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Crystal structures and absolute configurations of $(+)_{589}$-Li[Co(edtp)]·$3H_2O$ and $(+)_{589}$-Li[Cr(edtp)]·$3H_2O$ complexes of ethylenediamine-*N*,*N*,*N*′,*N*′-tetra-3-propionate ion and correlations with circular dichroism spectra

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Abstract

The complexes, $(+)_{589}$-Li[M(edtp)]·$3H_2O$ (M = Co or Cr; edtp = ethylenediamine-*N*,*N*,*N*′,*N*′-tetra-3-propionate ion) crystallize in the space group $P2_1$ of the monoclinic crystal system with $Z=2$. For M = Co, $a=8.824(2)$, $b=11.910(3)$, $c=8.7282(2)$ Å, $\beta=95.03(1)°$ and for M = Cr, $a=8.705(1)$, $b=11.940(2)$, $c=9.033(1)$ Å, $\beta=94.19(1)°$. The absolute configuration is $\Delta(\lambda\lambda)$ for each complex where λ designates the conformation of the axial β-alaninate rings. Significant sources of strain are found and discussed for both complexes. The distortion from octahedral coordination in these $[M(edtp)]^-$ complexes is greater for Co(III) than it is for Cr(III) which is unusual compared to other $[M(edta)]^-$-type complexes. The absolute configurations of the complexes are consistent with earlier reports of their circular dichroism spectra.

Introduction

The complex $[Co(edta)]^-$ (edta = ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate ion) and related edta-type complexes have been investigated extensively. Absolute configurations have been established by X-ray crystallography for $(+)_{546}$-Δ-$[Co(edta)]^-$ [1] and a few related complexes [2–5]. Absolute configurations have been assigned for many related complexes by correlation of their CD spectra with those of known configurations.

The CD spectra were compared for $(-)_{546}$-$[Co(edta)]^-$ and the corresponding isomers of $[Co(1,3\text{-pdta})]^-$, $[Co(edtp)]^-$, *cis*(*N*)-$[Co(ida)_2]^-$ [6], and *trans*(O_5O_6)-$[Co(eda3p]^-$ [7] (1,3-pdta = 1,3-propanediamine-*N*,*N*,*N*′,*N*′ -tetraacetate ion; edtp = ethylene-diamine-*N*,*N*,*N*′,*N*′-tetra-3-propionate ion; ida = iminodiacetate ion; eda3p = ethylenediamine-*N*-acetate-*N*,*N*′,*N*′-tri-3-propionate ion). The Λ absolute configurations are known for $(-)_{546}$-$[Co(edta)]^-$ and $(-)_{546}$-$[Co(1,3\text{-pdta}]^-$ [2] and the other complexes cited above were assigned the Λ configuration from CD spectra.

Fewer edta-type complexes of chromium(III) have had their absolute configurations established. The situation is complicated by the greater strain of the chelate rings for the larger Cr(III) ion resulting in the formation of pentadentate complexes with a water molecule in the sixth coordination site [8–13]. There is strong evidence, however, for hexadentate coordination with Cr(III) in solution from ^2H NMR and magnetic circular dichroism spectra [10, 11]. The unstable Cr(III) hexadentates were isolated as crystals and the expected strain of glycinate rings is apparent from the crystal structure determination of K[Cr(edta)]·$2H_2O$ [14] and Na[Cr(cdta)]·$4.5H_2O$ [15] (cdta = *trans*-cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetate ion).

Stable hexadentate edta-type Cr(III) complexes have been obtained with ligands having longer carboxylate or diamine chains. Stable hexadentate complexes were obtained for $[Cr(1,3\text{-pdta})]^-$ [16]

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and $[\mathrm{Cr(tdta)}]^-$ (tdta = tetramethylenediamine-*N,N,N′,N′*-tetraacetate ion) [17], but resolution was not achieved. A crystallographic study [18] reports, however, that the $[\mathrm{Cr(1,3\text{-}pdta)}]^-$ complex is spontaneously resolved. Three isomers of $[\mathrm{Cr(1,3\text{-}pddadp)}]^-$ (1,3-pddadp* = 1,3-propanediamine-*N,N′*-diacetate-*N,N′*-di-3-propionate ion) have been reported [19] with a crystal structure of one of the isomers. The structure and absolute configuration (Λ) of Li *trans*(O_5)-$(-)_{589}$-[Cr(eddadp)] was determined [20] (eddadp* = ethylenediamine-*N,N′*-diacetate-*N,N′*-di-3-propionate ion). CD data have been reported [21] for *trans*(O_5)-$[\mathrm{Cr(eddadp)}]^-$ and $[\mathrm{Cr}(S,S\text{-edds})]^-$ (S,S-edds = S,S-ethylenediamine-*N,N′*-disuccinate ion). As with S,S-edds, $[\mathrm{Cr}(S,S\text{-ptnta})]^-$ (S,S-ptnta = $2S,4S$-2,4-pentanediamine-*N,N,N′,N′*-tetraacetate ion) was formed stereospecifically [22]. Kaizaki *et al.* [11, 22] have used spin-forbidden transitions in CD spectra effectively in making absolute configuration assignments. The absolute configuration of $(+)_{589}$-$[\mathrm{Cr(edtp)}]^-$ was assigned the Δ absolute configuration [23] because of differences in CD splittings compared to $(-)_{589}$-Λ-*trans*(O_5)-$[\mathrm{Cr(eddadp)}]^-$ and $(+)_{589}$-Λ-*trans*(O_5)-$[\mathrm{Cr}(S,S\text{-edds})]^-$. All three have the (+, −) sequence of CD peaks with increasing energy in the region of the lower energy absorption band. The $(-)_{589}$-*trans*(O_5O_6)-$[\mathrm{Cr(eda3p)}]^-$ complex (eda3p = ethylenediamine-*N*-acetate-*N,N′,N′*-tri-3-propionate ion) gave a CD spectrum [24] similar to that of $(-)_{589}$-*trans*(O_5)-$[\mathrm{Cr(eddadp)}]^-$.

Experimental

Optical isomers are identified by (+) or (−) corresponding to the sign of the lowest energy CD peak in the region of spin-allowed transitions and/or by the sign of the optical rotation at a wavelength λ $[(+)_\lambda$ or $(-)_\lambda]$. The chirality is designated as Δ or Λ according to the IUPAC rules [25]. $\mathrm{Li[Cr(edtp)]\cdot 3H_2O}$ [23] and $\mathrm{Li[Co(edtp)]\cdot 3H_2O}$ [7] were prepared and resolved as reported.

Physical measurements

The X-ray analyses were performed on crystals that were allowed to grow slowly from alcoholic aqueous solutions. Cell constants and crystal orientation matrices were determined on an Enraf-Nonius CAD-4 diffractometer by a least-squares refinement following machine location and centering of 25 reflections in the range $10 < \theta < 15°$. The Mo Kα radiation was made monochromatic by the use of a graphite filter; intensities of three standard reflections were monitored at regular intervals for both crystals which showed no signs of deterioration over the period of data collection. Data for both crystals were corrected for Lorentz and polarization effects. Absorption corrections were ignored for the data on the chromium complex, but were applied to the data collected on the cobalt complex.

Crystal data summaries are given for each of the crystals in Table 1. The structure of the chromium complex was solved using the heavy-atom method and refined by full-matrix least-squares calculations initially with isotropic and finally with anisotropic temperature factors using SHELX '76 [26]. The structure of the cobalt complex was solved using direct methods (MULTAN '82) [27] and refined by full-matrix least-squares calculations with anisotropic temperature factors for the non-hydrogen atoms. Difference Fourier syntheses revealed all the hydrogen atoms in the chromium complex and all but those of the water molecules in the cobalt complex. For the chromium complex, H atoms were included in the refinement at fixed positions from the ΔF map and an overall isotropic temperature factor. For the cobalt complex, H atoms were included in the refinement in geometrically idealized positions (C–H and O–H 0.95 Å) and only overall isotropic thermal parameters were refined for these two types of H atoms.

In the final stages of refinement, a weighting factor of the form $w = 1/(\sigma^2 F + pF^2)$ was used. The p values

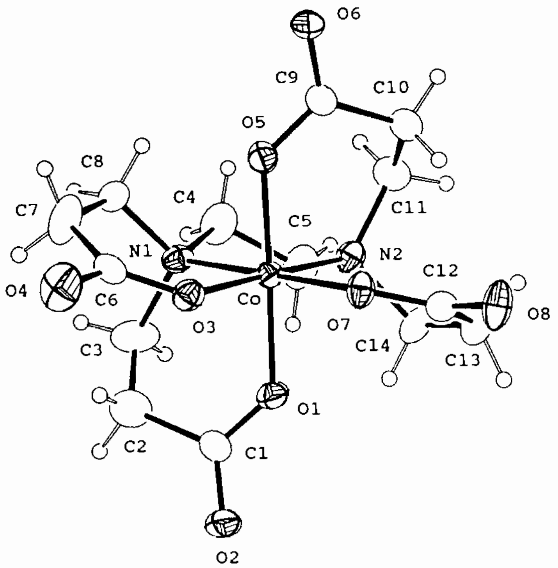

Fig. 1. Molecular structure (ORTEP) of $\Delta(\lambda\lambda)$-$[\mathrm{Co(edtp)}]^-$ in $(-)$-$(+)_{589}$-$\mathrm{Li[Co(edtp)]\cdot 3H_2O}$. The same numbering scheme is used for $[\mathrm{Cr(edtp)}]^-$.

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*The abbreviations used in earlier papers were pddda and eddda. These were changed to be consistent with systematic abbreviations.

TABLE 1. Crystal data summary for $(+)_{589}$-LiΔ(λλ)-[M(edtp)]·$3H_2O$

Formula	$C_{14}H_{26}N_2O_{11}LiCo$	$C_{14}H_{26}N_2O_{11}LiCr$
M	464.4	457.3
Space group	$P2_1$	$P2_1$
Cell type	monoclinic	monoclinic
Cell dimensions		
a (Å)	8.824(2)	8.705(1)
b (Å)	11.910(3)	11.941(2)
c (Å)	8.728(2)	9.033(1)
β	95.03(1)	94.19(1)
V (Å^3)	913.7	936.4
Z	2	2
D (g/cm^3)	1.687	1.622
Crystal size (mm)	0.20×0.10×0.36	0.23×0.25×0.37
λ (Mo Kα) (Å)	0.71073	0.71073
μ (cm^{-1})	9.968	15.38
Temperature data collection (K)	293	293
θ_{max} (°)	25	27
Scan method	$\omega/2\theta$	$\omega/2\theta$
ω-Scan speed (°/min)	0.82–3.3	1.5–3.3
ω-Scan width (°)	$(0.60+0.35 \tan \theta)$	$(1.20+0.35 \tan \theta)$
Absorption correction factors, min., max.	0.823, 0.998	
Octants data collected	h, $0 \rightarrow 10$; k, $0 \rightarrow 14$; l, $-10 \rightarrow 10$	h, $-11 \rightarrow 11$; k, $-15 \rightarrow 15$; l, $0 \rightarrow 11$
Data collected	1809	4541
Data used, $[I > 3\sigma(I)]$	1517	3912
$R = \Sigma[\lvert F_o\rvert - \lvert F_c\rvert]/\lvert F_o\rvert$	0.0406	0.042
$R_w = [\Sigma\Delta^2/\Sigma w F_o^2]^{1/2}$	0.0546	0.045
$(\Delta/\sigma)_{max}$ in last cycle	0.00	<0.1
$\Delta\rho$ in final ΔF-map (e Å^{-3})	0.672	0.70
Final p parameter in weighting scheme[a]	0.080	0.0028

[a] $w = [\sigma^2\lvert F_o\rvert + (p\lvert F_o\rvert)^2]^{-1}$.

for each of the crystals are shown in the corresponding summary tables. Scattering factors for H atoms were taken from those of Stewart *et al.* [28] and for the non-hydrogen atoms from Cromer and Mann [29], and allowance was made for anomalous dispersion [30].

Crystallographic results indicate that both crystals contain the metal edtp complexes with the Δ absolute configuration. Because ORTEP diagrams of both complexes are essentially identical, only that of the cobalt complex is shown (Fig. 1), with the same atom numbering scheme used for both complexes. For the chromium complex, refinement converged with $R = 0.042$ and $R_w = [\Sigma w\Delta 2/\Sigma w F_o^2]^{1/2} = 0.045$; the corresponding R values of the cobalt complex were determined to be 0.0406 and 0.0546, respectively. Independent and parallel rounds of calculations on the Λ enantiomer of the chromium complex gave R and R_w values of 0.052 and 0.055. Similar calculations on the Λ enantiomer of the cobalt complex gave $R = 0.0446$ and $R_w = 0.0587$. Therefore, all coordinates reported herein refer to the statistically favored Δ configurations [31]. Final difference maps were devoid of any other significant features.

Results and discussion

Crystal structures of (−)-(+)$_{589}$-LiΔ(λλ)-[Co(edtp)]·3H$_2$O (blue–violet) and (+)-(+)$_{589}$-LiΔ(λλ)-[Cr(edtp)]·3H$_2$O (red–violet)

The ORTEP diagram of Δ(λλ)-[Co(edtp)]$^-$ is shown in Fig. 1. The corresponding ORTEP diagram for the chromium complex is not shown because of its gross similarity to the cobalt complex. The same atom numbering scheme is used for both . Positional parameters and selected bond lengths and angles are listed in Tables 2–5.

One can readily see from the ORTEP diagram that the edtp^{4-} anion is hexadentate forming octahedral complexes. The highest symmetry axis of each is C_2 which bisects the N1–M–N2 bond angle making the two R rings (as well as the G rings) nearly identical. Any dissimilarity is probably due to the constraints imposed by the solid state. The main Cartesian axes (O1–M–O5, N1–M–O7 and N2–M–O3) for both complex ions are roughly equal but with those in the equatorial plane being a few percent longer (2% for the cobalt complex and 3% for the chromium) than the axis defined by the

TABLE 2. Positional parameters of $(-)$-$(+)_{589}$-LiΔ(λλ)-[Co(edtp)]·3H$_2$O

Atom	*x*	*y*	*z*
Co	0.58595(7)	0.54960[a]	0.15775(7)
O(1)	0.7140(4)	0.4457(4)	0.0651(4)
O(2)	0.9231(5)	0.3541(4)	0.0300(5)
O(3)	0.7566(4)	0.6498(4)	0.1705(4)
O(4)	0.9354(5)	0.7597(5)	0.2769(5)
O(5)	0.4739(4)	0.6674(3)	0.2395(4)
O(6)	0.2815(4)	0.7811(4)	0.2658(5)
O(7)	0.5358(4)	0.6079(3)	−0.0451(4)
O(8)	0.4174(5)	0.6247(4)	−0.2763(4)
O(9w)	0.9709(5)	0.4986(4)	−0.2595(5)
O(10w)	0.8636(5)	0.6879(4)	0.8635(5)
O(11w)	0.8293(5)	0.0952(5)	0.4801(5)
N(1)	0.6401(5)	0.4928(4)	0.3678(5)
N(2)	0.4125(5)	0.4467(4)	0.1389(5)
C(1)	0.8373(6)	0.4011(6)	0.1148(7)
C(2)	0.8885(8)	0.4199(8)	0.2839(8)
C(3)	0.7721(9)	0.4132(7)	0.3871(7)
C(4)	0.5043(7)	0.4282(6)	0.4101(7)
C(5)	0.4445(8)	0.3641(6)	0.2665(7)
C(6)	0.8265(6)	0.6941(6)	0.2862(6)
C(7)	0.7916(7)	0.6664(7)	0.4502(7)
C(8)	0.6639(6)	0.5880(5)	0.4798(6)
C(9)	0.3341(6)	0.6944(5)	0.2106(6)
C(10)	0.2337(6)	0.6173(5)	0.1091(7)
C(11)	0.2582(6)	0.4969(6)	0.1561(8)
C(12)	0.4501(6)	0.5688(5)	−0.1573(6)
C(13)	0.3756(8)	0.4543(6)	−0.1523(7)
C(14)	0.4102(7)	0.3821(5)	−0.0100(7)
Li	0.9154(10)	0.3516(9)	0.8056(12)

[a] Fixed to define the origin.

TABLE 3. Positional parameters of $(+)$-$(+)_{589}$-LiΔ(λλ)-[Cr(edtp)]·3H$_2$O

Atom	*x*	*y*	*z*
Cr	8.5035(4)	7.0300[a]	9.1090(4)
O(1)	0.7642(2)	0.5860(2)	1.0328(2)
O(2)	0.7359(3)	0.4759(2)	1.2229(2)
O(3)	1.0620(2)	0.6523(2)	0.9649(2)
O(4)	1.2859(3)	0.6340(2)	1.0895(3)
O(5)	0.9371(2)	0.8137(2)	0.7798(2)
O(6)	0.9689(2)	0.9073(2)	0.5736(2)
O(6)	0.8258(2)	0.6006(2)	0.7401(2)
O(7)	0.7121(3)	0.5021(3)	0.5576(3)
O(W1)	0.7417(3)	0.2612(2)	0.4738(3)
O(W2)	0.4798(3)	0.6671(3)	0.3351(3)
O(W3)	0.8583(3)	0.0688(2)	0.3657(3)
N(1)	0.8635(3)	0.8119(2)	1.0916(2)
N(2)	0.6300(3)	0.7677(2)	0.8578(2)
C(1)	0.7905(3)	0.5611(2)	1.1701(3)
C(2)	0.8876(4)	0.6407(2)	1.2653(3)
C(3)	0.8420(4)	0.7627(3)	1.2411(3)
C(4)	0.7364(4)	0.8932(3)	1.0570(4)
C(5)	0.5935(3)	0.8284(3)	0.9967(3)
C(6)	1.1676(3)	0,6890(2)	1.0560(3)
C(7)	1.1534(3)	0.8025(3)	1.1311(4)
C(8)	1.0123(3)	0.8743(2)	1.0921(3)
C(9)	0.8865(3)	0.8581(3)	0.6581(3)
C(10)	0.7152(4)	0.8399(4)	0.6097(4)
C(11)	0.6114(4)	0.8526(3)	0.7353(4)
C(12)	0.7052(3)	0.5634(2)	0.6660(3)
C(13)	0.5460(4)	0.6005(3)	0.6984(4)
C(14)	0.5182(3)	0.6726(3)	0.8330(3)
Li	0.8058(6)	0.4095(4)	0.4174(5)

[a] Fixed to define the origin.

trans(*O*)-coordination. Furthermore, these axes deviate only minimally from the ideal bond angle of 180° with the greatest deviation realized by the cobalt complex (O1–M–O5 = 172.7°). The [Co(edta)]$^-$ ion [1, 32] and related complexes all show an axial compression of 2–3%; apparently increasing the length of the carboxylate chain has little effect here. For the [Co(1,3-pdta)]$^-$ ion [2], increasing the size of the E ring by one carbon atom has the effect of increasing this axial compression to about 4%. The M–L, metal ion to ligating atom, distances in [Co(edta)]$^-$ are nearly the same as they are in [Co(edtp)]$^-$, but for one very important difference — the mean Co–N distance in [Co(edta)]$^-$ is shorter than the mean Co–O(equatorial) distance, 1.892 versus 1.945. The order is reversed in [Co(edtp)]$^-$ and other closely related edta-type cobalt(III) complexes [33]. Under similar conditions M–N distances are usually longer than M–O distances by a few percent. Absorption spectroscopy shows that the hexadentate edta ion imposes a stronger crystal field on the Co(III) ion than do all the other related ligands, and the shortened Co–N distance in [Co(edta)]$^-$ is assumed to be the main cause. When Cr is substituted for Co, the mean Cr–N distance is always longer than the mean Cr–O(eq) distance even for [Cr(edta)]$^-$ [33]. Hexadentate 1,3-pdta and eddadp ions with rhodium(III) show Rh–N bonds slightly shorter than Rh–O(eq) bonds similarly as in [Co(edta)]$^-$ [18, 34].

The idealized 90° octahedral bond angles vary from 86.4 to 93.9° in [Co(edtp)]$^-$ and from 86.9° to 92.9° in [Cr(edtp)]$^-$, the smallest distortions among the complexes in Table 6. The corresponding variation in [Co(edta)]$^-$ is 83.1 to 104.0° and in [Cr(cdta)]$^-$ [15] the variation is 80.9 to 112.9°. Increasing the size of the carboxylate rings allows the complexes to attain octahedral angles closer to the ideal with apparently less strain in the M–L bonds. Related Co(III) and Cr(III) complexes made with 1,3-pdta and eddadp show similar effects [2, 18, 20, 33].

The ethylenediamine ring is puckered as it usually is in these kinds of chelates, and the β-alaninate rings are in distorted boat conformations. The conformations of the axial (R) β-alaninate rings are specifically λ, which denotes the orientation of the

TABLE 4. Selected bond distances (Å) of $(+)_{589}$-LiΔ(λλ)-[M(edtp)]·3H_2O

	Co	Cr
M–O(1)	1.903(4)	1.961(2)
M–O(3)	1.917(4)	1.967(3)
M–O(5)	1.892(4)	1.962(2)
M–O(7)	1.917(4)	1.968(2)
M–N(1)	1.973(4)	2.084(2)
M–N(2)	1.956(5)	2.091(2)
O(1)–C(1)	1.254(7)	1.280(3)
O(2)–C(1)	1.238(8)	1.233(4)
O(3)–C(6)	1.253(7)	1.266(3)
O(4)–C(6)	1.247(7)	1.240(4)
O(5)–C(9)	1.278(6)	1.270(3)
O(6)–C(9)	1.246(7)	1.234(4)
O(7)–C(12)	1.272(6)	1.283(4)
O(8)–C(12)	1.246(7)	1.228(4)
N(1)–C(3)	1.500(9)	1.497(4)
N(1)–C(4)	1.497(8)	1.488(4)
N(1)–C(8)	1.500(8)	1.494(4)
N(2)–C(5)	1.494(8)	1.503(4)
N(2)–C(11)	1.506(8)	1.501(4)
N(2)–C(14)	1.509(8)	1.502(4)
C(1)–C(2)	1.522(9)	1.500(4)
C(2)–C(3)	1.426(9)	1.521(4)
C(4)–C(5)	1.522(9)	1.531(4)
C(6)–C(7)	1.526(8)	1.525(4)
C(7)–C(8)	1.504(9)	1.518(4)
C(9)–C(10)	1.508(8)	1.538(4)
C(10)–C(11)	1.502(9)	1.509(5)
C(12)–C(13)	1.516(9)	1.504(4)
C(13)–C(14)	1.519(8)	1.523(4)

β-alaninate ethylene C–C bonds with respect to the C_2 axis of the complex ion [24]. Mixed conformations can produce three conformers: Δ(λλ), *lel*$_2$; Δ(λδ), *lelob*; and Δ(δδ), *ob*$_2$. Only the most stable *lel*$_2$ forms were isolated in our work, but Kaizaki and Hayashi have reported the production and characterization of all three diastereomers of the chromium complex [35].

The equatorially coordinated β-alaninate rings (G) deviate more than the axially coordinated R rings from an ideal twist-boat conformation. These six-membered G rings have all the participating atoms very nearly co-planar except for the N atom. This means, essentially, that the three connected carbon atoms in these rings are flattened out away from the N atom; consider for example that the C(6)–C(7)–C(8) angle in the cobalt complex is 120.8°, and 119.3° in the chromium complex. This is a very large angular deviation from the ideal 109.5°. For the R rings, co-planarity is realized by all in the ring except the metal ion and the carbon atom opposed to it (as expected for a twist-boat conformation), but the carbon trinity still retains a higher than normal bond angle (mean angles of 113.4 and 113.2° for the cobalt and chromium complexes, respectively). Also, each of the carbonyl oxygen atoms of the four carboxylate rings is involved with either H-bonding (O8) to a water of crystallization or a lithium ion (O2, O4 and O6). What effects these interactions have on the conformations of the β-alaninate rings is uncertain.

Curiously, these complexes, which were synthesized to be relatively strain-free analogs of [M(edta)]$^-$, show other sources of strain that are just as significant. An M–O–C fragment of the β-alaninate rings is expected to attain a bond angle between 109.5 and 120°, depending on the degree of covalency of the M–O bond. These bond angles in the β-alaninate rings are as high as 132°, and the value is of the same order of magnitude for both kinds of rings, R or G, for both the cobalt and chromium chelates. It is tempting to conclude that this unusually high strain is the result of chelation constraints, but the corresponding edta complexes do not show anything quite like this, and furthermore, when β-alanine coordinates to metal ions, it forms rings with distorted boat conformations with the same unusually high M–O–C bond angles [36].

Table 6 contains results of a comparative study of the strain characteristics of a closely related series of cobalt(III) and related chromium(III) chelates made with hexadentate ligands. We consider the major contributions to strain for these complexes to be: (i) the octahedral angles around the central ion, (ii) the ring angle sums of the various kinds of rings, (iii) the M–O–C bond angles, (iv) the bond angles that the chelating nitrogen atom makes with its connectors.

A metal ion's immediate environment has the greatest effect on its chiroptical properties. The impetus, after all, for studies such as this one, is to reconcile molecular structure in a regular way to these chiroptical properties which usually means trying to understand variations in circular dichroism spectra. Several theories [38, 39] relate strain and rotatory strength, and the deviation from cubic symmetry becomes a major consideration. From the list in Table 6 we see that expanding the E ring and/or the glycinate ring lowers the octahedral strain. The octahedral distortion for the edtp complexes is less than for other edta-type complexes. The results are mixed, however, when a chromium ion is substituted for a cobalt ion. One expects for the complexes of edta and pdta that the octahedral strain should increase because the chromium ion is slightly larger than the cobalt ion. When edtp^{4-} is used, however, the chromium complex shows less strain

TABLE 5. Selected bond angles (°) of $(+)_{589}$-LiΔ(λλ)-[M(edtp)]·$3H_2O$

	Co	Cr		Co	Cr
O(1)–M–O(3)	86.4(2)	91.8(1)	M–N(2)–C(14)	110.1(4)	109.2(2)
O(1)–M–O(5)	172.7(2)	176.7(1)	C(5)–N(2)–C(11)	107.5(5)	105.8(2)
O(1)–M–O(7)	86.6(2)	88.5(1)	C(5)–N(2)–C(14)	107.1(5)	108.3(2)
O(1)–M–N(1)	93.9(2)	90.4(1)	C(11)–N(2)–C(14)	110.1(4)	111.6(2)
O(1)–M–N(2)	92.6(2)	90.6(1)	O(1)–C(1)–O(2)	122.9(5)	121.3(3)
O(3)–M–O(5)	87.1(2)	87.8(1)	O(1)–C(1)–C(2)	116.6(6)	117.5(2)
O(3)–M–O(7)	86.8(2)	92.8(1)	O(2)–C(1)–C(2)	120.1(5)	121.2(2)
O(3)–M–N(1)	92.0(2)	90.0(1)	C(1)–C(2)–C(3)	115.8(6)	113.2(2)
O(3)–M–N(2)	178.5(2)	176.2(1)	N(1)–C(3)–C(2)	119.2(6)	117.2(3)
O(5)–M–O(7)	89.6(2)	88.3(1)	N(1)–C(4)–C(5)	106.4(5)	108.6(2)
O(5)–M–N(1)	89.8(2)	92.9(1)	N(2)–C(5)–C(4)	108.2(5)	108.9(2)
O(5)–M–N(2)	93.8(2)	90.0(1)	O(3)–C(6)–O(4)	122.6(5)	121.7(3)
O(7)–M–N(1)	178.7(2)	176.9(1)	O(3)–C(6)–C(7)	122.7(5)	121.2(2)
O(7)–M–N(2)	91.9(2)	90.3(1)	O(4)–C(6)–C(7)	114.6(5)	117.1(2)
N(1)–M–N(2)	89.3(2)	86.9(1)	C(6)–C(7)–C(8)	120.8(5)	119.3(2)
M–O(1)–C(1)	131.1(4)	131.3(2)	N(1)–C(8)–C(7)	114.9(5)	113.9(2)
M–O(3)–C(6)	129.6(4)	132.6(2)	O(5)–C(9)–O(6)	121.1(5)	123.6(3)
M–O(5)–C(9)	129.7(4)	132.8(2)	O(5)–C(9)–C(10)	118.0(5)	117.1(3)
M–O(7)–C(12)	130.7(4)	131.4(2)	O(6)–C(9)–C(10)	120.8(5)	119.1(2)
M–N(1)–C(3)	116.4(4)	117.3(2)	C(9)–C(10)–C(11)	111.0(5)	113.1(3)
M–N(1)–C(4)	105.8(3)	104.2(2)	N(2)–C(11)–C(10)	117.5(5)	116.6(3)
M–N(1)–C(8)	110.8(3)	108.1(2)	O(7)–C(12)–O(8)	121.6(6)	122.5(3)
C(3)–N(1)–C(4)	106.1(5)	107.8(2)	O(7)–C(12)–C(13)	122.5(5)	121.8(2)
C(3)–N(1)–C(8)	110.0(4)	111.0(2)	O(8)–C(12)–C(13)	115.8(5)	115.5(3)
C(4)–N(1)–C(8)	107.2(4)	107.9(2)	C(12)–C(13)–C(14)	118.4(5)	121.6(3)
M–N(2)–C(5)	104.8(3)	103.5(2)	N(2)–C(14)–C(13)	113.8(5)	114.0(2)
M–N(2)–C(11)	116.8(4)	117.8(2)			

TABLE 6. Strain analysis of edta-type chelates of Co(III) and Cr(III)

Complex	ΣΔ[a]	ΔΣ[b, c, d]			Δ{M–O–C}[e, f]		ΣΔ[g]	Reference
	O_h	E	R	G	R	G	N	
$[Co(edta)]^-$	52	−7	−1	−15	+4	+3	15	1, 32
$[Co(eddadp)]^-$[h]	31	−11	−1	+38	+6	+18	13	33
$[Cr(eddadp)]^-$[h]	37	−15	−1	+37	+8	+21	16	20
$[Co(edtp)]^-$	29	−14	+42	+41	+21	+21	18	this work
$[Cr(edtp)]^-$	17	−16	+39	+39	+23	+23	22	this work
$[Co(1,3\text{-}pdta)]^-$	34	+36	+1	−12	+6	+5	15	2
$[Cr(1,3\text{-}pdta)]^-$	56	+35	+1	−10	+9	+7	14	18
$[Co(1,3\text{-}pddadp)]^-$[i]	38	+28	+33	−11	+17	+4	16	37
$[Cr(1,3\text{-}pddadp)]^-$[i]	42	+26	+33	−11	+19	+5	16	19

[a] ΣΔ(O_h) is the sum of the absolute values of the deviations from 90° of the L–M–L′ bite angles. All values rounded off to the nearest degree. [b] ΔΣ(E) is the deviation of the ethylenediamine or 1,3-propanediamine rings' bond angle sum from the ideal; 528° for the former and 637.5° for the latter. [c] ΔΣ(R) is the deviation from the ideal of the axial chelate rings'bond angle sum, 648° for a six-membered ring and 538.5° for a five. A mean value for the two rings is reported because the molecule is expected to have C_2 symmetry. [d] ΔΣ(G) is the deviation from the ideal of the axial chelate rings' bond angle sum, 648° for a six-membered ring and 538.5° for a five. [e] Δ{M–O–C}(R) is the mean value of the deviation of the R rings' M–O–C bond angle from 109.5°. Theoretically, this angle can vary from 109.5 to 120° depending on the degree of covalency of the M–O bond. [f] Δ{M–O–C}(G) is the mean value of the deviation of the G rings' M–O–C bond angle from 109.5°. [g] ΣΔ(N) is the sum of the absolute values of the six bond angles made by the chelate nitrogen atoms. A mean value for the two nitrogens is reported. [h] The *trans*(O_5)-isomer with glycinate rings coordinated axially. [i] The *trans*(O_6)-isomer with glycinate rings coordinated equatorially.

than the cobalt. We should point out, also, that a total deviation of 17° (for the [Cr(edtp)]$^-$ complex) indicates that the complex is relatively free of much octahedral angle strain because the mean angular deviation is only a little more than one degree per angle. We consider angular deviations to be significant only when they begin to approach 4°.

Table 6 shows further that replacing glycinate rings with β-alaninate rings increases the strain in the E ring. When the E ring is expanded by one carbon atom without replacing glycinates, the strain in this ring actually increases but in the opposite direction. For example, the E ring in [Cr(edta)]$^-$ shows a negative total deviation of 7°, but in [Co(1,3-pdta)]$^-$, the deviation is positive and 36°. Therefore, in the latter, the mean angular deviation in the ring made by the chelating nitrogens is actually larger (~6°/angle versus 1.4°/angle).

The strain in the β-alaninate rings in the edtp complexes are about the same regardless of ion or ring type, ~6–7°/angle, and as pointed out earlier, the main causes of strain are due to the M–O–C and C–C–C bond angles. There is little difference between the R and G rings because the M–N–C angle deviates minimally in the G ring when the C–C–C angle deviates more severely and vice versa for the R ring. These results suggest that strain in the chelate rings of the edtp complexes is actually greater than that measured for the corresponding edta complexes, at least for cobalt(III) and chromium(III).

Another important source of strain in edta-type complexes is the bonding geometry made by the chelating nitrogens. Halloran *et al.* [40] concluded that G ring strain in hexadentate edta-type complexes arises when the effect of chelation distorts the tetrahedral bonding geometry of the nitrogen atoms. Each N atom makes four bonds with six ideally 109.5° bond angles. In [Co(edtp)]$^-$ for example, the Co–N–C(R) mean bond angle is 116.4°, a deviation of nearly 7°. When each of the deviations is summed for the six angles, the total for this complex ion is 18°. Notice from Table 6 that the strain about the N atoms in [Co(edtp)]$^-$ is greater than that in [Co(edta)]$^-$. The greatest deviation about the N atoms in all the edta-type complexes in Table 6 is not consistently and specifically due to any one of the six bond angles. For example, in [Co(edta)]$^-$, the greatest deviation is realized for the C(G)–N–C(E) fragment, and in [Cr(edtp)]$^-$, two bond angles, Cr–N–C(R) and Cr–N–C(E), show very large deviations. These angles with their corresponding deviations are 117.6° (+8°) and 103.9° (−6°), respectively. The total deviation about the chelating N atoms in this Cr complex sums to roughly 20° and indicates that compared to the other complexes listed in Table 6, it contains N atoms with the most highly strained bonds.

It is now well known that hexadentate edta complexes are susceptible to substitution reactions in which certain monodentate ligands can displace a G glycinate ring. Recently, Kaizaki and Hayashi [35] reported that when *lelob*- or *ob*$_2$-[Cr(edtp)]$^-$ is heated in aqueous solution for 24 h at 60 °C, a neutral complex with ethylenediamine-*N*,*N*,*N*′-tri-3-propionate was obtained along with 3-hydroxypropionate as a major product. These results indicate a rather facile hydrolytic thermolysis of a C–N bond in a β-alaninate ring which could be indicative of an intrinsically weak and relatively highly strained N–C(R) bond as our crystallographic results show rather unequivocally.

Correlation of absolute configurations with circular dichroism spectra

Although there has been debate concerning whether in [Cr(edta)]$^-$ the edta is hexadentate in solution, hexadentate coordination of edta in the solid has been verified [14]. The edta-type ligands forming six-membered chelate rings are hexadentate in the case of 1,3-pdta [16], tdta [17], *S*,*S*-ptnta [22], *S*,*S*-edds [21], eddadp [20], 1,3-pddadp [19], eda3p [24] and edtp [23]. The complexes $(+)_{589}$-*trans*(O_5)-[Cr(*S*,*S*-edds)]$^-$, $(-)_{589}$-*trans*-(O_5)-[Cr(eddadp)]$^-$ and $(-)_{589}$-*trans*(O_5O_6)-[Cr(eda3p)]$^-$ give very similar CD spectra in the region of the $A_{2g}\rightarrow T_{2g}(O_h)$ absorption band. Each of these complexes has a positive CD peak at the lower energy extremity of the absorption band and an intense negative CD peak near the energy of the maximum of the absorption band. The complexes have been assigned the Λ configuration as required by the stereospecific *S*,*S*-edds ligand and confirmed by X-ray crystallography [20] for $(-)_{589}$-*trans*(O_5)-[Cr(eddadp)]$^-$. The CD spectrum of $(+)_{589}$-[Cr(*S*,*S*-ptnta)]$^-$ differs substantially from these others, but the lowest energy CD positive peak was assigned as $^4B(C_2)$ with $^4E(^4T_{2g})$ of either trigonal or tetragonal parentage [22]. On this basis the Λ configuration was assigned. The CD spectrum of $(+)_{589}$-[Cr(edtp)]$^-$ differs from the others in that it lacks a low energy peak near the extremity of the absorption maximum. This CD peak is assumed to be masked (effectively cancelled) by the intense positive peak near the absorption maximum. The $(+)_{589}$-[Cr(edtp)]$^-$ ion was assigned the Δ configuration because its dominant positive CD band of $A_{2g}\rightarrow T_{2g}(O_h)$ parentage is opposite compared to those similar complexes which have been shown to have the Λ configuration [23]. This Δ assignment for $(+)_{589}$-[Cr(edtp)]$^-$ is confirmed by the X-ray structure now reported. Kaizaki and Hayashi [35] reported the CD spectrum of *Λ*-[Cr(*S*-pdtp)]$^-$ (*S*-pdtp = 1,2-propanediamine-*N*,*N*,*N*′,*N*′-tetra-3-propionate ion) that is, as expected, nearly the mirror image of the CD spectrum of Δ-[Cr(edtp)]$^-$ [23].

The CD and absorption spectral data are summarized for [Co(edta)]$^-$-type complexes in Table 7. Absolute configurations have been determined by X-ray methods for $(+)_{546}$-KΔ-[Co(edta)] [1], $(-)_{546}$-K*Λ*-[Co(1,3-pdta)] [2], $(+)_{589}$-strychnine*Λ*-[Co(dhpta)] [5] (dhpta = 2-hydroxy-1,3-propanediamine-*N*,*N*,*N*′,*N*′-tetraacetate ion), and in this report $(+)_{589}$-LiΔ-[Co(edtp)]. The *Λ* configuration is assigned to these isomers that exhibit two well-defined CD peaks in the region of the first absorption band with the lowest energy CD peak positive and the next peak negative. The complexes $(+)_{546}$-K[Co(eda3p)] [7], $(+)$-$(-)_{589}$-Ag*trans*(O_5)-[Co(eddadp)] and $(+)$-$(-)_{589}$-Ag*trans*(O_5O_6)-[Co(eddadp)] [41], and $(+)$-Ag[Co(xdta)] [42] (xdta = xylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate ion) have CD spectra with the (+, −) sign pattern and such close similarity to one of the compounds of known configurations that these have been assigned *Λ* configurations. This crystallographic report for $(-)$-$(+)_{589}$-[Co(edtp)]$^-$ supports these assignments. The complex ions $(+)$-$(-)_{546}$-*Λ*-[Co{$(+)_{589}$-1,2-pdta}]$^-$ (1,2-pdta = 1,2-propanediamine-*N*,*N*,*N*′,*N*′-tetraacetate ion) [43], $(+)$-$(-)_{546}$-*Λ*-[Co{$(+)_{589}$-cdta}]$^-$ [44], and $(+)$-*Λ*-[Co{$(-)_{589}$-L-sdta}]$^-$ (sdta = stilbenediamine-*N*,*N*,*N*′,*N*′-tetraacetate ion) [42] are formed stereospecifically. These complexes give the now familiar (+, −) CD pattern for the lowest energy absorption band for the complexes with the *Λ* configuration (Table 7). The relative intensities of the CD peaks vary so the dominant CD peak and net sign are positive for $(-)_{546}$-*Λ*-[Co(edta)]$^-$, but these are negative for all the other *Λ* complexes cited. Variations in relative intensities

TABLE 7. Absorption (AB) and circular dichroism (CD) data for [Co(edta)]$^-$ and related hexadentate complexes

Complex	AB		CD		Reference
	$\tilde{\nu}$ (10^3 cm^{-1})	ϵ	$\tilde{\nu}$ (10^3 cm^{-1})	$\Delta\epsilon$	
$(+)$-$(-)_{546}$-K*Λ*-[Co(edta)]·$2H_2O$	18.63	347	17.10	+1.50	46
			19.80	−0.69	
	26.04	246	23.80	+0.28	
			25.60	−0.09	
			27.60	+0.29	
$(+)$-$(-)_{546}$-Ba*Λ*-[Co{$(+)_{589}$-1,2-pdta}]$_2$·$8H_2O$[a]	18.60	300	17.23	+1.58	43, 44
			19.70	−0.76	
	26.65	204	24.15	+0.32	
			26.00	−0.18	
			27.95	+0.34	
$(+)$-$(-)_{546}$-Na*Λ*-[Co(1,3-pdta)]·$3H_2O$	18.20	131	17.0	+1.91	6
			19.0	−2.41	
	26.40	115	24.6	+0.69	
$(+)$-$(-)_{589}$Ag*Λ*-*trans*(O_5)-[Co(eddadp)]·$2H_2O$	18.50	342	16.20	+0.40	41
			18.30	−2.78	
	25.70	186	24.20	+0.29	
			26.30	+0.36	
$(+)$-$(-)_{589}$Ag*Λ*-*trans*(O_5O_6)-[Co(eddadp)]·$3H_2O$	18.60	253	16.50	+2.25	41
			18.40	−3.12	
	25.80	142	24.40	+0.31	
			26.60	+0.56	
$(+)$-$(+)_{546}$K*Λ*-*trans*(O_5O_6)-[Co(eda3p)]·$3H_2O$	18.25	318	16.05	+0.90	7
			18.08	−3.18	
	25.19	147	23.81	+0.43	
			26.04	+0.58	
$(+)$-$(+)_{546}$-Li*Λ*-[Co(edtp)]·$3H_2O$	18.00	253	15.77	+1.05	7
			17.57	−3.68	
	24.80	110	23.30	+0.10	
			26.30	+0.20	

[a] The values of ϵ and $\Delta\epsilon$ were divided by two for comparison on a per molar complex ion basis.

of the CD peaks are not surprising with changes in strain resulting from ring size and various microsymmetries among the complexes of the group.

The S,S-edds and the S-eddams (eddams = S-ethylenediamine-N,N-diacetate-N′-succinate ion) ligands produce cobalt(III) complexes stereospecifically with the Λ configuration. Their complexes are closely related to the Λ-[Co(edta)]$^-$ ion [45], but have slightly different CD spectra from those of other edta-type complexes. The usual CD pattern has two-peaks (+, −) for the lowest energy absorption band, but Λ-[Co(S,S-edds)]$^-$ shows a three-peak (+, −, +) pattern, and Λ-[Co(S-eddams)]$^-$ shows only one negative peak for the lowest energy absorption band. A significant difference between the two types of complexes has to do with the branching of chelate rings. The chelate ring branching occurs on one octahedral face for [Co(eddams)]$^-$ and on two faces for [Co(S,S-edds)]$^-$. For the other edta-type complexes, the chelate rings branch at vertices and span the octahedral edges. Thus the molecular basis for defining chirality could be different for these two complexes.

The complex [Co(en)(mal)$_2$]$^-$ (mal = malonate ion) was prepared as a *cis*-[CoN$_2$O$_4$] strain-free model of [Co(edta)]$^-$ [46]. (−)$_{546}$-K[Co(en)(mal)$_2$] was assigned as Λ, and confirmed by crystallography [47]. Its CD spectrum shows a three-peak (+, −, +) pattern for the lower energy absorption band similar to the CD spectrum exhibited by the Λ-[Co(S,S-edds)]$^-$ complex. The symmetry is C_2 for [Co(en)(mal)$_2$]$^-$ and [Co(edta)]$^-$, and the chelate rings span the octahedral edges. But if the diamine chelate ring is disposed the same in the two complexes, the malonate ions span edges not spanned in [Co(edta)]$^-$. Thus the complexes share the same Λ designation, but they differ in the basis for chirality.

Figure 2 shows the absorption and CD spectra for (+)-Λ-[Co(edta)]$^-$, (+)-Λ-[Co(edtp)]$^-$ and (+)-Λ-*trans*(O_5O_6)-[Co(eda3p)]$^-$, and in Fig. 3 the spectra are compared for (+)-Λ-[Co(edta)]$^-$, (+)-Λ-[Co(1,3-pdta)]$^-$, (+)-Λ-*trans*(O_5)-[Co(eddadp)]$^-$ and (+)-Λ-*trans*(O_5O_6)-[Co(eddadp)]$^-$. For (+)-Λ-[Co(edta)]$^-$ and (+)-Λ-[Co(1,3-pdta)]$^-$ (Table 7), the first positive CD peak is at lower energy than that of the absorption maximum, and the second (negative) CD peak is at higher energy than that of ϵ_{max}. The CD spectra are very similar for the complexes involving propionate arms, (+)-Λ-[Co(edtp)]$^-$, (+)-Λ-*trans*(O_5O_6)-[Co(eda3p)]$^-$, and the two geometrical isomers of (+)-Λ-[Co(eddadp)]$^-$. For each of these complexes, the two lower energy CD peaks have energies lower than any defined by ϵ_{max}. The highest symmetry of any of the complexes is C_2, and the degeneracies are removed completely for spin-allowed transitions ($^1A_{1g} \rightarrow {}^1T_{1g}$, $^1T_{2g}$). For all of the complexes in Table 7, only two well-defined CD peaks are evident in the first absorption region and only [Co(edta)]$^-$ and [Co(1,2-pdta)]$^-$ show three distinct CD peaks in the T_{2g} absorption band region. Although it is possible that different combinations of components of $^1A_{1g} \rightarrow {}^1T_{1g}$ appear for the pattern for [Co(edta)]$^-$ (and the complexes with only acetate arms), and for [Co(edtp)]$^-$ (and the complexes with two or more

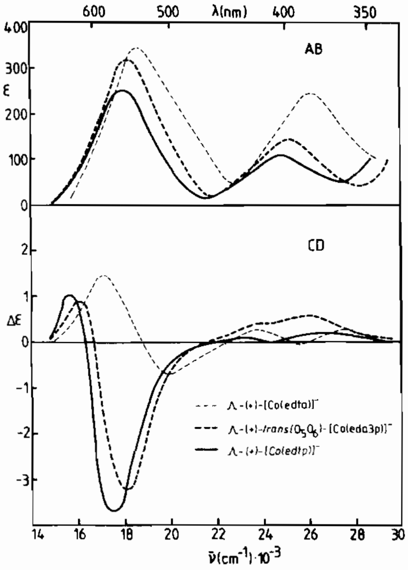

Fig. 2. Electronic absorption and CD spectra of (+)-Λ-[Co(edta)]$^-$, (+)-Λ-[Co(edtp)]$^-$ and (+)-Λ-*trans*(O_5O_6)-[Co(eda3p)]$^-$.

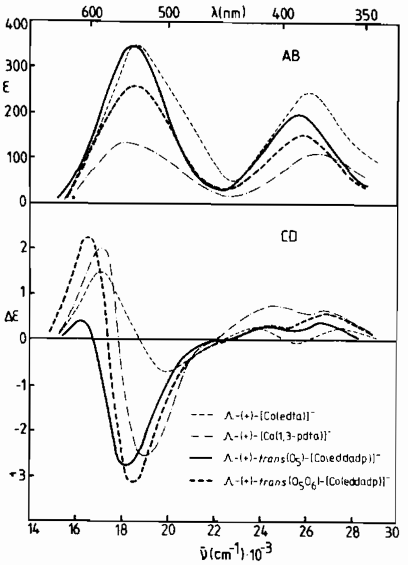

Fig. 3. Electronic absorption and CD spectra of (+)-Λ-[Co(edta)]$^-$, (+)-Λ-[Co(1,3-pdta)]$^-$, and the *trans*(O_5) and *trans*(O_5O_6) geometrical isomers of (+)-Λ-[Co(eddadp)]$^-$.

propionate arms), the Λ configuration is well established with the $(+, -)$ sign pattern for the entire series.

Supplementary material

Tables are available from the authors giving thermal parameters, H atom coordinates, least-square planes, and those listing observed and calculated structure factors.

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