H$_2$O (unresolved) (**B**)	1631	5, 6	This work
Li[Co(edtp)]·3H$_2$O	1590	6	46, 8

a) All spectra were obtained using KBr technique.

[Co(edta)]$^-$ and a series of related (Λ) complexes going from edta to edtp.[3,20)] The shapes of CD curves of these complexes[3)] 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 (Fig. 3) is mostly due to configurational effects associated with the distribution of the chelate rings of different size.

Differences between the CD curves of these complexes might show the contributions of structural changes. The difference CD curve in Fig. 3 (CD of Λ-*trans*(O$_5$)-[Co(ed3ap)]$^-$ (**A**) −CD of Λ-[Co(edta)]$^-$ (**1**)) gives one broad negative peak between two poorly defined weak positive peaks. This reflects the effect for one β-alaninate ring replacing a glycinate ring in an equatorial plane. However, the resolved CD peaks for these two complexes represent the lowest-energy component and combinations of the other two components (Table 6). The CD peaks for Λ-(+)-*trans*(O$_5$)-[Co(ed3ap)]$^-$ (**A**) and Λ-(+)-[Co(*u*-eddadp)]$^-$ (**B**) (Fig. 3, Table 6) correspond to the same lower energy components. The difference CD curve in Fig. 3 (CD of Λ-[Co(*u*-eddadp)]$^-$ (**B**) −CD of Λ-*trans*(O$_5$)-[Co(ed3ap)]$^-$ (**A**)) shows three well-defined peaks (+, −, +) in the lower-energy band region. The difference between the two components of these complexes results from the replacement in an axial position of a glycinate ring by a β-alaninate ring. This difference curve is similar to the CD curves for Λ-(+)-[Co(en)(mal)$_2$]$^-$,[1b)] Λ-(+)-[Co(*SS*-edds)]$^-$,[34)] and Λ-(+)-*trans*(O$_6$)-[Co(1,3-pddadp)]$^-$.[3,25)] These peaks probably correspond to the three C_2 components, as was also found in the difference CD curve (CD of Λ-[Co(edtp)]$^-$ −CD of Λ-*trans*(O$_5$O$_6$)-[Co(eda3p)]$^-$).[20)] These data suggest that structural changes in an axial position of [Co(edta-type)]$^-$ complexes affect the shape of CD spectra more than structural changes in an equatorial position (Fig. 3).

Infrared Spectra of Complexes. Infrared spectra (carboxylate region) for complexes **A** and **B** are also reported here. The asymmetric carbonyl stretching modes of ligand carboxylates have been used to analyze the environment of this functional group.[16a,17b,23a,32,43,44)] In general the following have been found: protonated carboxylate, >1700 cm^{-1}; coordinated carboxylate, ca. 1680—1560 cm^{-1}; ionic carboxylate, <1600 cm^{-1}. Also, in [M(edta-type)]$^{n-}$ complexes[16a,17b,23a,32,44)] containing ligands with mixed (five- and six-membered) carboxylate arms and having C_2 molecular symmetry, it was clearly demonstrated that the asymmetric stretching frequency of the carboxylate groups of the five-membered rings lies at a higher energy (ca. 1680—1600 cm^{-1}) than the corresponding frequency of the six-membered chelate rings (ca. 1600—1560 cm^{-1}) (Table 7).

The [Co(edta-type)]$^-$ complexes forming only four glycinate rings[43,45)] or four β-alaninate rings,[46)] have as expected, one band in the asymmetric carboxylate stretching region (at 1638 and 1590 cm^{-1} for five- and six-membered rings, respectively). The IR data (carboxylate region) for complexes **A** and **B** are given in Table 7. Both complexes **A** and **B** have C_1 molecular symmetry and four non-equivalent coordinated carboxylate groups. Instead of four bands, complex

A shows three bands in the expected asymmetric stretching carboxylate region, which is in agreement with its C_1 molecular symmetry. Two of these bands at higher energy (at 1651 and 1635 cm^{-1}) were assigned to the asymmetric stretch of coordinated carboxylate contained in the glycinate residue (R and G rings), and a band at lower energy (at 1579 cm^{-1}) was assigned to the moiety of the six-membered carboxylate arm. On the other hand, complex **B**, instead of four bands in the expected region, has only one very broad unresolved band (at 1631 cm^{-1}).

In the IR spectra reported, the bands appearing in the region 1420—1360 cm^{-1} (at 1418, 1384, and 1364 cm^{-1} for **A** and at 1377 cm^{-1} for **B** can be assigned tentatively to the $\nu_s(COO^-)$. In this sense the reported data are useful for identification of compounds.

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