

Coordination chemistry of hexadentate EDTA-type ligands with M(III) ions*

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ABSTRACT

In recent years, many edta-type ligands have been prepared and used to form hexadentate complexes with Co(III), Cr(III), and Rh(III). Absolute configurations have been determined by X-ray crystallography for representative complexes, substantiating assignments based on circular dichroism (CD) spectra. Within the first absorption band, the CD patterns for Co(III) complexes differ in energies of CD peaks relative to the absorption maximum, depending on the combinations of acetate and propionate arms. The overall pattern suggests that different combinations of three transitions usually appear. Some enlargement of chelate rings intended to relieve strain has been found to introduce other strain. Unexpected C–N bond cleavage for Cr(III) complexes of edta-type ligands with propionate arms led to the identification of conformational isomers.

1. INTRODUCTION

This is a review of studies of coordination chemistry of transition M(III) complexes with hexadentate aminopolycarboxylate edta-type (edta = ethylenediami-

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netetraacetate ion) ligands. It emphasizes work with cobalt(III) and chromium(III) in the period since a more comprehensive review [1]. There have been significant advances in structural data and in determining absolute configurations from X-ray crystallography. The ligands reviewed include edta-type ligands involving (a) structural changes in the diamine ring, (b) structural changes in carboxylate arms, and (c) a six-membered diamine ring with structural changes in carboxylate arms. Structural information for these complexes provide understanding of the influence of ligand configuration and conformation, and metal ion size on geometry and contributions to optical activity. The cobalt(III) complexes serve as models for complexes with other metal(III) ions. The complexes reviewed are of interest as possible simple structural models of active sites of metalloproteins [2–4].

Structures of the basic edta-type ligands are shown in Fig. 1. The edta is a hexadentate ligand in the complex $[\text{Co}(\text{edta})]^-$. Isomerism is possible for complexes of the hexadentate ligands where the carboxylate arms form non-equivalent chelate rings. The unsymmetrical ligands, such as ethylenediamine-*N,N'*-triacetate-*N'*-3-propionate (ed3ap) and ethylenediamine-*N*-acetate-*N,N',N'*-tri-3-propionate (eda3p)

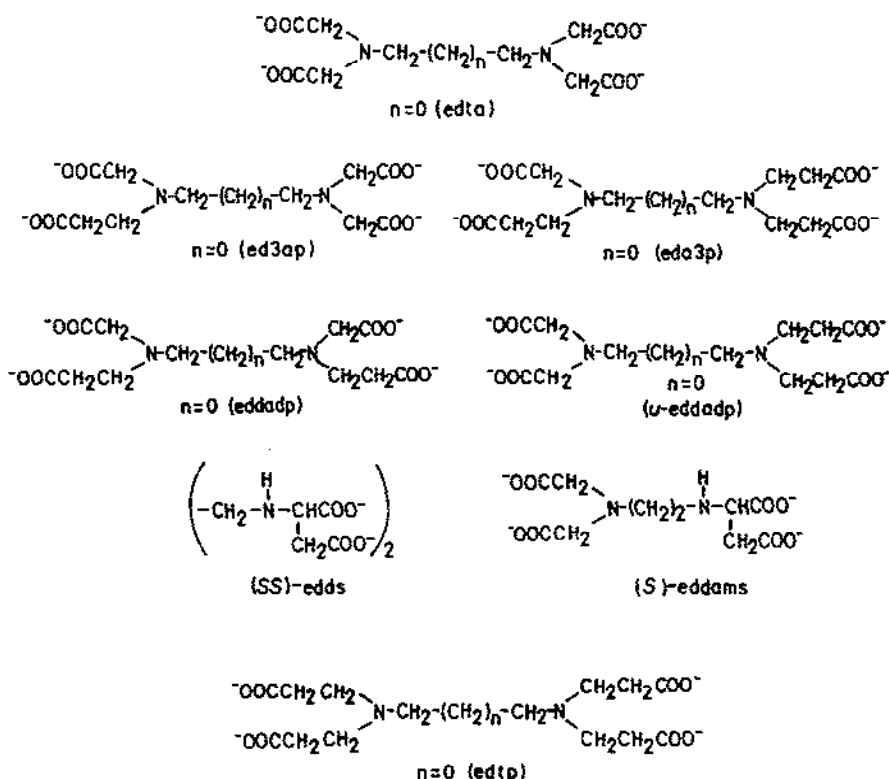


Fig. 1. Structures of the basic ligands.

ions on hexadentate coordination, form two geometrical isomers differing in the position of oxygen donors of six-membered rings: *trans*(O₅) (I) and *trans*(O₅O₆) (II) in the case of ed3ap [Fig. 2(a)] or *trans*(O₅O₆) (I) and *trans*(O₆) (II) in the case of eda3p [Fig. 2(b)]. The symmetrical ligands, structurally similar to edta having two longer carboxylate chains, such as (SS)-edds (*S,S*-ethylenediamine-*N,N'*-disuccinate ion) and eddarp (ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate ion) form isomers differing in the number of six-membered rings in the girdle plane. The optically active (SS)-edds ligand could, in principle, form two isomers, *trans*(O₅) (I) and *trans*(O₆) (II) having opposite absolute configurations about M(III) [Fig. 2(c)]. In the case of the coordinated ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate ion (eddarp) and 1,3-propanediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate ion (1,3-

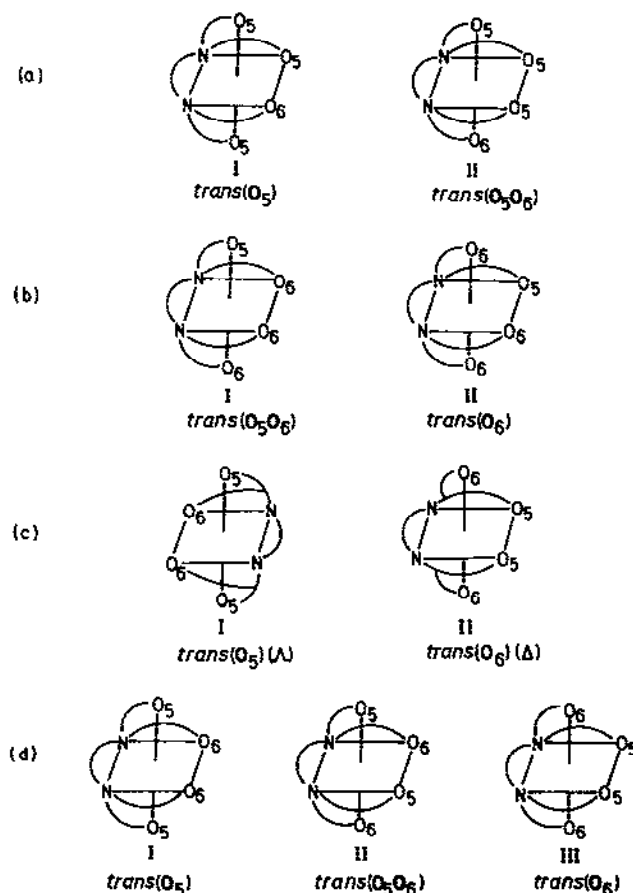


Fig. 2. Geometrical isomerism of six-coordinate complexes with hexadentate edta-type ligands.

pdadp), three isomers, differing in the number of six-membered rings in the girdle plane are possible: *trans*(O₅) (I), *trans*(O₅O₆) (II), and *trans*(O₆) (III) [Fig. 2(d)].

2. STRUCTURAL PARAMETERS IN RELATION TO STEREOCHEMISTRY

The multidentate ligands discussed in this review (Table 1) are all of the amino-polycarboxylate edta-type with N₂O₄ donor atoms. The most extensively studied ligands are those given as basic ligands (Fig. 1), and work with other ligands can be related to these studies.

Factors determining the structural types of M(III)-edta complexes include the d-electron configuration and the size of the central metal ion M[Co(III) < Cr(III) < Fe(III) < Rh(III)]. These influence differences in bond lengths (M–N and M–O), ring strain, and the ligand configuration [5–11].

Bonding parameters that greatly influence the coordination number (C.N.) of metal ions in edta and edta-type complexes have been discussed by Yamamoto et al. [5]. The radius of Fe(III) (≈ 0.79 Å) is the “critical” radius for determining the C.N. with edta-type ligands. When the ionic radius of the metal ion, with other than d⁰, d⁵, or d¹⁰ configurations, exceeds that of Fe(III), a C.N. 6 is preferred by ligand field stabilization, but edta cannot span the large ion as a hexadentate ligand. The complex is expected to contain pentadentate edta with water occupying the sixth position and one carboxylate ion not coordinated. Cr(III) (radius 0.76 Å) forms [Cr(Hedta)H₂O] [3,12] and hexadentate [Cr(edta)][−], [Cr(edtp)][−], [Cr(S)-pdta][−], and [Cr(S,S)-cdta][−] in solution [13,14], but hexadentate solid Li[Cr(edta)] [9,15] is well established. When the ionic radius of M, with d⁰, d⁵, or d¹⁰ configurations, exceeds 0.79 Å, the C.N. 6 is not imposed and its C.N. with edta can be expected to increase to 7 or 8. The edta complex of Fe(III) adopts a seven-coordinate structure with the seventh site occupied by H₂O [16]. The formation of the seven-coordinate complex suggests that the rings of edta are too small to surround the Fe(III) ion in an octahedral arrangement. A six-coordinate structure with Fe(III) has been reported under not well-established conditions [17,18]. Ligands with larger chelate rings (1,3-pdta or eddadp) form octahedral six-coordinate complexes with Fe(III) [5].

The low-spin Co(III) ion with an ionic radius of 0.69 Å forms an octahedral hexadentate complex with edta [19,20]. In [Co(edta)][−] the ethylenediamine (E) ring and two of the glycinate rings (G) are in the equatorial or girdle plane. The other two glycinate rings coordinate axially and are referred to as the out-of-plane or R rings. The G rings of [Co(edta)][−] are more strained than the E or R rings. Another ligand displaces a G ring more easily than an R ring [3].

X-ray structural studies have been reported for very closely related hexadentate edta-type M(III) complexes*. These are [Cr(edta)][−] [9,15], [Cr(cdta)][−] [21], [Fe(1,3-

* See Table 1 for ligands identified here by abbreviations. The currently used abbreviation is given along with some used earlier. Extensions of early abbreviations became awkward, so more systematic abbreviations have been used recently. In several cases, new systematic abbreviations are suggested in Table 1.

TABLE I

Hexadentate edta-type and structurally related ligands

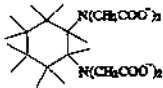
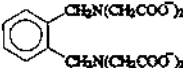
Ligand	Abbreviation
Ethylenediaminetetraacetate $(^-OOCCH_2)_2NC_2H_4N(CH_2COO^-)_2$	edta
1,2-Propanediaminetetraacetate (propylenediaminetetraacetate) $(^-OOCCH_2)_2NCH(CH_3)CH_2N(CH_2COO^-)_2$	pdta
meso-2,3-Butanediaminetetraacetate $(^-OOCCH_2)_2NCH(CH_3)CH(CH_3)N(CH_2COO^-)_2$	bdta
trans-1,2-Cyclohexanediaminetetraacetate	cdta
	
1,2-Diphenyl-1,2-ethanediaminetetraacetate (stilbenediaminetetraacetate) $(^-OOCCH_2)_2NCH(C_6H_5)CH(C_6H_5)N(CH_2COO^-)_2$	sdta
α, α' -Diamino-o-xylenetetraacetate (xylylenediaminetetraacetate)	xdtta
	
Ethylenediamine-N,N,N'-triacetate-N'-3-propionate $(^-OOCCH_2)_2NC_2H_4N(C_2H_4COO^-)(CH_2COO^-)$	ed3ap
Ethylenediamine-N-diacetate-N'-di-3-propionate $(^-OOCCH_2)_2NC_2H_4N(C_2H_4COO^-)_2$	u-eddadp
Ethylenediamine-N,N'-diacetate-N,N'-di-3-propionate $(^-OOCCH_2)(^-OOCCH_2)NC_2H_4N(C_2H_4COO^-)(CH_2COO^-)$	edddap (eddda)
Ethylenediamine-N-acetate-N,N',N'-tri-3-propionate $(^-OOCCH_2)(^-OOCCH_2)NC_2H_4N(C_2H_4COO^-)_2$	eda3p
Ethylenediamine-tetra-3-propionate $(^-OOCCH_2)_2NC_2H_4N(C_2H_4COO^-)_2$	edtp
1,2-Propanediamine-tetra-3-propionate $(^-OOCCH_2)_2NCH(CH_3)CH_2N(C_2H_4COO^-)_2$	S-pdtp
trans-1,2-Cyclohexanediaminetetrapropionate $(^-OOCCH_2)_2NC_6H_{10}N(C_2H_4COO^-)_2$	cdtp (S,S-cydt)
Ethylenediamine-N,N'-disuccinate $[^-OOC(^-OOCCH_2)CH]NHC_2H_4NH[CH(CH_2COO^-)COO^-]$	SS-edds
N-Methylethylenediamine-N,N'-disuccinate $[^-OOC(^-OOCCH_2)CH]N(CH_3)C_2H_4NH[CH(CH_2COO^-)COO^-]$	medds
N,N'-Dimethylethylenediamine-N,N'-disuccinate $[^-OOC(^-OOCCH_2)CH]N(CH_3)C_2H_4(CH_3)N[CH(CH_2COO^-)COO^-]$	dmedds
Ethylenediamine-N,N'-diacetate-N'-monosuccinate $(^-OOCCH_2)_2NC_2H_4NH[CH(CH_2COO^-)COO^-]$	eddams
1,3-Propanediaminetetraacetate (trimethylenediaminetetraacetate) $(^-OOCCH_2)_2NC_3H_6N(CH_2COO^-)_2$	1,3-pdta (trdta)
1,3-Butanediaminetetraacetate $(^-OOCCH_2)_2NC_2H_4CH(CH_3)N(CH_2COO^-)_2$	1,3-mpdta (suggest 1,3-bdta)

TABLE 1 (continued)

Ligand	Abbreviation
2,4-Pentanediaminetetraacetate ($^- \text{OOCCH}_2)_2 \text{NCH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)\text{N}(\text{CH}_2\text{COO}^-)_2$	2,4-ptnta
2-Hydroxy-1,3-propanediaminetetraacetate ($^- \text{OOCCH}_2)_2 \text{NCH}_2\text{CH}(\text{OH})\text{CH}_2\text{N}(\text{CH}_2\text{COO}^-)_2$	dhpta (suggest hpdta)
1,3-Propanediamine- <i>N,N,N'</i> -triacetate- <i>N'</i> -3-propionate ($^- \text{OOCCH}_2)_2 \text{NC}_3\text{H}_6\text{N}(\text{C}_2\text{H}_4\text{COO}^-)(\text{CH}_2\text{COO}^-)$	1,3-pd3ap
1,3-Propanediamine- <i>N,N'</i> -diacetate- <i>N,N'</i> -di-3-propionate ($^- \text{OOCCH}_2)(^- \text{OOCCH}_2)\text{NC}_3\text{H}_6\text{N}(\text{C}_2\text{H}_4\text{COO}^-)(\text{CH}_2\text{COO}^-)$	1,3-pddadp
<i>cis</i> -2-Butene-1,4-diaminetetraacetate ($^- \text{OOCCH}_2)_2 \text{NCH}_2\text{CH}=\text{CHCH}_2\text{N}(\text{CH}_2\text{COO}^-)_2$	dcbita
1,4-Butanediaminetetraacetate (tetramethylenediaminetetraacetate) ($^- \text{OOCCH}_2)_2 \text{NC}_4\text{H}_8\text{N}(\text{CH}_2\text{COO}^-)_2$	tdta (suggest 1,4-bdta)
1,5-Pentanediaminetetraacetate (pentamethylenediaminetetraacetate) ($^- \text{OOCCH}_2)_2 \text{NC}_5\text{H}_{10}\text{N}(\text{CH}_2\text{COO}^-)_2$	1,5-ptnta (pmdta) (suggest 1,5-pdta)
1,6-Hexanediaminetetraacetate (hexamethylenediaminetetraacetate) ($^- \text{OOCCH}_2)_2 \text{NC}_6\text{H}_{12}\text{N}(\text{CH}_2\text{COO}^-)_2$	hdta

pdta)]⁻ [5], [Rh(1,3-pdta)]⁻ [22], [Co(1,3-dhpta)]⁻ [23], *trans*(O₅)-[Co(SS)-edds]⁻ [24], *trans*(O₅)-[Fe(eddadp)]⁻ [5], *trans*(O₅)-[Rh(eddadp)]⁻ [25], and those cited in Table 2.

Table 2 contains results of a comparative study of the strain characteristics of a closely related series of Co(III) and related Cr(III) chelates made with hexadentate ligands [11]. Indications of strain for these complexes were considered as:

- (a) the octahedral angles around the central ion,
- (b) the ring angle sums of the various kinds of ring,
- (c) the M–O–C bond angles, and
- (d) the bond angles that the coordinated nitrogen atom makes with its connectors.

The [Co(edta)]⁻ complex ion and related complexes all show axial compression of 2–3% relative to the equatorial Co–O bonds. Increasing the length of the carboxylate chain has little effect here. For the [Co(1,3-pdta)]⁻ ion, increasing the size of the E ring by one carbon atom has the effect of increasing the axial compression by about 4%. The M–L (metal ion to donor atom) distances in [Co(edta)]⁻ are nearly the same as those in [Co(edtp)]⁻, but with one very important difference: the mean Co–N distance (1.925 Å) in [Co(edta)]⁻ is shorter than the mean Co–O(eq) distance (1.946 Å). The order is reversed [Co–N longer than Co–O(eq)] in [Co(edtp)]⁻ and other closely related complexes [9]. When Cr is substituted for Co, the mean Cr–N distance is always longer than the mean Cr–O(eq) distance, even

TABLE 2

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

Complex	$\Sigma\Delta(\text{O}_b)^a$	$\Delta\Sigma(\text{E})^b$	$\Delta\Sigma(\text{R})^c$	$\Delta\Sigma(\text{G})^d$	$\Delta\{\text{M}-\text{O}-\text{C}\}(\text{R})^e$	$\Delta\{\text{M}-\text{O}-\text{C}\}(\text{G})^f$	$\Sigma\Delta(\text{N})^g$	Ref.
$[\text{Co}(\text{edta})]^-$	52	-7	-1	-15	+4	+3	15	19,20
$[\text{Co}(\text{eddadp})]^{-h}$	31	-11	-1	+38	+6	+18	13	9
$[\text{Cr}(\text{eddadp})]^{-h}$	37	-15	-1	+37	+8	+21	16	27
$[\text{Co}(\text{edtp})]^-$	29	-14	+42	+41	+21	+21	18	11
$[\text{Cr}(\text{edtp})]^-$	17	-16	+39	+39	+23	+23	22	11
$[\text{Co}(1,3\text{-pdta})]^-$	34	+36	+1	-12	+6	+5	15	26
$[\text{Cr}(1,3\text{-pdta})]^-$	56	+35	+1	-10	+9	+7	14	22
$[\text{Co}(1,3\text{-pddadp})]^{-i}$	38	+28	+33	-11	+17	+4	16	10
$[\text{Cr}(1,3\text{-pddadp})]^{-i}$	42	+26	+33	-11	+19	+5	16	39

^a $\Sigma\Delta(\text{O}_b)$ 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 $\Delta\Sigma(\text{E})$ is the deviation of the bond angle ring sum from the ideal en(528°) or 1,3-pn(637.5°).^c $\Delta\Sigma(\text{R})$ is the deviation (mean values) from the ideal bond angle sum of axial chelate rings (six-membered ring 648°) and (five-membered ring 538.5°).^d $\Delta\Sigma(\text{G})$ is the deviation from the ideal bond angle sum of equatorial chelate rings.^e $\Delta\{\text{M}-\text{O}-\text{C}\}(\text{R})$ is the mean value of the deviation of M-O-C bond angles from 109.5° for R rings.^f $\Delta\{\text{M}-\text{O}-\text{C}\}(\text{G})$ deviation for G rings.^g $\Sigma\Delta(\text{N})$ is the sum of mean absolute values of the six bond angles made by the nitrogen atoms.^hThe *trans*(O₅) isomer with axial glycinate rings.ⁱThe *trans*(O₆) isomer with equatorial glycinate rings.

for $[\text{Cr}(\text{edta})]^-$ [9]. The hexadentate Rh(III) complexes of 1,3-pdta and eddadh [22,25] show Rh–N bonds slightly shorter than Rh–O(eq) bonds, as in $[\text{Co}(\text{edta})]^-$.

Each of the M–O bond distances [9] increases with the increasing size of the M(III) ion for a particular edta-type ligand. In contrast, the M–N bonds are longer and shorter in the Fe(III) and Rh(III) complexes, respectively, than are expected from ionic radii; they increase in the order $\text{Co} < \text{Rh} < \text{Cr} < \text{Fe}$, which reflects a weaker affinity of Fe(III) and stronger affinity of Rh(III) ions for nitrogen donors than for oxygen donors.

Increasing the size of the carboxylate chains allows the complexes to attain octahedral angles closer to the ideal with apparently less strain in the M–L bonds. Detailed comparison of the structural parameters among $\text{trans}(\text{O}_5)-[\text{M}(\text{eddadh})]^-$ (M(III) = Co, Cr, Fe, and Rh) and other related complexes of edta-type ligands [9] revealed that the Co(III) and Rh(III) complexes are less distorted from a regular octahedral structure than the Cr(III) complexes and much less than the Fe(III) complexes. The ligand eddadh surrounds the M(III) ions more favorably than 1,3-pdta and much more than edta, both of which are capable of forming only five-membered glycinate rings. Related Co(III) and Cr(III) complexes made with 1,3-pdta and eddadh show similar effects [9,22,26,27]. A total deviation of octahedral angles by 17° for the $[\text{Cr}(\text{edtp})]^-$ complex (Table 2) indicates that the complex is relatively free of octahedral angle strain.

The $[\text{M}(\text{edtp})]^-$ complexes (M = Co or Cr) [11], which were synthesized to be relatively ring-strain-free analogs of $[\text{M}(\text{edta})]^-$, show other significant sources of strain. An M–O–C fragment of the 3-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 3-alaninate rings are as high as 132° , and the value is of the same order of magnitude for both kinds of ring, R or G, for both the cobalt and chromium complexes. 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. Furthermore, when 3-alaninate coordinates to metal ions, it forms rings with distorted boat conformations with the same unusually high M–O–C bond angles [28].

Table 2 shows further that replacing glycinate rings with 3-alaninate rings increases the strain in the E ring. When the E ring is expanded by one carbon atom without replacing glycinate, the strain in this ring actually increases but in the opposite direction. The E ring in $[\text{Cr}(\text{edta})]^-$ shows a total deviation of -7° , but in $[\text{M}(1,3\text{-pdta})]^-$ (M = Co or Cr) the deviation is $+35\text{--}36^\circ$. Therefore in the latter, the mean angular deviation in the ring made by chelating nitrogens is actually larger ($\approx 6^\circ/\text{angle}$ vs. $1.4^\circ/\text{angle}$).

The strain in the 3-alaninate rings in the edtp complexes are about the same regardless of ion or R or G ring type, $\approx 6\text{--}7^\circ/\text{angle}$. There is little difference between the R and G rings for M–O–C and C–C–C bond angles 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 for Co(III) and Cr(III) is actually greater than that measured for the corresponding edta complexes.

Another important source of strain in edta-type complexes involves the bonds to coordinated nitrogen. Halloran et al. [29] 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 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 is 18°. Notice from Table 2 that the strain about N in [Co(edtp)][−] is greater than that in [Co(edta)][−]. The greatest deviation about the N atoms in all the edta-type complexes (Table 2) is not consistently and specifically due to any one of the six bond angles. The total deviation about the chelating N atoms in this [Cr(edtp)][−] sums to roughly 20° and indicates that, compared with the other complexes listed in Table 2, it contains N atoms with the most highly strained bonds.

For the ligands having mixed five- and six-membered carboxylate arms (ed3ap [30], 1,3-pd3ap [31], eddarp [5,9,25,27,32–35], (SS)-edds [24,34–36], (S)-eddams [37], eda3p [38], and 1,3-pddarp [10,31,39–41]) geometrical isomers are possible that differ in the number (0, 1, or 2) of six-membered rings lying in the girdle plane. These ligands generally minimize strain by forming isomers that have a six-membered ring in the G plane.

Two ligands (the eddarp and 1,3-pddarp), differing in size of the diamine backbone ring, can form three geometrical isomers [Fig. 2(d)]. The six-membered 3-propionate chelate serves better for the formation of less-strained G rings, favoring *trans*(O₅)-[M(eddarp)][−] complexes. [Rh(1,3-pddarp)][−] [41] was identified as the *trans*(O₅) isomer. Curiously, in hexadentate [M(1,3-pddarp)][−] complexes (M = Cr(III) [39] or Co(III) [10,31,40]), the dominant isomer was found to be the *trans*(O₆) isomer with the 3-propionate rings in axial positions. This is unexpected since the equatorial rings are generally more strained for five-membered rings. The *trans*(O₆) geometry was verified by X-ray crystallography [10,39].

For the same configuration of the complex, changing from *trans*(O₅) to *trans*(O₆) for [M(eddarp)][−] or [M(1,3-pddarp)][−] involves inversion at chiral nitrogen centers. Either process, nitrogen inversion or inversion of configuration for the complex, requires an exchange of in-plane substituents for out-of-plane substituents [40].

The effect of the asymmetric centers of ligands on the stereochemistry of a complex is greater than the effect of chelate chain length. The presence of asymmetric centers on the ligand determines the geometrical configuration of the complex, the conformations of the chelate rings, and controls the absolute configuration of the complex as a whole. For the optically active (SS)-edds ligand in Fig. 2(c), two

geometrical isomers are shown having opposite absolute configurations, but only one, Λ -*trans*(O₅) was found [24,34–36].

3. CARBON–NITROGEN BOND CLEAVAGE IN [M(edta-type)][−] COMPLEXES

Thermal decomposition of hexadentate [M(edta-type)][−] complexes involves decarboxylation of the ligand, involving C–N bond cleavage to form diamine-*N,N,N'*-triacetato or diamine-*N,N'*-diacetato complexes [42,43]. Studies on thermal hydrolytic activation of the C–N bond in inert Cr(III) complexes showed anomalous facile C–N bond cleavage in one of the 3-alaninate arms of the novel diastereoisomers of [Cr(edtp)][−] and [Cr(S-pdtp)][−] complexes (Fig. 3) [13]. As reported, when *lelob* or *ob₂*-[Cr(edtp)][−] is heated in aqueous solution for 24 h at 60°C, a neutral complex with ed3p was obtained along with 3-hydroxypropionate as a major product. These results reveal a rather facile hydrolytic thermolysis of a C–N bond in a 3-alaninate ring which could be indicative of a weak and strained N–C(R) bond as shown by crystallography [11].

The *lel₂* isomers of [Cr(edtp)][−] or [Cr(S-pdtp)][−] are stable in acidic solution, without decomposition involving C–N bond cleavage, or displacement of a carboxylate arm to form the pentadentate complex, in contrast to the case of the edta-type complexes [14]. Recently [44], two isomers of the [Cr(Hedtp)(H₂O)] obtained from the stable *lel₂* form were reported. The geometrical structure of one isomer was found to be *cis-eq* (Scheme 1). The rechelation from the *cis-eq* as well as *cis-polar* isomer to the *lel₂* form may occur easily by interchanging of one uncoordinated 3-propionate and the aqua ligand. However, the reaction from the *trans-eq* isomer to *lel₂* requires the interchange among two 3-propionates and the aqua ligand, even in the shortest pathway thorough *cis-polar* intermediate. From the fact that both isomers revert to *lel₂* completely, these pentadentate complexes should be much more unstable than *lel₂* in aqueous (or acidic) solution. This might be the reason

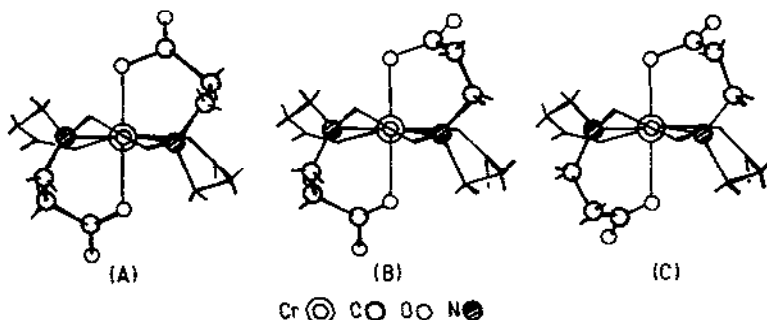
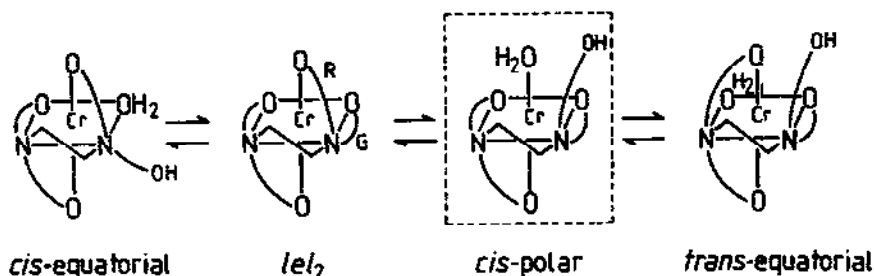


Fig. 3. The three diastereoisomers of edtp or (S)-pdtp complexes: (A) *lel₂* $\Delta(\delta\delta)$; (B) *lelob* $\Delta(\delta\lambda)$; (C) *ob₂* $\Lambda(\lambda\lambda)$.



why the Hedtp complex could not be found in the acidic solution of the lel_2 form, in contrast to the case of $[Cr(Hedta)(H_2O)]$ [3,12,14].

4. SYMBOLISM

Many forms of notation have been used for describing absolute configurations of chelate complexes and conformations of individual chelate rings [45–54]. The symbols used to denote the absolute configurations and conformations of individual chelate rings of metal complexes used here are according to the IUPAC proposal [46]:

- Δ, Λ the absolute configurations of metal complexes describing the helicity of the spiral arrangement of one octahedral edge spanned by a chelate ring relative to another.
- δ, λ the conformations of individual chelate rings. The description of the conformation corresponds to that for the absolute configuration of a metal complex.
- R, S the absolute configuration of tetrahedral carbon and nitrogen atoms [55].
- $(+)_\lambda, (-)_\lambda$ the optical rotation at a wavelength λ .
- $(+), (-)$ the sign of the lowest energy or the dominant circular dichroism (CD) peak in the ligand field region.

5. OPTICAL ACTIVITY OF COMPLEXES

The reviewed complexes possess a symmetric chromophore placed in a dissymmetric environment and complexes of Co(III) provide a particularly comprehensive series of stable coordination compounds. The immediate environment of a metal ion has the greatest effect on its chiroptical properties. Circular dichroism (CD) spectra are used as a probe of chiroptical properties in order to understand the relationship to molecular structure. Explanation of optical activity requires information about the electronic states and structures of the complexes. Theories of optical activity of coordination compounds have been reviewed [56,57]. Several theories [58,59] relate strain and rotatory strength, and the deviation from cubic symmetry at the metal ion as the chromophore.

Mason's work on $[\text{Co}(\text{en})_3]^{3+}$ and $\text{cis-}[\text{Co}(\text{en})_2\text{L}_2]^{n+}$ (L_2 represents two monodentate ligands or a didentate ligand) [49] relates the absolute configuration to CD spectra. These complexes can be related to $[\text{Co}(\text{edta})]^-$ by their common C_2 axis, allowing their configurations to be related.

Yamatera and co-workers [60] considered a tetragonal (D_{4h}) model of the $[\text{M}(\text{A})_4(\text{B})_2]$ type complex and calculated relative intensities of the ligand-field transition bands in Cr(III) and Co(III) complexes. They found a correlation of the band intensities in tetragonal complexes by applying a modified treatment of Dubicki and Day [61].

The method outlined by Mason and co-workers [49] and other methods [51,52,59] have been employed for complexes discussed in this review and the results obtained have been strongly supported by the assignments made directly by X-ray crystallography or indirectly by using stereospecific ligands of known absolute configuration. Absolute configurations of complexes are described as tentative when they are assigned on the basis of CD spectra alone.

6. ABSOLUTE CONFIGURATIONS OF $[\text{M}(\text{edta-type})]^-$ COMPLEXES

The determination of absolute configurations of metal complexes by X-ray crystallography is the only unequivocal procedure available. Such absolute configurations of complexes serve as references and checks for the assignment of absolute configurations from CD data using empirical methods for closely related complexes. The absolute configuration of the parent complex $(+)\text{_{546}}-[\text{Co}(\text{edta})]^-$ has been determined to be $\Delta(\Delta\Delta)$ [20]. The diamine chelate ring has an asymmetric gauche form with the λ conformation. One of the two out-of-plane glycinate chelate rings has a strained asymmetric envelope form with the λ conformation, and the other one is δ . Both of the in-plane glycinate chelate rings have an asymmetric envelope form with δ conformation.

The complexes of 1,3-pdta and its derivatives (1,3-mpdta, 2,4-ptnta, and dhpta) involve six-membered chelate diamine rings with puckered skeletal structures. Four conformations of the diamine rings are possible: chair, two twist (δ) and (λ), and a boat form. For a stable octahedral complex with the ligand hexadentate, a δ twist form gives a complex with the Λ configuration and the λ twist gives the Δ configuration, as verified crystallographically. The absolute configuration around the cobalt atom is Λ for $(-)\text{_{546}}-[\text{Co}(1,3\text{-pdta})]^-$ [26], as shown in Fig. 4. The same Λ configuration was established [22] for $(-)\text{_{589}}-[\text{Rh}(1,3\text{-pdta})]^-$ and the configuration is Δ for $(+)\text{_{589}}-[\text{Co}(\text{dhpta})]^-$ [23]. The six-membered chelate ring has the δ -skew boat conformation in complexes of Λ configuration and the λ -skew boat conformation in complexes having the Δ configuration. In all cases, the G and R rings have envelope conformations (the R rings are relatively flat for the Rh(III) complex).

The geometries of eddadp ligands in the crystal structures of $(-)\text{_{589}}\text{-trans}(\text{O}_5)\text{-}[\text{Cr}(\text{eddadp})]^-$ [27] (Fig. 5) and $(-)\text{_{589}}\text{-trans}(\text{O}_5)\text{-}[\text{Rh}(\text{eddadp})]^-$ [25] are essentially

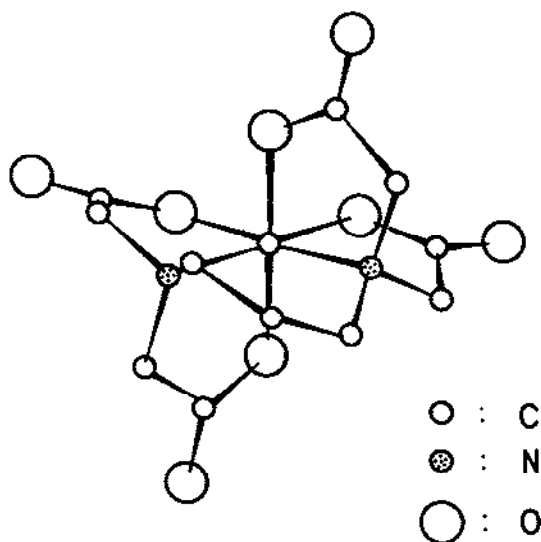


Fig. 4. Crystal structure of $(-)_546\text{-K}[\text{Co}(1,3\text{-pdta})]\cdot 2\text{H}_2\text{O}$ (orthorhombic, $B22_12$, $a = 10.984 \text{ \AA}$, $b = 16.638 \text{ \AA}$, $c = 8.853 \text{ \AA}$, $Z = 4$), $\Lambda(\Delta\Delta\Delta)$ configuration. Conformation of the diamine ring is δ skew boat [26].

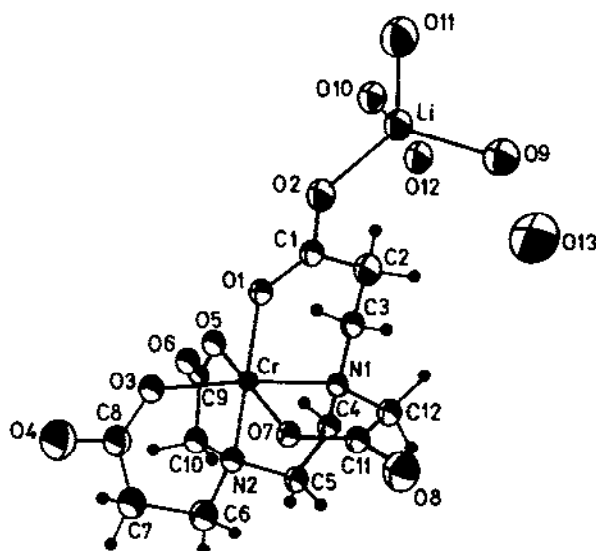


Fig. 5. Crystal structure of $(-)_599\text{-Li}[\text{Cr}(\text{eddarp})]\cdot 5\text{H}_2\text{O}$ (orthorhombic, $P2_12_12_1$, $a = 11.635 \text{ \AA}$, $b = 13.309 \text{ \AA}$, $c = 12.633 \text{ \AA}$, $Z = 4$). Absolute configuration of the complex is $\Lambda(\Delta\Delta\Delta)$ [27].

the same. These structures are isomorphous with the Λ absolute configuration. The analysis of the conformation parameters shows that one of the glycinate rings lying out-of-plane of the diamine ring is relatively flat. The other glycinate ring shows a significant deviation from planarity with a λ conformation. The puckered diamine

ring (E) has a δ conformation. The conformation of the two six-membered rings lying in the plane of the diamine ring is close to half-chair (λ).

The complexes $(+)\text{-}_{589}\text{-Li}[\text{M}(\text{edtp})] \cdot 3\text{H}_2\text{O}$ ($\text{M} = \text{Co}$ or Cr) [11] (Fig. 6) are isomorphous. The ethylenediamine ring is puckered as usual in such chelates and the 3-alaninate rings are in distorted boat conformations. The conformations of the axial (R) 3-alaninate rings are λ , denoting the orientation of the ethylene C–C bonds with respect to the C_2 axis of the complex ion [13,62]. Mixed conformations can produce three conformers (A) $\text{lel}_2 \Lambda(\delta\delta)$; (B) $\text{lelob} \Lambda(\delta\lambda)$; (C) $\text{ob}_2 \Lambda(\lambda\lambda)$ (Fig. 3) [13]. However, the most stable lel_2 form was found to dominate in complexes $[\text{M}(\text{edtp})]^-$ [62,63], having $\Delta(\lambda\lambda)$ absolute configurations (Fig. 6).

The equatorially coordinated 3-alaninate rings (G) (Fig. 6) deviate more than the axially coordinated R rings from an ideal twist-boat conformation. These six-membered G rings have all the participating atoms nearly coplanar except for the N atom. Thus, the three connected carbon atoms in these rings are flattened out away from the N atom. Each of the carbonyl oxygen atoms of the four carboxylate rings is involved with either H-bonding to a water (O8) of crystallization or a lithium ion (O2, O4, and O6). The effects of these interactions on the conformations of the 3-alaninate rings are uncertain.

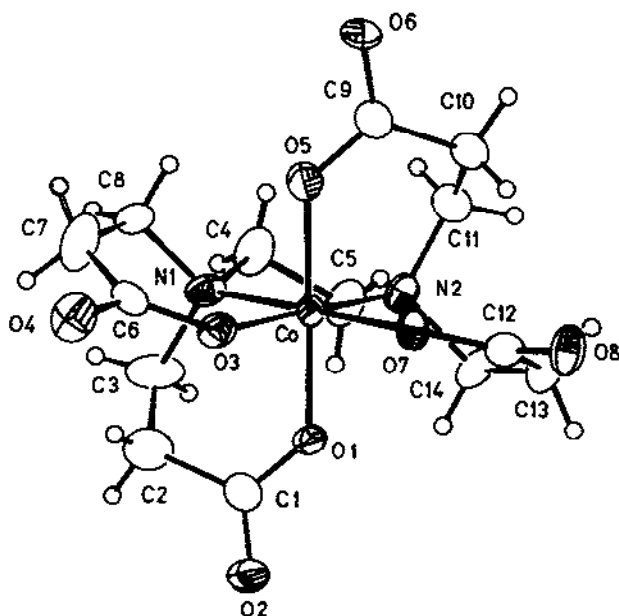


Fig. 6. Crystal structures of $(+)\text{-}_{589}\text{-Li}[\text{M}(\text{edtp})] \cdot 3\text{H}_2\text{O}$ (monoclinic with $Z = 2$, $\text{M} = \text{Co}$, $a = 8.824 \text{ \AA}$, $b = 11.910 \text{ \AA}$, $c = 8.728 \text{ \AA}$; $\text{M} = \text{Cr}$, $a = 8.705 \text{ \AA}$, $b = 11.940 \text{ \AA}$, $c = 9.033 \text{ \AA}$). Absolute configuration is $\Delta(\lambda\lambda)(\Delta\Delta\Delta)$ for each complex [11].

7. CORRELATION OF ABSOLUTE CONFIGURATIONS WITH CD SPECTRA

The two spin-allowed ligand field transitions in a low-spin d^6 system [Co(III) and Rh(III)] in an octahedral field are $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ in order of increasing energy. In a tetragonal field, these transitions split into two components each, i.e. $^1T_{1g} = ^1A_{2g} + ^1E_g^a$ and $^1T_{2g} = ^1B_{2g} + ^1E_g^b$. Most of the complexes considered in this article are treated to have holohedrized D_{4h} *cis*-[N₂O₄] symmetry with the weaker field along the z (O–O) axis. The energy of $^1E_g^a$ is lower than that of $^1A_{2g}$ [64]. The splitting of $^1T_{2g}$ is smaller, but the energy of $^1E_g^b$ is lower than that of $^1B_{2g}$.

The two spin-allowed transitions in O_h for Cr(III) complexes (d^3) are $^4A_{2g} \rightarrow ^4T_{2g}$ (at lower energy) and $^4A_{2g} \rightarrow ^4T_{1g}$. In D_{4h} , the ground state is $^4B_{1g}$ and the O_h transition $^4A_{2g} \rightarrow ^4T_{2g}$ splits to give $^4B_{1g} \rightarrow ^4E_g^a$ (at lower energy) and $^4B_{1g} \rightarrow ^4B_{2g}$. The D_{4h} splitting of $^4A_{2g} \rightarrow ^4T_{1g}$ is smaller and the ordering depends on the signs and relative values of tetragonal parameters.

The empirical rules for assigning the absolute configurations of d^3 and low-spin d^6 transition metal complexes are consistent with the results for D_{4h} symmetry if there are two CD peaks in the region of the low-energy spin-allowed transition, one on each side of the absorption maximum. For C_2 symmetry, three peaks are expected, but usually only two peaks appear in this region, both on the low-energy side of or near the absorption maximum. In a third case, a single CD peak appears in the first absorption band region because of complete cancellation or masking of weak peaks by the dominant peak.

Although many cases of [M(edta-type)][−] complexes show CD spectra indicating symmetry lower than D_{4h} , i.e. C_2 , it is useful to use the centrosymmetric holohedrized D_{4h} symmetry when that splitting pattern appears. In particular, the *effective* selection rules for the absorption spectra involving electric-dipole transitions correspond to a centrosymmetric point group as judged from the low intensities. Since the operators are *ungerade* for O_h and D_{4h} and all $d \rightarrow d$ transitions are *gerade*, the transitions are electric-dipole forbidden. Rotational strength requires a product involving integrals for the electric- and magnetic-dipole transitions. The magnetic-dipole operators are *gerade*. For D_{4h} the two components of the first absorption band are magnetic-dipole allowed and only the E component of the higher energy absorption band is magnetic-dipole allowed for d^3 and d^6 . For the non-centrosymmetric C_2 point group, all of these transitions are electronic- and magnetic-dipole allowed [65,66].

The CD and absorption spectral data are summarized for Co(III) and Cr(III) complexes in Table 3. The shapes of the absorption bands of [M(edta-type)][−] complexes suggest pseudo-octahedral symmetry since the broad bands obscure small splittings. Only two complexes (*trans*(O₆)-[Co(1,3-pddadp)][−] [31,40] and *trans*(O₆)-[Co(cda3p)][−] [67]) show some splitting of the lower-energy absorption band. These two complexes have two 3-propionate rings in axial positions and presumably the ligand field along the z axis is weak enough to show the splitting expected for D_{4h} symmetry.

TABLE 3

Absorption (AB) and circular dichroism (CD) data for hexadentate [M(edta-type)] complexes

Complex	AB		CD		Ref.
	ν (10^3 cm^{-1})	ϵ	ν (10^3 cm^{-1})	$\Delta\epsilon$	
$\Lambda(-)_{546}\text{-[Co(edta)]}^-$	18.63	347	17.10	+1.50	20,71
			19.80	-0.69	
	26.04	246	23.80	+0.28	
			25.60	-0.09	
			27.60	+0.29	
$\Lambda(-)_{546}\text{-[Co(S-pdta)]}^-$	18.60	300	17.23	+1.58	68,69
			19.70	-0.76	
			(21.75)	-(0.23)	
	26.04	204	24.15	+0.32	
			26.00	-0.18	
$\Lambda(-)_{546}\text{-[Co(SS-cdta)]}^-$	18.50	316	27.95	+0.34	69
			16.80	+1.43	
	26.20	221	18.80	-1.72	
			$\approx 23.8^a$	$\approx +0.3^a$	
			$\approx 27.2^a$	$\approx +0.4^a$	
$\Lambda(+)\text{-[Co(SS-sdta)]}^-$	18.42	295	16.81	+0.95	70
			18.80	-2.57	
	26.18	219	24.10	+0.43	
			27.78	+0.42	
$\Lambda(+)\text{-[Co(xdta)]}^-$	16.61	158	15.87	+6.43	70
			17.86	-6.32	
	25.00	201	22.73	+0.83	
			25.77	+1.80	
$\Lambda(-)_{546}\text{-trans(O}_5\text{)-R-[Co(ed3ap)]}^-$	18.65	286	16.53	+0.91	30
			18.62	-1.98	
	26.04	196	24.09	+0.33	
			27.55	+0.30	

$\Lambda-(+)_546\text{-[Co}(u\text{-eddadp})]^-$	18.45	279	16.31	+1.11	30
			18.25	−2.66	
	25.57	166	23.81	+0.26	
			26.95	+0.36	
$\Lambda-(-)_{589}\text{-trans}(\text{O}_5\text{O}_6)\text{-SR}\cdot\text{[Co(eddadp)]}^-$	18.60	253	16.50	+2.25	33
			18.40	−3.12	
	25.80	142	24.40	+0.31	
			26.60	+0.56	
$\Lambda-(-)_{589}\text{-trans}(\text{O}_5)\text{-RR}\cdot\text{[Co(eddadp)]}^-$	18.50	342	16.20	+0.40	32,33
			18.30	−2.78	
	25.70	186	24.20	+0.29	
			26.30	+0.36	
$\Lambda-(+)_546\text{-trans}(\text{O}_5\text{O}_6)\text{-R}\cdot\text{[Co(eda3p)]}^-$	18.25	318	16.05	+0.90	38
			18.08	−3.18	
	25.19	147	23.81 sh	+0.43	
			26.04	+0.58	
$\Lambda-(+)_546\text{-[Co(edtp)]}^-$	18.00	253	15.77	+1.05	11,68
			17.57	−3.68	
	24.80	110	23.30	+0.10	
			26.30	+0.20	
$\Lambda-(+)\text{-trans}(\text{O}_5)\text{-RR}\cdot\text{[Co(SS-edds)]}^-$	19.40	$\approx 300^a$	16.47	+0.39	36,65
			18.25	−2.31	
	26.24	$\approx 115^a$	$\approx 20.0^a$	$\approx +0.7^a$	
			25.64	+0.95	
$\Lambda-(-)\text{-trans}(\text{O}_5)\text{-R}\cdot\text{[Co(S-eddams)]}^-$	19.36	260	26.20	+1.0	37
			18.40	−1.98	
	26.35	150	26.30	+0.58	
			17.00	+1.91	
$\Lambda-(-)_{546}\text{-[Co(1,3-pdta)]}^-$	18.20	131	19.00	−2.41	63
			24.60	+0.69	
$\Delta-(+)_{589}\text{-[Co(RR-2,4-ptnta)]}^-$	26.40	115	17.04	−2.19	66
	18.02	123	18.94	+2.02	

TABLE 3 (continued)

Absorption (AB) and circular dichroism (CD) data for hexadentate [M(edta-type)] complexes

Complex	AB		CD		Ref.
	ν (10^3 cm^{-1})	ϵ	ν (10^3 cm^{-1})	$\Delta\epsilon$	
$\Delta(+)_589\text{-[Co(RR-2,4-ptnta)]}^-$	26.18	100	24.55	-0.70	23
			32.26	+0.13	
	43.86	23 988	40.32	-6.38	
			44.44	+8.30	
$\Delta(+)_589\text{-[Co(dhpta)]}^-$	18.25	142	16.72	-2.12	40
			18.73	+3.01	
			24.39	-0.80	
$\Lambda(+)_546\text{-trans(O}_6\text{)-SS-[Co(1,3-pddadp)]}^-$	26.46	121	16.08	+3.02	40
	16.34 sh	≈ 25	20.41	-3.21	
	18.42	58	17.92	+0.41	
	25.77	71	23.15	+0.19	
			26.18	-1.40	
			29.00 sh	-0.12	
$\Lambda(+)_546\text{-trans(O}_5\text{O}_6\text{)-SR-[Co(1,3-pddadp)]}^-$	17.76	114	15.92	+1.20	40
			17.86	-3.20	
			24.10	+0.58	
$\Delta(+)_589\text{-[Co(dcbta)]}^-$	25.19	88	24.10	+0.58	1
	$\approx 17.6^a$	$\approx 95^a$	$\approx 16.5^a$	$\approx -1.5^a$	
			$\approx 18.8^a$	$\approx +3.3^a$	
	$\approx 25.6^a$	$\approx 83^a$	$\approx 23.6^a$ sh	$\approx -0.6^a$	
			$\approx 25.6^a$	$\approx -0.8^a$	
$\Lambda(-)_589\text{-trans(O}_5\text{)-RR-[Cr(eddadp)]}^-$	$\approx 42.4^a$	$\approx 17\,400^a$	$\approx 42.5^a$	$\approx +0.2^a$	27,35,75
	18.90	214	16.53	+0.20	
			18.62	-0.77	
			20.33 sh	-0.20	
	25.30	107	22.17 sh	-0.05	
			24.10	-0.08	
			26.53	+0.23	

$\Lambda(-)_{589}\text{-trans}(\text{O}_5\text{O}_6)\text{-R-[Cr(eda3p)]}^-$	18.69	194	16.58	+0.09	62
			18.76	-0.64	
			21.05 sh	-0.14	
	25.12	86.6	23.53	+0.07	
			26.67	+0.23	
$\Delta(\lambda\lambda)(+)\text{-}_{589}\text{-[Cr(edtp)]}^-$	18.55	183	18.24	+0.37	62
			20.08	-0.04	
			21.01	-0.02	
	25.11	77	23.20	-0.14	
			26.52	-0.18	
$\Lambda(\delta\delta)\text{-[Cr(S-pdtp)]}^-$	18.55	189	$\approx 18.40^*$	$\approx -0.19^*$	13
			$\approx 20.90^*$	$\approx +0.02^*$	
			$\approx 25.90^*$	$\approx -0.04^*$	
$\Lambda(+)\text{-}_{589}\text{-trans}(\text{O}_5)\text{-RR-[Cr(SS-edds)]}^-$	25.11	67			
	19.60	175	17.54	+0.41	35,75
			19.33	-0.39	
			21.83	+0.45	
	26.00	57	23.50 sh	+0.34	
			26.99	+0.38	
$\Lambda(+)\text{-}_{589}\text{-[Cr(SS-ptnta)]}^-$	19.64	110	18.00 sh	+0.20	75
			19.67	+0.44	
			21.67	-0.06	
	25.97	77	24.00	+0.44	
			25.25 sh	+0.27	
			29.66	-0.02	
$\text{trans}(\text{O}_5)\text{-[Cr(1,3-pddadp)]}^-$	18.50	127			39
	24.80	81			
$\text{trans}(\text{O}_5\text{O}_6)\text{-[Cr(1,3-pddadp)]}^-$	18.90	118			39
	25.60	70			
$\text{trans}(\text{O}_6)\text{-[Cr(1,3-pddadp)]}^-$	19.60	90			39
	26.10	45			

*Values estimated from spectra.

The complexes of $[M(\text{edta-type})]^-$ ($M = \text{Cr}$ or Co) exhibit similar CD splitting and sign patterns. The transition to the $A(C_2)$ state, derived from the $E_g^*(D_{4h})$ state is expected to retain the CD sign. The lowest energy CD components of these complexes is positive for the $\Lambda(\Lambda\Lambda\Lambda)$ configuration.

Absolute configurations have been determined by X-ray methods for $\Delta-(+)_546-[\text{Co}(\text{edta})]^-$ [20], $\Lambda-(-)_546-[\text{Co}(1,3\text{-pdta})]^-$ [26] (Fig. 4), $\Delta-(+)_589-[\text{Co}(\text{dhpta})]^-$ [23], and $\Delta-(+)_589-[\text{Co}(\text{edtp})]^-$ [11] (Fig. 6). The general sign pattern in the region of the lower energy absorption band for Co complexes in Table 3 is a lowest energy positive CD peak followed by a negative peak for the Λ configuration. For three of the complexes in Table 3, data with opposite signs are given for the Δ configuration as reported in the references cited. For the Co complexes with only acetate arms, the second CD peak is at higher energy than that of the absorption maximum for en or larger diamine rings.

For $(-)_546\text{-trans}(\text{O}_5)-[\text{Co}(\text{ed3ap})]^-$, the second CD peak is at almost the same energy as the maximum of the first absorption band. For all complexes containing 2-, 3-, or 4-propionate arms, except for $(+)_546\text{-trans}(\text{O}_5\text{O}_6)-[\text{Co}(1,3\text{-pddadp})]^-$, the second CD peak is at lower energy than the maximum of the absorption band.

The CD spectra of two groups of complexes giving very similar CD curves in the region of the first absorption band are shown in Fig. 7. For each group the CD curve for $[\text{Co}(\text{edta})]^-$ is shown for comparison. Figure 8 shows CD spectra for two isomers of $[\text{Co}(1,3\text{-pddadp})]^-$ and $[\text{Co}(1,3\text{-pdta})]^-$ along with the absorption spectra. The second CD peak ($17\,860\text{ cm}^{-1}$) for $(+)_546\text{-trans}(\text{O}_5\text{O}_6)-[\text{Co}(1,3\text{-pddadp})]^-$ is very nearly at the energy of the absorption maximum ($17\,760\text{ cm}^{-1}$). The $(+)_546\text{-trans}(\text{O}_6)-[\text{Co}(1,3\text{-pddadp})]^-$ is the only complex of ligands other than $[\text{Co}(\text{edds})]^-$ that shows three CD peaks in the first absorption band region. It also shows a shoulder of the absorption band, indicating more splitting of the components than for the other complexes. It is likely that three components are present in general for $[M(\text{edta-type})]^-$ complexes, but fewer CD peaks appear because of small splitting and masking weak peaks.

The relative intensities of the CD peaks vary. The dominant CD peak and net sign are positive in the first absorption band region for $(-)_546\text{-}\Lambda-[\text{Co}(\text{edta})]^-$ and $(-)_546\text{-}\Lambda-[\text{Co}(\text{pdta})]^-$, but these are negative for all other Λ complexes cited except as follows. The net sign is nearly zero for $(+)-[\text{Co}(\text{xtda})]^-$ and $(+)_546\text{-trans}(\text{O}_6)-[\text{Co}(1,3\text{-pddadp})]^-$. The CD intensities for $(+)-[\text{Co}(\text{xtda})]^-$ are unusually high, probably involving intensity borrowing from an allowed transition. The splitting of $(+)_546\text{-trans}(\text{O}_6)-[\text{Co}(1,3\text{-pddadp})]^-$ has been noted to be unusual. Variations in relative intensity of the CD peaks are not surprising with changes in strain resulting from ring size and various microsymmetries among the complexes.

The complex ions $(-)_546-[\text{Co}(\text{S-pdta})]^-$ [68], $(-)_546-[\text{Co}(\text{SS-cdta})]^-$ [69], and $(+)-[\text{Co}(\text{SS-sdta})]^-$ [70] are formed stereospecifically as Λ . They also give the familiar $(+, -)$ CD pattern for the lowest energy band. The (SS)-edds and the (S)-eddams ligands also produce Co(III) complexes stereospecifically with the Λ configuration

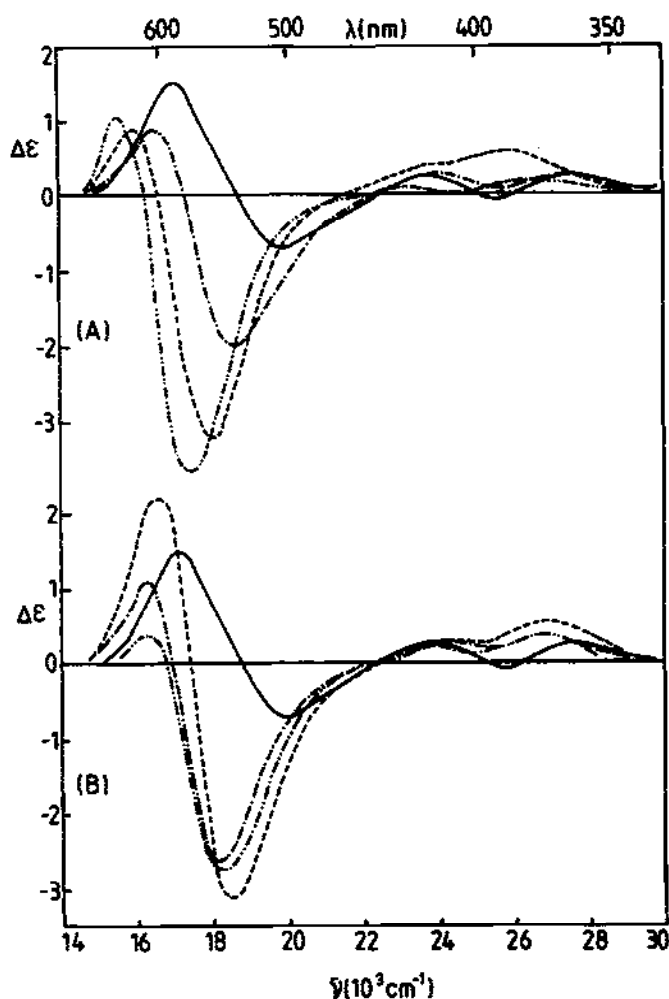


Fig. 7. CD spectra of $[\text{Co}(\text{edta-type})]^-$ complexes forming five-membered diamine rings. (A) —, $\Lambda-(+)-(-)_{546}-[\text{Co}(\text{edta})]^-$; ---, $\Lambda-(+)-(-)_{546}-[\text{Co}(\text{ed3ap})]^-$; - · - ·, $\Lambda-(+)-(-)_{546}-[\text{Co}(\text{eda3p})]^-$; and · · · ·, $\Lambda-(+)-(-)_{546}-[\text{Co}(\text{edtp})]^-$. (B) —, $\Lambda-(+)-(-)_{546}-[\text{Co}(\text{edta})]^-$; ---, $\Lambda-(+)-(-)_{546}-[\text{Co}(\text{u-eddadp})]^-$; - · - ·, $\Lambda-(+)-(-)_{589-\text{trans}}(\text{O}_5\text{O}_6)-[\text{Co}(\text{eddadp})]^-$; and · · · ·, $\Lambda-(+)-(-)_{589-\text{trans}}(\text{O}_5\text{O}_6)-[\text{Co}(\text{eddadp})]^-$.

[36,37]. Their complexes are closely related to the $\Lambda-[\text{Co}(\text{edta})]^-$ ion, but have slightly different CD spectra from those of the other edta-type complexes. The usual CD pattern has two peaks (+, -) for the lowest energy absorption band, but $\Lambda-[\text{Co}(\text{SS-edds})]^-$ shows a three-peak (+, -, +) pattern, and $\Lambda-[\text{Co}(\text{S-eddams})]^-$ shows only one negative peak for the lowest energy absorption band. A significant difference between the two types of complex has to do with the branching of chelate rings. The chelate ring branching occurs on one octahedral face for $[\text{Co}(\text{S-eddams})]^-$ and on two faces for $[\text{Co}(\text{SS-edds})]^-$. For the other edta-type complexes, the chelate

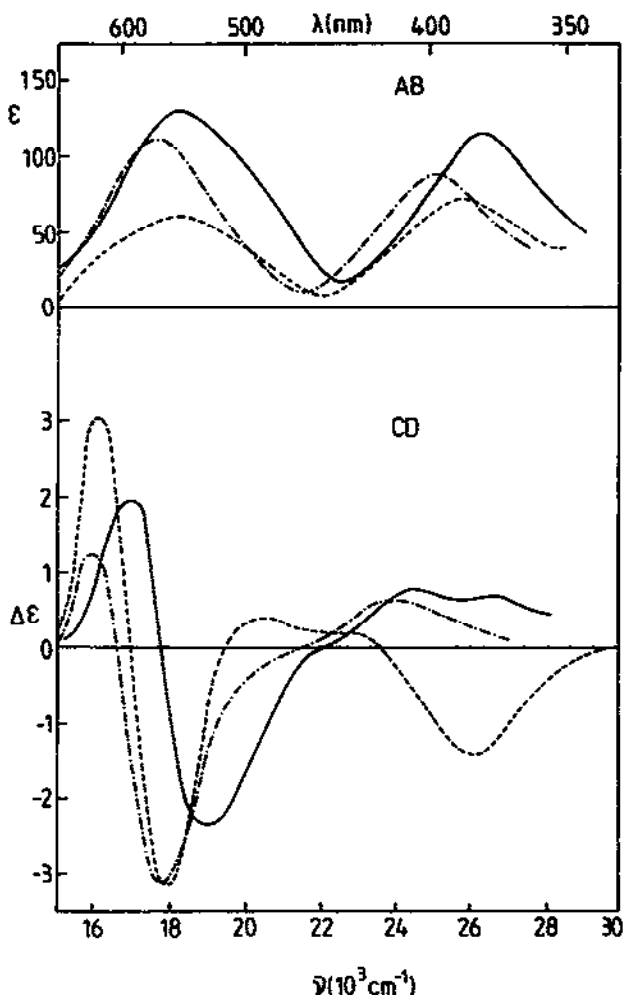


Fig. 8. Electronic absorption and CD spectra of $[\text{Co}(\text{edta-type})]^-$ complexes forming six-membered diamine rings. —, $\Lambda-(+)(-)\text{-(})_{546}\text{-}[\text{Co}(1,3\text{-pdta})]^-$; - - - -, $\Lambda-(+)(+)\text{-(})_{546}\text{-trans}(\text{O}_5\text{O}_6)\text{-}[\text{Co}(1,3\text{-pddadp})]^-$; and - · - ·, $\Lambda-(+)(+)\text{-(})_{546}\text{-trans}(\text{O}_6)\text{-}[\text{Co}(1,3\text{-pddadp})]^-$.

rings branch at vertices and span the octahedral edges. Thus the molecular basis for defining chirality is different for these complexes.

The complex $[\text{Co}(\text{en})(\text{mal})_2]^-$ (mal = malonate ion) was prepared as a *cis*- $[\text{Co}(\text{N})_2(\text{O})_4]$ strain-free model of $[\text{Co}(\text{edta})]^-$, both having C_2 symmetry [71]. The Λ configuration was assigned for $(-)\text{-(})_{546}\text{-}[\text{Co}(\text{en})(\text{mal})_2]^-$ as confirmed by crystallography [72]. Its CD spectrum shows a three-peak (+, −, +) pattern for the lower energy absorption band similar to the CD spectrum of $\Lambda\text{-}[\text{Co}(\text{S,S-edds})]^-$. If the diamine rings and C_2 axes of $[\text{Co}(\text{en})(\text{mal})_2]^-$ and $[\text{Co}(\text{edta})]^-$ are disposed in

the same way, the malonate ions span edges not spanned in $[\text{Co}(\text{edta})]^-$. Thus, the complexes share the same Λ designation, but they differ in the basis for chirality.

Stable hexadentate edta-type Cr(III) complexes are formed with ligands having longer carboxylate or diamine chains. The hexadentate complexes include those of 1,3-pdta [22,73], (S)-pdtp [13], tdtta [74], (SS)-ptnta [75], (SS)-edds [35], eddadp [27,35], 1,3-pddadp [39], eda3p [62], and edtp [11,62]. The complexes $(+)\text{}_{589}\text{-trans}(\text{O}_5)\text{-}[\text{Cr}(\text{SS-edds})]^-$, $(-)\text{}_{589}\text{-trans}(\text{O}_5)\text{-}[\text{Cr}(\text{eddadp})]^-$, and $(-)\text{}_{589}\text{-trans}(\text{O}_5, \text{O}_6)\text{-}[\text{Cr}(\text{eda3p})]^-$ give very similar CD spectra in the region of the lower energy absorption band [$A_{2g} \rightarrow T_{2g}(\text{O}_h)$ parentage] (Table 3 and Fig. 9). 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 corresponding absorption band. The complexes have been assigned the Λ configuration as required by the stereospecific (SS)-edds ligand and confirmed by X-ray crystallography for $(-)\text{}_{589}\text{-trans}(\text{O}_5)\text{-}[\text{Cr}(\text{eddadp})]^-$ [27] (Fig. 5). The CD spectrum of $(+)\text{}_{589}\text{-}[\text{Cr}(\text{SS-ptnta})]^-$ differs substantially from these others but the lowest energy CD positive peak was assigned as ${}^4B(C_2)$ from ${}^4E({}^4T_{2g})$ of either trigonal or tetragonal parentage [75]. On this basis, the Λ configuration was assigned. The CD spectrum of $(+)\text{}_{589}\text{-}[\text{Cr}(\text{edtp})]^-$ (Fig. 9) 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 or canceled by the intense positive peak near the absorption maximum. The $(+)\text{}_{589}\text{-}[\text{Cr}(\text{edtp})]^-$ ion was assigned the Δ configuration [62] because its dominant positive CD peak band of $A_{2g} \rightarrow T_{2g}(\text{O}_h)$ parentage is opposite compared with the dominant bands of those similar complexes which have been shown to have the Λ configuration. This Δ configuration for $(+)\text{}_{589}\text{-}[\text{Cr}(\text{edtp})]^-$ was confirmed by the X-ray structure [11]. Kaizaki et al. [13] reported that the CD spectrum of $\Lambda\text{-}[\text{Cr}(\text{S-pdtp})]^-$ is nearly the mirror image of the spectrum of $\Delta\text{-}[\text{Cr}(\text{edtp})]^-$.

8. SUMMARY

Recent structural and spectral studies of edta-type complexes of Co(III), Cr(III), and Rh(III) have provided data for a wide range of compounds and give a good overall view. The determination of absolute configurations by X-ray crystallography of representative complexes have made spectral assignments more certain. Some structural changes in chelate ring sizes intended to relieve strain have introduced other strain. The study of conformational isomers of Cr(III) and the unexpected C–N bond cleavage for some of these complexes have been important advances.

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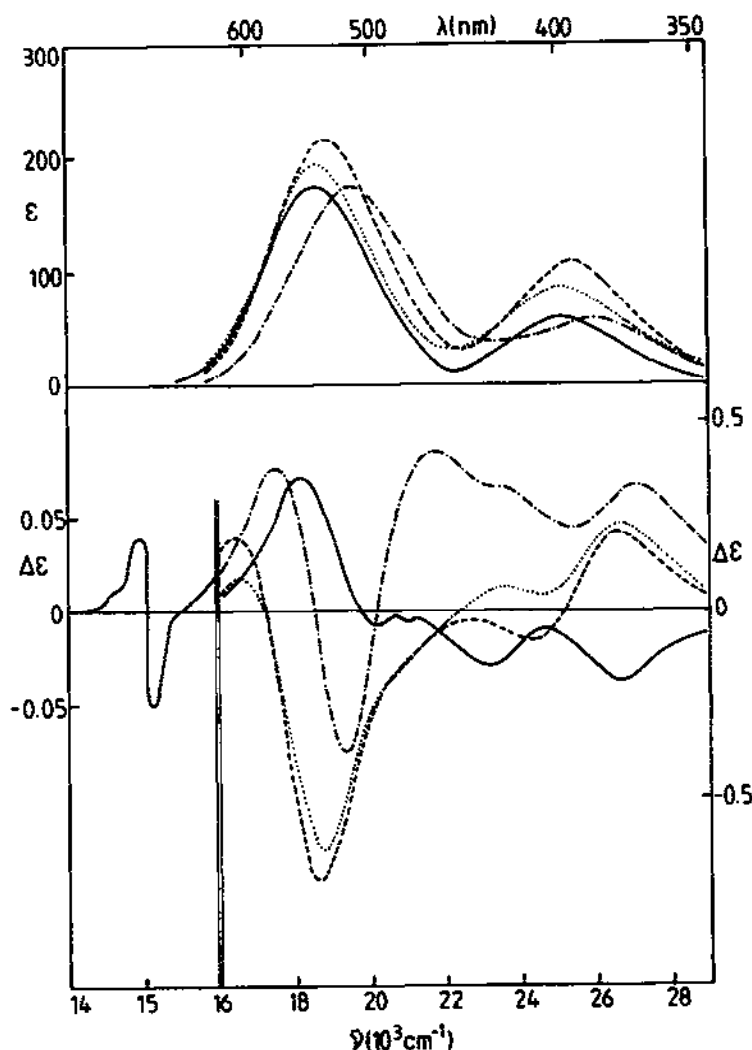


Fig. 9. Electronic absorption and CD spectra of $[\text{Cr}(\text{edta-type})]^-$ complexes. —, $\Lambda(+)(+)_\text{589-trans}(\text{O}_5)-[\text{Cr}(\text{SS-edds})]^-$; ---, $\Lambda(+)(-)_\text{589-trans}(\text{O}_5)-[\text{Cr}(\text{eddadp})]^-$; ····, $\Lambda(+)(-)_\text{589-trans}(\text{O}_5\text{O}_6)-[\text{Cr}(\text{eda3p})]^-$; and —, $\Lambda(+)_\text{589}-[\text{Cr}(\text{edtp})]^-$.

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