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OPTICAL ACTIVITY OF COBALT(III), CHROMIUM(III) AND RHODIUM(III) COMPLEXES WITH AMINOPOLYCARBOXYLATE EDTA-TYPE AND RELATED LIGANDS

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CONTENTS

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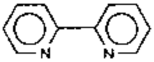
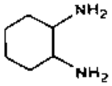
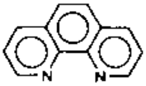
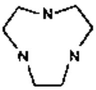
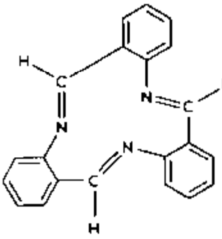
ABBREVIATIONS

ala	alaninate	$H_2NCH(CH_3)COO^-$
asp	aspartate	$H_2NCH(CH_2COO^-)COO^-$
bipy	2,2′-bipyridine	
bn	*meso*-2,3-butanediamine	$H_2NCH(CH_3)CH(CH_3)NH_2$
chxn	1,2-cyclohexanediamine	
dcb	*cis*-2-butene-1,4-diamine	$H_2NCH_2CH{=}CHCH_2NH_2$
deen	*N*,*N*′-diethylethylenediamine	$(CH_3CH_2)HNCH_2CH_2NH(CH_2CH_3)$
dmen	*N*,*N*′-dimethylethylenediamine	$(CH_3)HNCH_2CH_2NH(CH_3)$
edma	ethylenediaminemonoacetate	$H_2NCH_2CH_2NH(CH_2COO^-)$
een	*N*-ethylethylenediamine	$H_2NCH_2CH_2NH(CH_2CH_3)$
elam	2-aminoethanol (ethanolamine)	$H_2NCH_2CH_2OH$
en	ethylenediamine	$H_2NCH_2CH_2NH_2$
glu	glutamate	$H_2NCH(CH_2CH_2COO^-)COO^-$
gly	glycinate	$H_2NCH_2COO^-$
ida	iminodiacetate	$NH(CH_2COO^-)_2$
ileu	isoleucinate	$H_2NCH[CH(CH_3)(CH_2CH_3)]COO^-$
mal	malonate	$^-OOCCH_2COO^-$
men	*N*-methylethylenediamine	$H_2NCH_2CH_2NH(CH_3)$
nta	nitrilotriacetate	$N(CH_2COO^-)_3$
OAc	acetate anion	CH_3COO^-
ox	oxalate	$^-OOCCOO^-$
phen	1,10-phenanthroline	
pn	1,2-propanediamine (propylenediamine)	$H_2NCH(CH_3)CH_2NH_2$
pro	prolinate	$HN(CH_2)_3CHCOO^-$
ptn	2,4-pentanediamine	$H_2NCH(CH_3)CH_2CH(CH_3)NH_2$
py	pyridine	
stien	1,2-diphenyl-1,2-ethanediamine (stilbenediamine)	$H_2NCH(C_6H_5)CH(C_6H_5)NH_2$
tacn	1,4,7-triazacyclononane	
tart	tartrate	$^-OOCCH(OH)CH(OH)COO^-$

tmd	1,4-butanediamine	$H_2NCH_2CH_2CH_2CH_2NH_2$
tn	1,3-propanediamine (trimethylenediamine)	$H_2NCH_2CH_2CH_2NH_2$
tri	tribenzo[b,f,j]-[1,5,9]triazacycloduodecine	
val	valinate	$H_2NCH[CH(CH_3)_2]COO^-$

A. INTRODUCTION

The present work is a review of the studies of optical activity and stereochemistry of the transition metal complexes (M^{III} = Co, Cr and Rh) with aminopolycarboxylate edta-type and related ligands. It includes those papers which were published or submitted for publication by the end of August 1982. The basic ligands reviewed include: (a) the hexadentate edta-type and structurally related ligands which differ in ligand donating atoms, varying from N_4O_2 for triethylenetetraamine-N^2,N^3-diacetate (ttda, $(^-OOCCH_2)(H_2NCH_2CH_2)NCH_2CH_2N(CH_2CH_2NH_2)(CH_2COO^-)$), to N_2O_4 for ethylenediaminetetraacetate (edta, $(^-OOCCH_2)_2NCH_2CH_2N(CH_2COO^-)_2$), 1,3-propanediaminetetraacetate (trimethylenediaminetetraacetate) (1,3-pdta or trdta, $(^-OOCCH_2)_2NCH_2CH_2CH_2N(CH_2COO^-)_2$), ethylenediaminetetrapropionate (edtp, $(^-OOCCH_2CH_2)_2NCH_2CH_2N(CH_2CH_2COO^-)_2$), (*S*,*S*)-ethylenediamine-*N*,*N*′-disuccinate (*SS*-edds, $[^-OOC(^-OOCCH_2)CH]NHCH_2CH_2NH[CH(CH_2COO^-)COO^-]$), ethylenediamine-*N*,*N*-diacetate-*N*′-monosuccinate (*S*-eddams, $[^-OOC(^-OOCCH_2)CH]NHCH_2CH_2N(CH_2COO^-)_2$), and ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate (eddda, $(^-OOCCH_2)(^-OOCCH_2CH_2)NCH_2CH_2N(CH_2CH_2COO^-)(CH_2COO^-)$); (b) the quinquedentate ed3a-type ligands such as ethylenediamine-*N*,*N*,*N*′-triacetate (ed3a, $(^-OOCCH_2)NHCH_2CH_2N(CH_2COO^-)_2$), and 1,3-propanediamine-*N*,-*N*,*N*′-triacetate (1,3-pd3a, $(^-OOCCH_2)NHCH_2CH_2CH_2N(CH_2COO^-)_2$); (c) the quadridentate edda-type ligands such as ethylenediamine-*N*,*N*′-diacetate (edda, $(^-OOCCH_2)NHCH_2CH_2NH(CH_2COO^-)$), and 1,3-propanediamine-*N*,*N*′-diacetate (trimethylenediamine-*N*,*N*′-diacetate) (1,3-pdda or tmdda, $(^-OOCCH_2)NHCH_2CH_2CH_2NH(CH_2COO^-)$) and various alkyl-substituted derivatives and some analogues of the above ligands.

Structural determinations have provided data leading to some understanding of the influence of ligand configuration and conformation, and metal ion size on the geometry and number of ligand sites attached to the metal ion. Considerable information pertaining to the conformation and properties of five-membered and six-membered chelate rings have been obtained from PMR, ^{13}C NMR and IR studies and steric considerations of complexes.

The most important aspect of the studies of these complexes has been directed to determine the influence of various structural changes of the ligand and the relative effects of these and other factors on optical activity. The important structural types are provided by complexes of hexadentate (edta-type), quinquedentate (ed3a-type) and quadridentate (edda-type) ligands. Most of the data available has been obtained for complexes of cobalt(III), which serve as useful models for complexes with other metal ions. Finally, the complexes chosen to be reviewed are not only of interest for the understanding of their stereochemistry but also for their applications in the bioinorganic field because they provide simple structural models of the active sites of metalloproteins [1].

B. GENERAL CONSIDERATIONS

(i) Geometry of complexes

The flexible edta ligand is hexadentate in the complex $[Co(edta)]^-$, giving only one geometric isomer, the *cis*(N)-isomer (Fig. 1). The structure of the (ethylenediaminetetraacetato)cobaltate(III) ion has been determined crystallographically by Weakliem and Hoard [2a]. Structural parameters of this chelate system show notable departures from regular octahedral coordination and imply that the system is strained. The two glycinate rings (desig-

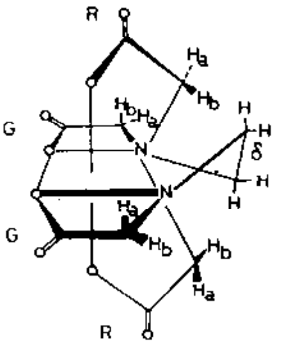


Fig. 1. The structure of $\Lambda(\delta)$-$(-)_{546}$-$[Co(edta)]^-$ complex.

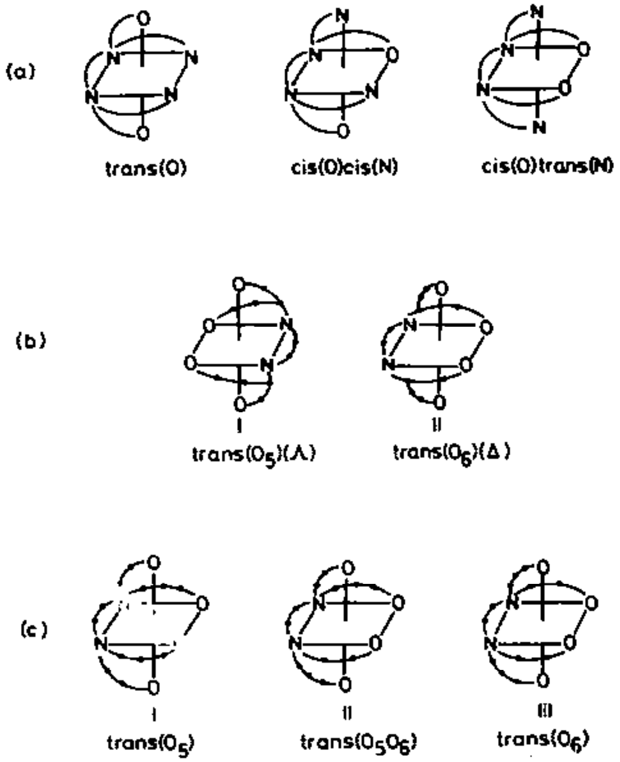


Fig. 2. Possible geometrical isomers of hexadentate complexes including various edta-type ligands: (a) ttda; (b) *SS*-edds; and (c) eddda.

nated as G, see Fig. 1) lying in the plane of the diamine ring are considerably more strained than the out-of-plane glycinate rings (designated as R rings). The ethylenediamine "backbone" ring of the [Co(edta)]$^-$ complex is locked in one conformation (δ for the structure shown in Fig. 1 having Λ configuration) [2b].

Structural variations of the edta framework involve increasing the size or rigidity of the chains, or omitting one or more of the carboxylate arms. In the case of the edta-type ligand with an extremely long diamine backbone chain, the hypothetical *trans*(N)-isomer (Fig. 3(a)) has been reported *.

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* The chromium(III) edta-type complexes of 1,5-pentanediaminetetraacetate (1,5-ptnta, $(^-OOCCH_2)_2N(CH_2)_5N(CH_2COO^-)_2$), oxybis(ethyleneaminediacetate) (eedta, $O[CH_2CH_2N(CH_2COO^-)_2]_2$), and thiobis(ethyleneaminediacetate) (tedta, $S[CH_2CH_2N(CH_2COO^-)_2]_2$) have recently been examined [3]. The authors have shown that the tedta ligand forms two isomers assigned as *cis* and *trans* with respect to the coordinated nitrogen atoms. In the *trans* isomer the ligand is hexadentate and the thioether sulfur atom occupies a coordination position. Its formation results from the maximum chelation achieved by the tedta ligand.

Isomerism is possible for complexes of hexadentate ligands where the carboxylate arms are replaced so as to form nonequivalent chelate rings. The triethylenetetraamine-N^2,N^3-diacetate ion (ttda) has ethylamine groups replacing two of the glycinate arms. Three isomers of [M(ttda)]$^+$ are possible: *trans*(O), *cis*(O)*cis*(N) and *cis*(O)*trans*(N) (Fig. 2(a)). Other ligands, structurally similar to edta, such as *SS*-edds ((*S,S*-ethylenediamine-*N,N'*-disuccinate) and eddda (ethylenediamine-*N,N'*-diacetate-*N,N'*-di-3-propionate) having two longer carboxylate chains, form isomers differing in the number of six-membered rings in the girdle plane. The optically active *SS*-edds ligand could theoretically form two isomers: *trans*(O_5) (I) and *trans*(O_6) (II) having opposite absolute configuration (Fig. 2(b)). In the case

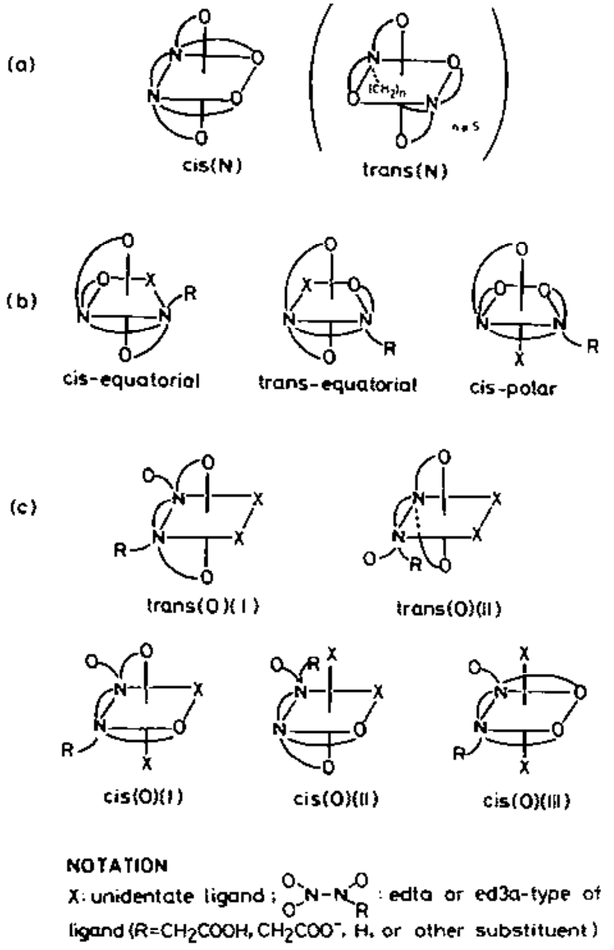

Fig. 3. Geometrical isomerism of six-coordinate complexes with diamine-tetra- or -triacetate ligands: (a) hexadentate; (b) quinquedentate; (c) quadridentate.

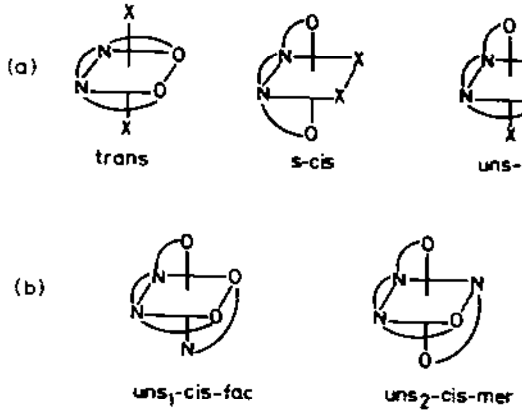

Fig. 4. Geometrical isomerism of six-coordinate complexes including (a) a flexible quadridentate edda-type ligand, and (b) isomerism introduced in a mixed unsymmetrical bidentate flexible quadridentate ligand complex of uns-*cis* configuration.

of the coordinated eddda ligand, three isomers, differing in the number (0, 1 or 2) of six-membered rings in the girdle plane are possible: *trans*(O_5) (I), *trans*(O_5O_6) (II), and *trans*(O_6) (III) (Fig. 2(c)).

In many cases where the number of donor atoms bound to the metal ion is less than six, the quinquedentate or quadridentate ligand admits the possibility of further isomerism. In general, when edta or ed3a (ethylenediamine-N,N',N'-triacetate) are quinquedentate, three possible geometric isomers are expected. The isomers are assigned as *cis*-equatorial, *trans*-equatorial and *cis*-polar (Fig. 3(b)). Furthermore, the two unidentate ligands with respect to the edta or ed3a acting as a quadridentate make possible the isomerism shown in Fig. 3(c) (*trans*(O) (I), *trans*(O) (II), *cis*(O) (I), *cis*(O) (II) and *cis*(O) (III)).

A linear flexible edda-type ligand can occupy four coordination sites with three geometric isomers possible: *trans*, s-*cis* und uns-*cis* (Fig. 4(a)) *. An unsymmetrical bidentate ligand coordinated along with a quadridentate edda-type ligand in the uns-*cis* configuration admits the possibility of isomerism shown in Fig. 4(b).

The chelate rings formed by multidentate ligands are likened to the saturated heterocyclic systems in organic chemistry. The geometric isomer-

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* Abbreviations of the ligands and the nomenclature used for most edta-type and related complexes are those most commonly used. For the complexes of a flexible edda-type ligand the symmetrical-*cis*/unsymmetrical-*cis* (s-*cis*/uns-*cis*) nomenclature has been suggested by Worrell and Busch [4] as an alternative to the α-*cis*/β-*cis* nomenclature employed by Sargeson and Searle [5] or the *trans*/*cis* nomenclature of Legg and Cooke [6].

ism and number of isomers strongly depends on steric constraints, which can be explained by consideration of the conformations of the various possible isomers using the method of Corey and Bailar [7] and the principle of conformational analysis applied to multidentate ligand systems by Buckingham et al. [8] and Gollogly and Hawkins [9]. Certainly, the most elegant applications of conformational analysis to complexes containing multidentate ligands have recently appeared in support of X-ray structure determinations.

Most of the complexes exhibiting configurations shown in Figs. 2–4 have been isolated and characterized. All of them are optically active and many have been resolved.

(ii) Summary of adopted symbolism

The following symbols are used throughout the present article:

Λ, Δ	to describe the absolute configurations of metal complexes in accordance with IUPAC rules [10] (the tangent describes a right-handed (Δ) or a left-handed (Λ) helix with respect to the axis of the helix).
δ, λ	to describe the conformations of individual chelate rings according to the IUPAC rules (the tangent describes a right-handed (δ) or a left-handed (λ) helix with respect to the axis of the helix).
R,S	to describe the absolute configurations of tetrahedral carbon and nitrogen atoms according to the method of Cahn et al. [11].
d,l	to describe the rotation at the sodium D line.
$(+)_X$,$(-)_X$	to describe the rotation at a wavelength X.
$(+)$-[ ],$(-)$-[ ]	to describe the sign of the CD peak in the ligand field region (the lowest energy or the dominant CD peak)

For the assignment of the absolute configuration of the chelate complexes and conformations of individual chelate rings many forms of notation have been used [7,10,12–19]. Relationships between the adopted symbols (IUPAC) and those in earlier use are given in Table 1.

(iii) Stereochemically significant centers of the ligands

The structure of the basic ligands discussed here is shown in Fig. 5. As can be seen, some of ligands possess optically active centers at the coordinated nitrogen donor atoms (the stereospecific *SS*-edds and (S)-eddams ligands also possess asymmetric carbon atoms). The bonds from the nitrogen atoms are directed approximately tetrahedrally and contribution of their dissymme-

TABLE 1

Relationships between the adopted symbols (IUPAC) and those in earlier use

Absolute configuration [a]

IUPAC [10]	T.S. Piper [12] (C_3 axis)	Saito et al. [13]	Mason et al. [14]	Gillard [15]	Hawkins and Larsen [16]	Legg and Douglas [17]
Δ	Δ	L	$P(C_3)$ or $M(C_2)$	$R(C_3)$ or $S(C_2)$	Negative octant sign	$\Lambda(C_2)$
Λ	Λ	D	$M(C_3)$ or $P(C_2)$	$S(C_3)$ or $R(C_2)$	Positive octant sign	$\Delta(C_2)$

Conformation of the ring

IUPAC	A.D. Liehr [18]	Corey and Bailar [7]	Sargeson [19]	Hawkins and Larsen [16]
δ	δ	k′	k	Positive octant sign
λ	λ	k	k′	Negative octant sign

[a] The configurations of the chelate complexes are related to the helix described by any pair of chelate rings of $[Co(en)_3]^{3+}$ complex. The chirality is left-handed for $(+)_{589}$-$[Co(en)_3]^{3+}$ and this isomer is designated Λ [10,12]. The designation using the C_3 or pseudo-C_3 axis to relate the helix of the $[(Co(en)_3]^{3+}$ complex is equivalent to the IUPAC nomenclature except that in the case of multidentate complexes where IUPAC suggests that all skew lines pairs must be given. It is important to note that the helix is opposite if one uses the C_2 or pseudo-C_2 axis as the reference axis.

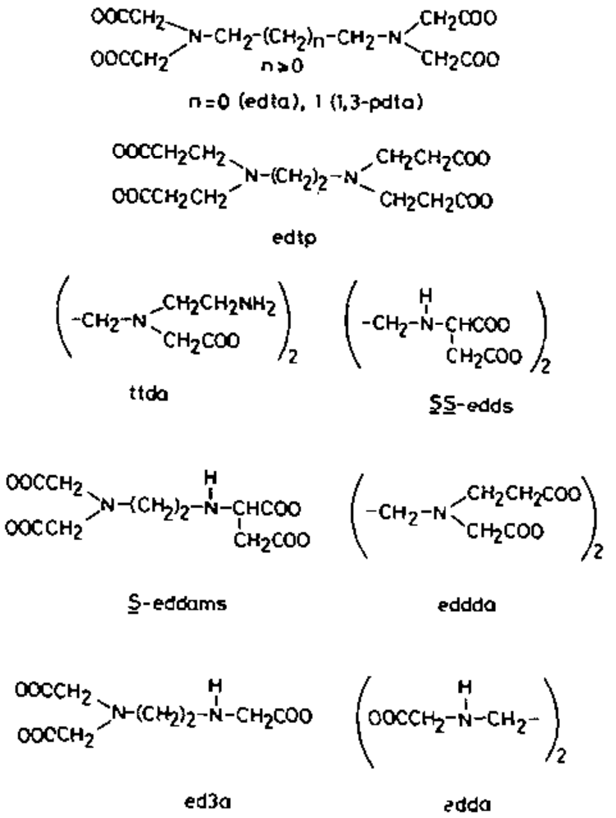


Fig. 5. The structure of the basic ligands. Optically active centers at the coordinated nitrogen donor atoms (ttda, *SS*-edds, *S*-eddams, eddda, ed3a and edda ligands).

try to the optical activity is not usually separable from chelate ring conformation contributions. In only a few complexes discussed here have the effects been dealt with separately.

The complexes with edta-type and related ligands, in which alkyl substituents are introduced to generate additional dissymmetric centers on the ligands will be discussed as derivatives of the parent ligands where appropriate. Such ligands having asymmetric carbon atoms exhibit absolute stereospecificity in the formation of metal complexes. The other ligands included in this review, which are not covered by the above classification, will be described as analogues of the basic ligands.

(iv) Optical activity and absolute configurations

There are two limiting cases for the origin of the optical activity exhibited by dissymmetric transition metal complexes: (a) when a symmetric chromophore is placed in a dissymmetric molecular field (in which case the origin of the optical activity is described in a number of theories [20–27]); and (b) when an optically active complex is regarded as a dissymmetric ensemble of symmetric chromophores formed by coordination to a central metal atom [28–31]. The reviewed complexes possess a symmetric chromophore placed in a dissymmetric environment and complexes of cobalt(III) provide a particularly comprehensive series of stable coordination compounds.

From the theoretical point of view, the fundamental theory of optical activity requires information about the electronic states and structures of individual molecules. Therefore, a number of complexes have been investigated and several surveys have appeared dealing with the application of optical activity to the study of coordination compounds [32].

It may be worthwhile to note here that the absolute configurations of complexes discussed in this article could not be assigned a priori from ORD or CD data. X-ray analysis is the only method for unequivocal assignment of the absolute configuration of metal complexes. Absolute configurations determined in this way serve as references and checks for the assignment of absolute configurations from CD data using empirical methods.

There are, then, essentially three methods available for assigning absolute configuration of related complexes: (1) by analysis of the mechanism of a reaction which converts a complex of known absolute configuration to one of unknown absolute configuration; (2) by comparison of ORD and CD data between complexes of known and unknown absolute configuration and (3) by stereochemical analysis of complexes formed from stereospecific ligands whose absolute configurations have been determined by X-ray crystallography.

The absolute configuration of the tris(ethylenediamine)cobalt(III) ion, which is dextrorotatory at the sodium D-line, $(+)_{589}$-$[Co(en)_3]^{3+}$, was determined to be Λ by X-ray analysis [13]. McCaffery and Mason [33] measured the circular dichroism of single crystals of Na-$(+)_{589}$-$[Co(en)_3]_2Cl_7 \cdot 6H_2O$. Since the optical axis is parallel to the C_3 axis of the complex ion and the electric vector of the light is perpendicular to the C_3 axis, only the $A_1 \rightarrow E$ transition is allowed. They assigned the longer wavelength band to that of E symmetry and the shorter wavelength component to that of A_2 symmetry. Crystal measurements show that the rotational strength of the E component of the octahedral T_{1g} transition is positive for the $(+)_{589}$-$[Co(en)_3]^{3+}$ complex of known Λ configuration [13] and similar tris(bidentate) d^6 complex ions having positive sign of the E component have been assigned the Λ absolute configuration. Application of this criterion requires the unambiguous identification of the symmetries of the electronic transitions which give rise to the observed Cotton effects.

Various rules, purely empirical or with theoretical justification, have been proposed to correlate circular dichroism data with absolute configurations.

Mason and co-workers [14b] proposed a method for relating absolute configurations of [Co(en)$_2$L]$^{n+}$ (L = two unidentate ligands or a bidentate ligand) to [Co(en)$_3$]$^{3+}$ of known absolute configuration [13]. The electronic transitions of these complexes with C_2 symmetry are related to those of [Co(en)$_3$]$^{3+}$ (D_3) which McCaffery and Mason had assigned from the polarized CD spectrum [33]. The relationship is illustrated in Fig. 6. Mason recognized that the A state (C_2 symmetry) had $E_a(D_3)$ parentage and that the A component should be dominant in the CD spectrum of [Co(en)$_2$L]$^{n+}$. As can be seen (Fig. 6) the isomer of [Co(en)$_2$L]$^{n+}$ is configurationally related to the corresponding isomer of [Co(en)$_3$]$^{3+}$ complex if the sign of the A component in the former is the same as that of the E_a component in the

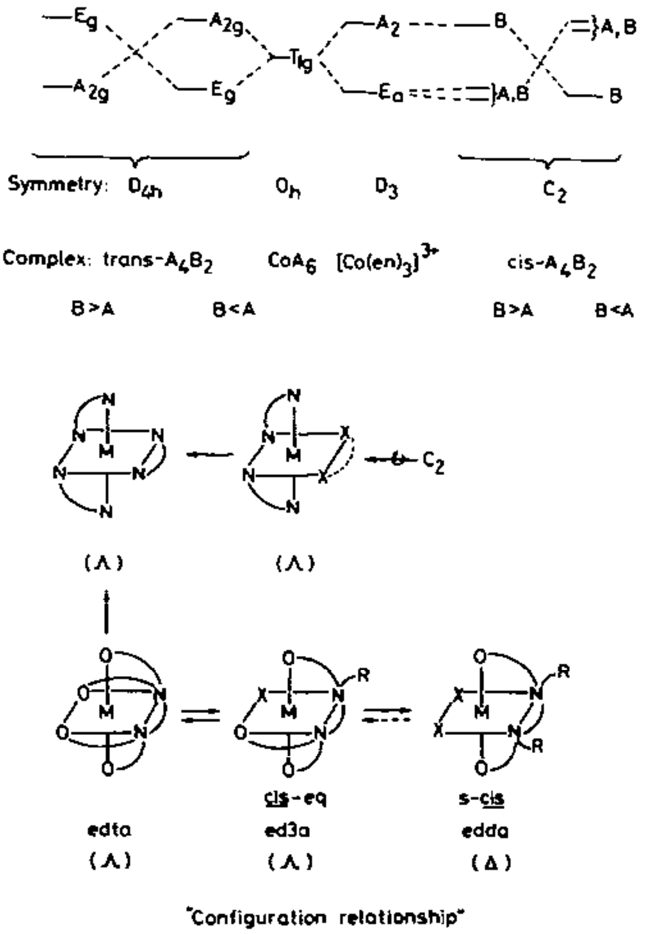


Fig. 6. Correlation of energy levels in the $^1T_{1g}(O_h)$ region for (top) strong-field Co(III) in various symmetries and (bottom) "configuration relationship" between Λ-[Co(en)$_3$]$^{3+}$ and Λ-[Co(en)$_2$(L)]$^{n+}$, Λ-[M(edta-type)]$^-$ and related complexes.

latter. The order of the states in the C_2 complexes is a function of the relative ligand strengths of the ligands involved.

The statement that two complexes are "configurationally related" has certain hidden implications and complex chelates such as those discussed in this review (Fig. 6) offer some interesting problems. In many cases their "configurational relationship" to $[Co(en)_3]^{3+}$ is not obvious (see later discussions).

Legg and Douglas [17] developed a "ring pairing" scheme to relate the configuration of multidentate complexes. This method is similar to the "octant sign" method for relating configurations proposed earlier by Hawkins and Larsen [16] and is closely related to the IUPAC rules [10]. Both methods are essentially empirical and equivalent. They cover the main symmetry types of cobalt(III) and other metal complexes and the sign of the Cotton effect due to a particular component descended from the octahedral T_{1g} transition in a trigonal, tetragonal or orthorhombic environment is correlated with the octant sign or net chirality.

The scheme of Mason and co-workers for relating absolute configurations (Fig. 6) [14b] presumes that the correct theoretical model for optical activity should be derived from a consideration of metal–ligand orbital overlap where the ligand orbitals are the antibonding orbitals on the nonligating atoms. On the other hand, Piper and Karipides [24] calculated the rotatory strength of some trigonal complexes using a static one-electron model earlier proposed by Moffitt [20]. This theory predicts that the sign of rotatory strength does not depend upon the absolute configuration of the chelate ring around the metal ion but is determined by the displacement of the coordinating atoms from the apices of a regular octahedron.

Wing and Eiss [34] determined the absolute configuration of bis(tribenzo[b,f,j]-[1,5,9]triazacycloduodecine)cobalt(III) ion, $(+)_{546}$-$[Co(tri)_2]^{3+}$. In addition, Shibata and co-workers [35] prepared and resolved $[(Co(tacn)(tri)]^{3+}$ complex (tacn = 1,4,7-triazacyclononane). From the CD spectral similarity of $(+)_{500}$-$[Co(tacn)(tri)]^{3+}$ with $(+)_{546}$-$[Co(tri)_2]^{3+}$, it has been suggested that the metal-centered optical activity of both complexes is derived from a chiral arrangement of (benzene ring)–C=N– moieties. $(+)_{546}$-$[Co(tri)_2]^{3+}$ is a "sandwich" type complex formed by six nitrogen atoms which possess a small twist distortion about the threefold axis in the counterclockwise direction as in the case of Λ-$(+)_{589}$-$[Co(en)_3]^{3+}$. This complex cannot be "configurationally related" to $[Co(en)_3]^{3+}$ (it has no "ring pairs") but has a remarkably similar CD spectrum in the region of the first absorption band to that of Λ-$(+)_{589}$-$[Co(en)_3]^{3+}$. The above facts constitute experimental support for Piper's model of optical activity in trigonal complexes and suggest that the "ring pairing" scheme may be limited to complexes with constraining ligands (in which the ligand–metal–ligand bond angles are less than 90°). The single crystal $d \rightarrow d$ CD studies of tris(trimethylenediamine)cobalt(III) ion [36], $[Co(tn)_3]^{3+}$, and tris(tetramethylenediamine)cobalt(III) ion [37], $[Co(tmd)_3]^{3+}$, also seem to support Piper's model. In these complexes it appears that the E_a and A_2 transitions are interchanged, leading to a reversal in the sign of E_a. In both cases crystal structure study revealed that the N–Co–N bond angles were greater than 90° and thus the observations on the CD spectra are consistent with Piper's prediction.

Shinada [25] calculated the optical rotatory dispersion of D_3 complexes by means of a purely ionic model. Schäffer [26] discussed the optical activity of D_3 complexes of Co(III) and Cr(III) in terms of the angular overlap model of bonding in complexes proposed by Yamatera [38]. The recent study of the vibronic fine structure in the CD of metal complexes could lead to a more rapid advance in this subject [32e].

Mason [39] devised regional rules correlating the position of a substituent added to the tetragonal chromophores, $[CoA_5B]$ and *trans*-$[CoA_4B_2]$ and the octahedral chromophore $[CoA_6]$. These rules are founded on the general symmetry aspects of the theory of the symmetric chromophore in a dissymmetric environment developed by Schellman [40] and have been applied to many amine complexes of Co(III) and analogous metal ions. The octant sign has been calculated by employing the coordinate function $z(x^2 - y^2)$ for each substituent.

A similar octahedral rule also has been used by Bosnich and Harrowfield [41]. They presented a rule for the optical activity of the $d \rightarrow d$ transitions of the conformational isomers of octahedral complexes. The effect of donor atom distortion and the contributions of the amino hydrogen atom, which were ignored in the previous regional rules, are taken into account.

Richardson [27a] examined the optical activity of trigonally distorted ML_6 clusters on the basis of an ionic model. According to this theory, the trigonal splitting parameter of the ${}^4A_{2g} \rightarrow {}^4T_{2g}$(Cr(III)) and of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$(Co(III)) transition may be controlled by an angle θ [42]. Strickland and Richardson [27d] also calculated rotatory strength for trigonally distorted complexes of Co(III) and Cr(III) using a molecular orbital model. Chirality is introduced into the ML_6 cluster either by a Piper representation (trigonal nuclear geometry) or by a Liehr representation (ligand donor orbitals canted from the M–L axes in an octahedral ML_6 cluster). This calculation supports the contention that trigonal dihedral transition metal complexes gain substantial optical activity in the visible region by the dissymmetric positioning of the ligating atoms. The theoretical interpretations explained above have enjoyed some success in explaining or rationalizing the observed CD spectra of a few specific systems or in providing a possible procedure for calculating the rotatory strengths of $d \rightarrow d$ transitions. However, these theories are not sufficiently explicit or general to permit widespread use in making spectra-structure correlations.

Richardson [27c] also used a model in which both ligand field theory and the one-electron static-coupling theory of optical activity were incorporated. He proposed sector rules which relate the sign of the total or net $d \rightarrow d$ rotatory strength (or the sign of the algebraic sum of the $d \rightarrow d$ CD band areas) to the distribution of ligand perturber sites (atoms or groups of atoms) about the metal ion.

Recently, Yamatera and co-workers [43] considered a tetragonal (D_{4h}) model of the $[M(A)_4(B)_2]^+$ 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 [44]. Such a correlation of energy states is given in Table 2.

TABLE 2

Correlation of representations in tetragonal Co(III) and Cr(III) complexes given by Yamatera [43]

O_h Co(III) complex	D_{4h} Co(III)	D_{4h} Cr(III)
$T_{1g}(t_{2g}{}^5e_g)$	E_g	$E_g\,(t_{2g}{}^2e_g)$
	A_{2g}	$B_{2g}(t_{2g}{}^2e_g)$
$T_{2g}(t_{2g}{}^5e_g)$	E_g	$E_g\,(t_{2g}{}^2e_g)$
	B_{2g}	$A_{2g}(t_{2g}{}^2e_g)$
$A_{1g}(t_{2g}{}^6)$	A_{1g}	$B_{1g}\,(t_{2g}{}^3)$
T_{1u}(CT) [a]	E_u	E_u (CT)
	A_{2u}	B_{2u}(CT)
T_{2u}(CT)	E_u	E_u (CT)
	B_{2u}	A_{2u}(CT)

[a] CT-charge-transfer bands.

The foregoing discussion serves only to point out the general state in the study of optical activity of complexes and its relationship to the assignment of electronic states and absolute configurations. The method outlined by Mason and co-workers [14b] and other methods [16,17,27c], have been employed for complexes discussed in this review and the results obtained have been strongly supported by the assignments made directly by crystallographic analysis or indirectly by using stereospecific ligands of known absolute configuration. Absolute configurations are described as "tentative" only when they are assigned on the basis of relative optical activity alone.

C. HEXADENTATE COMPLEXES WITH EDTA-TYPE LIGANDS

The hexadentate ligands discussed in this review are listed in Table 3. These multidentate ligands are all of the aminopolycarboxylate edta-type

TABLE 3

Hexadentate edta-type and structurally similar ligands

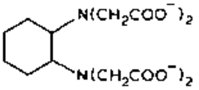
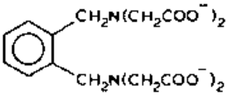
Ligand	Abbreviation
Ethylenediaminetetraacetate $(^-OOCCH_2)_2NCH_2CH_2N(CH_2COO^-)_2$	edta
1,2-Propanediaminetetraacetate (propylenediaminetetraacetate) $(^-OOCCH_2)_2NCH(CH_3)CH_2N(CH_2COO^-)_2$	pdta
meso-2,3-Butanediaminetetraacetate $(^-OOCCH_2)_2NCH(CH_3)CH(CH_3)N(CH_2COO^-)_2$	bdta
trans-1,2-Cyclohexanediaminetetraacetate 	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) 	xdta
1,3-Propanediaminetetraacetate (trimethylenediaminetetraacetate)- $(^-OOCCH_2)_2NCH_2CH_2CH_2N(CH_2COO^-)_2$	1,3-pdta (trdta)
1,3-Butanediaminetetraacetate $(^-OOCCH_2)_2NCH_2CH_2CH(CH_3)N(CH_2COO^-)_2$	1,3-mpdta
2,4-Pentanediaminetetraacetate $(^-OOCCH_2)_2NCH(CH_3)CH_2CH(CH_3)N(CH_2COO^-)_2$	2,4-ptnta
cis-2-Butene-1,4-diaminetetraacetate $(^-OOCCH_2)_2NCH_2CH{=}CHCH_2N(CH_2COO^-)_2$	dcbta
1,4-Butanediaminetetraacetate (tetramethylenediaminetetraacetate) $(^-OOCCH_2)_2NCH_2CH_2CH_2CH_2N(CH_2COO^-)_2$	tdta
1,5-Pentanediaminetetraacetate (pentamethylenediaminetetraacetate) $(^-OOCCH_2)_2NCH_2CH_2CH_2CH_2CH_2N(CH_2COO^-)_2$	1,5-ptnta (pmdta)
1,6-Hexanediaminetetraacetate (hexamethylenediaminetetraacetate) $(^-OOCCH_2)_2NCH_2CH_2CH_2CH_2CH_2CH_2N(CH_2COO^-)_2$	hdta
Thiobis(ethyleneaminediacetate) $S[CH_2CH_2N(CH_2COO^-)_2]_2$	tedta
Oxybis(ethyleneaminediacetate) $O[CH_2CH_2N(CH_2COO^-)_2]_2$	eedta
Ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-di-α-propionate $(^-OOCCH_2)[^-OOC(CH_3)CH]NCH_2CH_2N[CH(CH_3)COO^-](CH_2COO^-)$	edpa
Ethylenediaminetetrapropionate $(^-OOCCH_2CH_2)_2NCH_2CH_2N(CH_2CH_2COO^-)_2$	edtp
Ethylenediamine-*N*,*N*′-disuccinate $[^-OOC(^-OOCCH_2)CH]NHCH_2CH_2NH[CH(CH_2COO^-)COO^-]$	edds
N-Methylethylenediamine-*N*,*N*′-disuccinate $[^-OOC(^-OOCCH_2)CH]N(CH_3)CH_2CH_2NH[CH(CH_2COO^-)COO^-]$	medds

TABLE 3 (continued)

Ligand	Abbreviation
N,*N*′-Dimethylethylenediamine-*N*,*N*′-disuccinate $[^-OOC(^-OOCCH_2)CH]N(CH_3)CH_2CH_2(CH_3)N$-$[CH(CH_2COO^-)COO^-]$	dmedds
Ethylenediamine-*N*,*N*-diacetate-*N*′-monosuccinate $(^-OOCCH_2)_2NCH_2CH_2NH[CH(CH_2COO^-)COO^-]$	eddams
Ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate $(^-OOCCH_2)(^-OOCCH_2CH_2)NCH_2CH_2N(CH_2CH_2COO^-)$-$(CH_2COO^-)$	eddda
Triethylenetetraamine-N^2,N^3-diacetate $(^-OOCCH_2)(H_2NCH_2$-$CH_2)NCH_2CH_2N(CH_2CH_2NH_2)(CH_2COO^-)$	ttda
1,9-Diamino-3,7-diazanonane-3,7-diacetate $(^-OOCCH_2)(H_2$-$NCH_2CH_2)NCH_2CH_2CH_2N(CH_2CH_2NH_2)(CH_2COO^-)$	ddda
1,9-Diamino-4-methyl-3,7-diazanonane-3,7-diacetate $(^-OOCCH_2)(H_2NCH_2CH_2)NCH_2CH_2CH(CH_3)$-$N(CH_2CH_2NH_2)(CH_2COO^-)$	mddda

with ligand donating atoms varying from N_2O_4 for the ethylenediaminetetraacetate (edta) series to N_4O_2 for the triethylenetetraamine-N^2,N^3-diacetate (ttda) series. The most extensively studied ligand is edta and the work with the other ligands can be related to these studies directly or indirectly.

(i) Ethylenediaminetetraacetate (edta) and its substituted derivatives

This section includes the complexes with ethylenediaminetetraacetate ligand and its C-substituted derivatives such as 1,2-propanediaminetetraacetate (pdta), *trans*-1,2-cyclohexanediaminetetraacetate (cdta), *meso*-2,3-butanediaminetetraacetate (bdta) and stilbenediaminetetraacetate (sdta) (see structural formula of the ligands in Table 3). The ligands have been prepared generally by reactions of the diamines with chloro- or bromoacetic acid.

Complexes of ethylenediaminetetraacetic acid and other carboxylic acids have provided an impressive number and variety of studies [45] including those of thermochemical [46], kinetic [47] and many studies concerning stereochemical orientations.

Schwarzenbach [48] was the first to report the synthesis of a hexadentate $[Co(edta)]^-$ complex oxidizing the resulting cobalt(II) complex with bromine in glacial acetic acid. This procedure was later improved by Kirschner [49] who used hydrogen peroxide for the oxidation. Alkali metal salts of this complex were also prepared by bromine [48,50], chlorite [51], or hydrogen peroxide [52] oxidation of the appropriate cobalt(II) complexes.

Sawyer and McKinnie [53] reported the preparation of a hexadentate $[Cr(edta)]^-$ complex. In addition, Hoard et al. [54] have suggested that in the pH range 5 to 9, both $[Cr(edta)(H_2O)]^-$ and $[Cr(edta)(OH)]^{2-}$ are converted into the hexadentate $[Cr(edta)]^-$ and isolated the hexadentate complex in the solid state. However, the formation of a hexadentate $[Rh(edta)]^-$ complex has been indicated only from PMR solution studies by Smith and Sawyer [55].

The presence of the glycinate unit in the $[Co(edta)]^-$ and related compounds offers a unique probe into chelate stereochemistry. The methylene protons of the chelated glycinate ring are labilized selectively to isotopic deuterium exchange in D_2O solutions, thus enhancing the NMR probe and the assignments of complexes. Deuterium exchange techniques [56c–g], H–N–C–H spin-spin coupling [56b,56e] and anisotropy arguments [6,56b] have been used to assign the PMR spectra and consequently the stereochemistries of a large number of cobalt(III) complexes related to the $[Co(edta)]^-$ chelate system.

Day and Reilley [56a] discussed and interpreted PMR spectra for a series of complexes of cobalt(III) with ethylenediaminetetraacetate ligand and its derivatives (pdta, 2,3-bdta and cdta). The differences in lability have been ascribed to structural effects within the ligand. The two octahedral configurations have been predicted for the $[Co(2,3\text{-bdta})]^-$ complex having one axial substituent on the diamine backbone.

Terrill and Reilley [56d] have shown from PMR studies that acid-catalyzed deuterium exchange of the methylenes of $[Co(edta)]^-$ at 85–103°C in the acidity range 0.05–0.5 M occurs most rapidly at the out-of-plane glycinate methylenes, with the in-plane glycinate rings exchanging very slowly. They found that the ethylenediamine methylenes do not undergo any observable exchange under these conditions. Similar trends were also observed for $[Co(cdta)]^-$ and $[Co(pdta)]^-$.

Legg and co-workers [56f] compiled PMR data and classified the chemical shifts observed for the various types of glycinate rings in a manner which is helpful to stereochemists working with multidentate aminopolycarboxylate chelates. Sudmeier et al. [56g] completed assignments of the individual glycinate methylene protons in $[Co(pdta)]^-$ and $[Co(edta)]^-$ hexadentate complexes. "Tickling" experiments were used to establish the identities of the overlapping *AB* patterns in complexes. Stereospecific acid- and base-catalyzed deuterations of glycinate protons were carried out, leading to the assignment of the individual glycinate proton resonances. They demonstrated that the magnitudes of the glycinate proton geminal coupling constants provide a valuable diagnosis for assignment of out-of-plane ($J \approx -18$ Hz) and in-plane ($J \approx -16$ Hz) *AB* patterns.

The observations of Terrill and Reilley [56d] have been utilized by Blackmer and Vickrey [57] in their ^{13}C NMR studies of the kinetics of deuterium exchange for three hexadentate cobalt(III) aminopolycarboxylates: $[Co(edta)]^-$, $[Co(cdta)]^-$ and $[Co(pdta)]^-$. Howarth et al. [58–60] also used the conclusions of Terrill and Reilley in interpreting the ^{13}C NMR spectra of $[Co(edta)]^-$, $[Co(Hedta)]$ and $[Co(cdta)]^-$ complexes (Hedta denotes a quinquedentate ethylenediaminetetraacetate ligand with a free acetate branch). Recently, Chang and Douglas [61] provided detailed assignments of the ^{13}C NMR spectra of a series hexadentate edta-type complexes with cobalt(III). They considered the strain effects in the complexes with respect to the chemical shift ranges of similar carbons in related compounds. The chemical shifts have been correlated with the C–N–C bond angles made between the methylene carbons of the side ring and of the backbone ring at the coordinated nitrogen.

The resolution of $[Co(edta)]^-$ has been reported by several methods: by selective adsorption on optically active quartz [50]; by spontaneous resolution of its ammonium or rubidium salts [2a] and using the resolving agent to form diastereoisomers [52,62–66].

Dwyer and Garvan [63] demonstrated the utility of *d*- or *l*-*cis*-dinitrobis(ethylenediamine)cobalt(III) chloride as the resolving agent, to achieve rapid resolution of $[Co(edta)]^-$ ($[\alpha]_{546} = \pm 1000°$). In addition, the resolution of this complex with $[Co(en)_2(ox)]^+$ was suggested by Dwyer et al. [64]. The same agent was used by Douglas and co-workers [65] who demonstrated an extremely convenient method for the resolution of $[Co(edta)]^-$. Recently, Gillard et al. [66] also reported an extremely convenient method for the resolution of $[Co(edta)]^-$ which involves the differing solubilities of the diastereoisomers with *S*-histidine.

Dwyer and Garvan [67] prepared *dl*-1,2-propanediaminetetraacetic acid and its optically active forms by the condensation of the racemic and active bases [68] with sodium chloroacetate at 20°C (the optical isomers gave $[\alpha]_D = \pm 47°$). The pure optical forms of the acid were also obtained from the cobalt(III) complex by its resolution through the *cis*-dinitrobis(ethylenediamine)cobalt(III) salt.

Later, Dwyer and Garvan [69] considered stereospecific influences in metal complexes containing optically active ligands. Only the *trans* form of cyclohexanediaminetetraacetic acid with both amino groups in equatorial positions (1e;2e) has been considered as a ligand since with the amino groups in axial positions both amino groups cannot coordinate to the metal ion. The resolution of the acid ($[\alpha]_D = \pm 53°$) has been achieved by the decomposition of the cobalt(III) complex resolved through the *cis*-dinitrobis(ethylenediamine)cobalt(III) salt. Two optical isomers of the hexadentate complex containing one optical form of the ligand (Λ and Δ, assigned in the original paper as *Ll* and *Dl*) have been considered and the isomer Λ involving considerable distortion of the cyclohexane ring has been excluded. *l*-*trans*-1,2-Cyclohexanediamine (*l*-chxn) (having the *RR* configura-

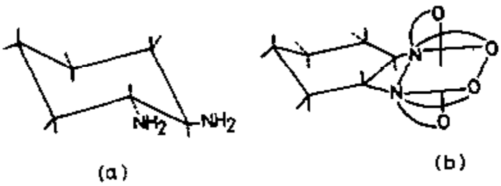


Fig. 7. The structure of (a) *RR-trans*-1,2-cyclohexanediamine, and (b) coordinated *RR-trans*-1,2-cyclohexanediaminetetraacetate in Δ-$(+)_{546}$-[Co(RR-cdta)]$^-$ complex.

tion [70], Fig. 7(a)) reacts with sodium chloroacetate to give *l-trans*-1,2-cyclohexanediaminetetraacetic acid with full retention of configuration and this ligand coordinates stereospecifically, giving only the structure shown in Fig. 7(b). Dwyer and Garvan also considered two optical isomers of a hexadentate complex which arise from *l*-1,2-propanediaminetetraacetic acid (Λ and Δ, assigned in the original paper as *Ll* and *Dl*) *. Since molecular models suggested that one isomer (Δ) should be preferred (a free-energy difference 3 kcal mol^{-1}) the strained Λ isomer has been excluded. *l*-Propanediamine (*l*-pn), having the *R* configuration [71,72], reacts with sodium chloroacetate to give *R*-1,2-propanediaminetetraacetic acid which coordinates stereospecifically, giving only one optical isomer of the resulting chelate. A similar effect has been predicted in the complexes of *meso*-2,3-butanediaminetetraacetic acid in which case the isomers are formed by the alignment of two asymmetric carbons, *R* and *S*, for each of the absolute configurations, Δ and Λ.

In a recent paper, Pavelčik and Majer [73] have employed molecular mechanics calculations for the study of the stereochemistry and relative energy of diastereoisomers of Λ-[Co(bdta)]$^-$ complex containing the ligand of known (*SS* or *RR*) absolute configuration. The calculated thermodynamic stabilities of the complexes decrease in the order (*SS*)-bdta > (*RS*)-bdta > (*RR*)-bdta. In the Λ-[Co(RR-bdta)]$^-$ isomer there are large repulsion interactions between the axial groups and the atoms of the R and G rings and the formation of this isomer in solution is thermodynamically improbable. The bdta exhibits high, possibly absolute stereoselectivity. *RR*-bdta coordinates to form a complex with absolute Δ configuration and *SS*-bdta with absolute Λ configuration.

Dwyer and MacDermott [74] considered the stereochemistry of the [Co(R-pdta)]$^-$ complex using the method of Corey and Bailar [7] and demonstrated four possible isomers: 1a, 2a, 1e and 2e (Fig. 8). They

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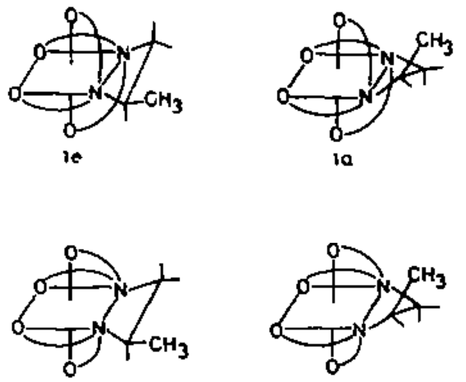
* In this work [69] the notation *L*, *D* refers to the sign of rotation of complexes at 546 nm. The given figure represents two different configurations of ligand in the same (Δ) absolute configuration of complex, contrary to the explanation in the legend.



1e 1a 2e 2a

Fig. 8. Four possible isomers of $[Co(R\text{-pdta})]^-$ complex.

concluded that the most stable isomer, obtained in the previous studies [67,69], is probably isomer 1e, as the first two forms (1a and 2a) are of the unstable axial type, and 2e suffers appreciable steric distortion. $(+)_{546}$-$[Co(R\text{-pdta})]^-$, assigned the 1e configuration on the basis of the preceding discussion [7,19], serves as a standard for the assignment of configurations of the $[Co(edta)]^-$ type and related complexes.

MacDermott and Sargeson [75] used the expected stereospecificity in the formation of $[Co(l\text{-pdta})]^-$ and $[Co(l\text{-cdta})]^-$ complexes to assign their absolute configurations. As the conformation of the l-pn ring (Λ [10] or k in Bailar's notation [7]) with the methyl group equatorial is the most stable form, they reasoned that the $(+)_{546}$-$[Co(l\text{-pdta})]^-$ complex must adopt the configuration shown in Fig. 9(a) and this was assigned as L by comparison with L-$[Co(en)(ox)_2]^-$ (Fig. 9(b)), and L-$[Co(en)_3]^{3+}$ (Fig. 9(c)). The $(+)_{546}$-$[Co(l\text{-cdta})]^-$ (Fig. 7(b)) has also been assigned L from comparison of ORD curves. Since L-$(+)_{546}$-$[Co(l\text{-pdta})]^-$, $(+)_{546}$-$[Co(edta)]^-$ and $(+)_{546}$-$[Co(en)(ox)_2]^-$ complexes had practically identical ORD curves, it was concluded that all of them have the same L configuration. As the ions $[Co(edta)]^-$ and $[Co(en)_3]^{3+}$ have widely differing symmetry properties, the authors chose to designate "b" as L (Fig. 10) and to relate "b" and "c"

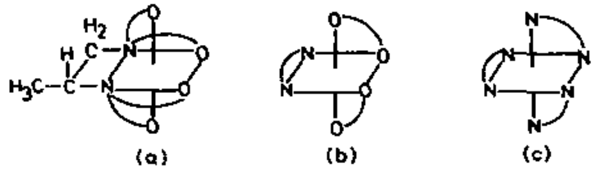


Fig. 9. Comparison between (a) Δ-$(+)_{546}$-$[Co(R\text{-pdta})]^-$, (b) Δ-$(+)_{546}$-$[Co(en)(ox)_2]^-$ and (c) Δ-$(-)_{589}$-$[Co(en)_3]^{3+}$ (assigned the same L configuration [75]).

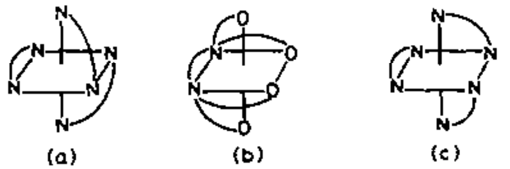
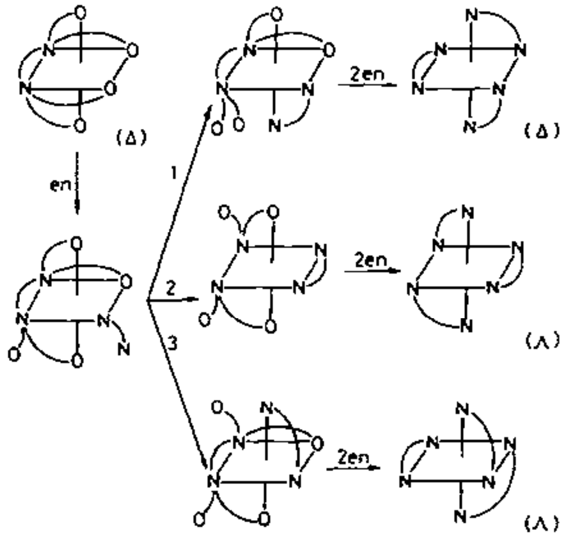

(a) (b) (c)

Fig. 10. Relationship between (a) Λ-$(+)_{589}$-$[\mathrm{Co(en)_3}]^{3+}$, (b) Δ-$(+)_{546}$-$[\mathrm{Co(edta)}]^-$ and (c) Δ-$(-)_{589}$-$[\mathrm{Co(en)_3}]^{3+}$ complex. (Reproduced with permission from ref. 75; copyright 1963 CSIRO, Australia.)

through the $(+)_{546}$-$[\mathrm{Co(en)(ox)_2}]^-$ ion which had a similar ORD spectrum and diastereoisomer solubility, to $(+)_{546}$-$[\mathrm{Co(edta)}]^-$ whose symmetry could be easily related to the *L*-$[\mathrm{Co(en)_3}]^{3+}$ ion.

Busch et al. [47a] reached the same conclusion regarding the structure of $(+)_{546}$-[Co(*l*-pdta)]$^-$ and $(+)_{546}$-$[\mathrm{Co(edta)}]^-$ complexes from kinetic studies but have designated the absolute configurations as *D*. The difference arises because of the arbitrary choice to be made in relating the $[\mathrm{Co(edta)}]^-$ complex to one of the isomers of $[\mathrm{Co(en)_3}]^{3+}$, since they differ in the number and arrangement of chelate rings *. Additionally, Busch et al. [47b] proposed the mechanism of the replacement of the edta or pdta by ethylenediamine (see Scheme I). In anhydrous ethylenediamine, Δ-$[\mathrm{Co(edta)}]^-$ produces Δ-



Scheme I. Proposed mechanism by Busch et al. [47b].

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* This confusion in the use of the *D*,*L* notation indicates the need for introducing new notation. In this case both research groups agreed on the structure of $(+)_{546}$-$[\mathrm{Co(edta)}]^-$ as that in Fig. 10(b), but they disagreed on how to relate it to $[\mathrm{Co(en)_3}]^{3+}$. On the basis of the IUPAC rules [10] $(+)_{546}$-$[\mathrm{Co(edta)}]^-$ has ΔΛΔ or net Δ chirality.

and Λ-$[Co(en)_3]^{3+}$ in the ratio of 1:2 [47b], while Δ-$[Co(R\text{-pdta})]^-$ gives almost 100% of Δ-$[Co(en)_3]^{3+}$ [47c], that is, the reaction of Δ-$[Co(edta)]^-$ proceeds through paths 1, 2 and 3 in equal probability, while that of Δ-$[Co(R\text{-pdta})]^-$ only goes through the path retaining the configuration.

Hidaka et al. [76] reported the electronic absorption and ORD spectrum of $(-)_{546}$-$[Co(edta)]^-$. Since two Cotton effects were identified in the low-energy region, the tetragonal crystal field about cobalt(III) was suggested.

Douglas et al. [77] discussed the electronic absorption ORD and CD spectra of $(-)_{546}$-$[Co(edta)]^-$, $(+)_{546}$-$[Co(en)(ox)_2]^-$ and $(-)_{546}$-$[Co(en)(mal)_2]^-$ complexes (the electronic absorption and CD data for $(-)_{546}$-$[Co(edta)]^-$ and its derivatives are summarized in Table 4). Two absorption bands were observed for each compound (suggesting an effectively cubic field), but their ORD curves show two components in the region of the lower energy band and the CD curves can be interpreted in terms of three components for each band (see Fig. 11). The CD spectrum of $(-)_{546}$-

TABLE 4

Absorption (AB) and circular dichroism (CD) data for hexadentate $[M(edta)]^-$ and directly related complexes

Complex	AB		CD		Ref.
	$\tilde{\nu} \times 10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu} \times 10^{-3}$ (cm^{-1})	$\Delta\epsilon$	
Λ-$(-)_{546}$-$[Co(edta)]^-$	18.60	347	17.10	+1.50	77,83
			19.80	−0.69	
	26.65	246	23.80	+0.28	
			25.60	−0.09	
			27.60	+0.29	
Λ-$(-)_{546}$-$[Co(S\text{-pdta})]^-$	18.60	300	17.23	+1.58	81
			19.70	−0.76	
			(21.75)	−(0.23)	
	26.65	204	24.15	+0.32	
			26.00	−0.18	
			27.95	+0.34	
Λ-$(-)_{546}$-$[Co(SS\text{-cdta})]^-$	18.50	316	16.80	+1.43	81
			18.80	−1.72	
	26.20	221	23.80 [a]	+0.35 [a]	
			27.20 [a]	+0.43 [a]	
Λ-$(+)$-$[Co(SS\text{-sdta})]^-$	18.42	295	16.81	+0.95	85
			18.80	−2.57	
	26.18	219	24.10	+0.43	
			27.78	+0.42	
$[Cr(edta)]^-$					53,54
$[Cr(cdta)]^-$	18.25	215			84
	25.38	103			

[a] Estimated from spectra.

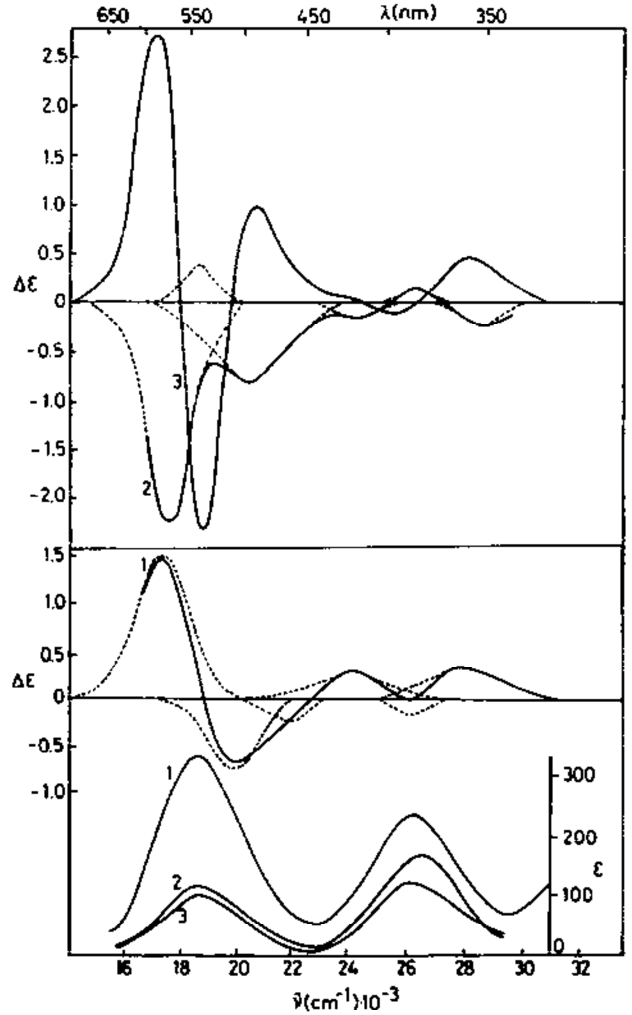


Fig. 11. CD and absorption spectra for (1) Λ-(−)$_{546}$-[Co(edta)]$^-$, (2) Δ-(+)$_{546}$-[Co(en)(ox)$_2$]$^-$ and (3) Λ-(−)$_{546}$-[Co(en)(mal)$_2$]$^-$ (observed curves (———), gaussian analysis (— — —)).

[Co(edta)]$^-$ was discussed in terms of C_2 symmetry in relating it to the model complexes [Co(en)(ox)$_2$]$^-$ and [Co(en)(mal)$_2$]$^-$. The *A* (lowest energy) component is dominant and has the same sign for all three complexes. On the basis of the positive CD sign *A*, ORD curves and diastereoisomer solubility data, the (−)$_{546}$ isomers have been assigned the Λ configuration. Later, this result was verified by X-rays in the case of (+)$_{546}$-[Co(edta)]$^-$ [2b] and (+)$_{546}$-[Co(en)(mal)$_2$]$^-$ [78] complexes having Δ configuration.

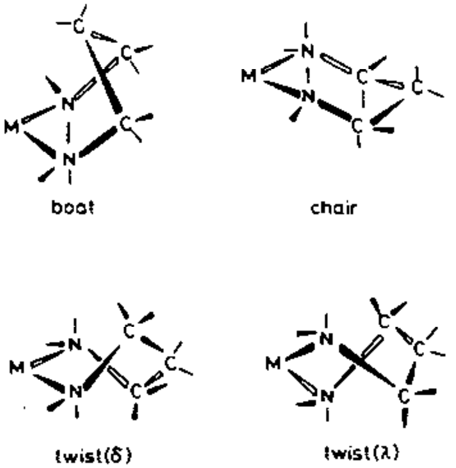
The (−)$_{546}$-[Co(*d*-pdta)]$^-$ and (−)$_{546}$-[Co(edta)]$^-$ complexes were also studied by Gillard [79] who discussed the electronic absorption, ORD and

CD spectra of these complexes. The CD spectra were interpreted in terms of two components for each absorption band. Later, Gillard [80a] reported the electronic absorption spectra (and IR data [80b]) for several complexes of ethylenediaminetetraacetate and *d*-1,2-propanediaminetetraacetate ligands with cobalt(III), rhodium(III) and chromium(III) in which the ligands act as a quadridentate (for rhodium(III)), quinquedentate and also hexadentate in the case of cobalt(III). The CD spectra were measured for $(-)_{546}$-$[Co(edta)]^-$ and $(-)_{546}$-$[Co(d\text{-pdta})]^-$ complexes for which the same configuration was found. Since the configuration of $(-)_{546}$-$[Co(d\text{-pdta})]^-$ is known [69] from the stereospecific requirement of the methyl group, this configuration was described as Δ (the notation used in the original paper is $S(C_2)$). The assignment is opposite to that made by MacDermott and Sargeson [75] and Douglas et al. [77]. Again, the difference arises because of the arbitrary choice to be made in relating the $[Co(edta)]^-$ complex to one of the isomers of $[Co(en)_3]^{3+}$.

Brennan et al. [81] studied the contributions to the CD spectra for the optically active ligands in $(-)_{546}$-$[Co(d\text{-cdta})]^-$ and $(-)_{546}$-$[Co(d\text{-pdta})]^-$ complexes. The $(-)_{546}$-$[Co(d\text{-cdta})]^-$ complex was included for comparison to earlier $(-)_{546}$-$[Co(edta)]^-$ [77], $(-)_{546}$-$[Co(d\text{-pdta})]^-$ [82] and other model complexes [83]. They found that the spectrum of the $(-)_{546}$-$[Co(d\text{-pdta})]^-$ complex was very similar to the spectrum of $(-)_{546}$-$[Co(edta)]^-$, whereas the spectrum of the $(-)_{546}$-$[Co(d\text{-cdta})]^-$ complex, while similar to the other two, showed a high-energy peak with greater intensity (see Table 4). The authors concluded that the asymmetric carbon in the $(-)_{546}$-$[Co(d\text{-pdta})]^-$ complex has little effect on the CD spectrum. On the other hand, there was a greater contribution from the *d-trans*-1,2-cyclohexanediaminetetraacetate ligand to the CD spectra. The overall effect on the second peak intensity is comparable to that of structural changes in the edta framework for less strained models [83] of $[Co(edta)]^-$ complex. The $(-)_{546}$ isomers of these complexes (Table 4) were assigned the Λ configuration, as concluded from ORD data [75].

Tanaka et al. [84] have reported the preparation and characterization of sodium *trans*-1,2-cyclohexanediaminetetraacetatochromate(III) tetrahydrate, $Na[Cr(cdta)]\cdot 4H_2O$. The preparation of this complex strongly depends on pH. The isolated complex was characterized by means of electronic absorption and IR spectra.

Douglas and co-workers [85] have synthesized the cobalt(III) complex containing the *l*-stilbenediaminetetraacetate ion, $[Co(l\text{-sdta})]^-$, and studied the effects of the benzene rings on the CD spectra. *l*-Stilbenediaminetetraacetate (*l*-sdta) coordinates stereospecifically because the two benzene rings prefer the equatorial position. Since the ligand was prepared from *l*-stilbenediamine (*l*-stien) of known *SS* configuration [86] the formation of



boat

chair

twist(δ)

twist(λ)

Fig. 12. Possible conformations of six-membered 1,3-diamine chelates.

the complex is stereoselective, yielding only one optical isomer of known Λ configuration. The absorption, circular dichroism, ^{1}H NMR and ^{13}C NMR spectra have been used to characterize the complex and data obtained were compared to those of other cobalt(III) hexadentate complexes. The CD spectrum of $[Co(l\text{-sdta})]^-$ is more similar to those of the less strained model complexes [83] than to that for $[Co(edta)]^-$.

(ii) Analogues of ethylenediaminetetraacetate with lengthened diamine chains

(a) 1,3-Propanediaminetetraacetate (1,3-pdta or trdta) and its derivatives

Complexes with ligands related to ethylenediaminetetraacetate, but with lengthened diamine backbone chains, have been reported. The complexes of 1,3-propanediaminetetraacetic acid and its derivatives, (1,3-butanediaminetetraacetate (1,3-mpdta), and 2,4-pentanediaminetetraacetate (2,4-ptnta) ligands, see Table 3) involve six-membered chelate diamine rings with puckered skeletal structures. Four conformers of the diamine chelate rings are possible: chair, two twist (δ) and (λ), and a boat form, as shown in Fig. 12. Molecular models show that a stable octahedral complex with the ligand hexadentate should have a twist form and that the δ twist gives a complex with the Λ configuration and the λ twist gives the Δ configuration, as has been crystallographically confirmed [87,88]. Absorption and CD spectra obtained for the complexes described in this section are summarized in Table 5.

In 1964, Tanaka and Ogino [89] reported the synthesis of potassium 1,3-propanediaminetetraacetatocobaltate(III) dihydrate, $K[Co(1,3\text{-pdta})] \cdot 2H_2O$. The electronic absorption and IR spectra were used to characterize

TABLE 5

Absorption (AB) and circular dichroism (CD) data for hexadentate [M(1,3-pdta)]$^-$ and related complexes

Complex	AB		CD		Ref.
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	$\Delta\epsilon$	
Λ-$(-)_{546}$-[Co(1,3-pdta)]$^-$	18.20	131	17.00	+1.91	83
			19.00	−2.41	
	26.40	115	24.60	+0.69	
Λ-$(-)_{546}$-[Co(edtp)]$^-$	18.00	253	15.80	+0.88	83
			17.60	−3.28	
	24.80	110	23.30	+0.09	
			26.30	+0.18	
Λ-$(-)_{546}$-[Co(ida)$_2$]$^-$ "Model complex"	17.80	152	17.10	+2.72	83
			19.60	−2.94	
	26.30	135	26.30	+0.79	
[Cr(1,3-pdta)]$^-$	19.64	118			92,93b
	25.97	83			
Λ-$(-)_{589}$-[Rh(1,3-pdta)]$^-$	27.94 sh	284	25.51	−1.03	95,96
	29.58 sh	274	30.03	+2.05	
	34.13	243	34.01	−0.65	
			38.02	+0.09	
Δ-$(+)_{589}$-[Co(*RR*-2,4-ptnta)]$^-$	18.02	123	17.04	−2.19	99
			18.94	+2.02	
	26.18	100	24.55	−0.70	
			32.26	+0.13	
	43.86	23988	40.32	−6.38	
			44.44	+8.30	
Λ-$(+)_{589}$-[Cr(*SS*-ptnta)]$^-$	19.64	100[a]	18.00 sh	+0.20	100
			19.67	+0.442	
			21.67	−0.064	
	25.97	73[a]	24.00	+0.435	
			25.25 sh	+0.27	
			29.66	−0.024	
[Cr(tdta)]$^-$	17.98	55			93
	25.19	53			
Λ-$(+)$-[Co(xdta)]$^-$	16.61	158	15.87	+6.43	85
			17.86	−6.32	
	25.00	201	22.73	+0.83	
			25.77	+1.80	
Δ-$(+)_{589}$-[Co(dcbta)]$^-$	17.65[a]	95[a]	16.47[a]	−1.50[a]	104
			18.83[a]	+3.31[a]	
	25.59[a]	83[a]	23.60[a] sh	−0.62[a]	
			25.59[a]	−0.76[a]	
	42.35[a]	17378[a]	42.47[a]	+0.15[a]	

[a] Values estimated from spectra.

the complex and comparisons were made with the spectra of other [Co(edta)]$^-$ type complexes. The preparation and resolution of [Co(1,3-pdta)]$^-$ complex has also been reported by Ogino et al. [90]. The conformation of [Co(1,3-pdta)]$^-$ complex was inferred from the measurement of PMR spectra. It was found that K[Co(1,3-pdta)]$\cdot$2H_2O crystals are a mixture consisting of equimolar amounts of the crystals of $(+)_{546}$-K[Co(1,3-pdta)]$\cdot$2H_2O and $(-)_{546}$-K[Co(1,3-pdta)]$\cdot$2H_2O. The absolute configuration for optically active forms has been determined by the measurements of ORD and CD curves and by the reaction with ethylenediamine to form tris(ethylenediamine)cobalt(III) cation. In connection with this work, the assignment of the absolute configurations has been refuted by X-ray structure analysis and the $\Lambda\Delta\Lambda$ configuration was found for the $(-)_{546}$-[Co(1,3-pdta)]$^-$ complex [87].

Van Saun and Douglas [83] studied the influence of various structural changes in the ligand on the rotational strengths of $d \rightarrow d$ transitions of cobalt(III) in a series of model complexes for [Co(edta)]$^-$. The series included (1,3-propanediaminetetraacetato)cobaltate(III), [Co(1,3-pdta)]$^-$, *cis*(*N*)-bis(iminodiacetato)cobaltate(III), [Co(ida)$_2$]$^-$ and (ethylenediaminetetrapropionato)cobaltate(III), [Co(edtp)]$^-$ complexes where the strain in the chelate ring system was varied, but the same arrangement of ligand atoms was retained. The intensities of the visible absorption bands (see Fig. 13, Table 5) are lower for the model compounds, as might be predicted because of the decrease in ring strain. However, the CD spectra show an increase in net rotational strength for the less strained complexes, a result not expected from some theories of optical activity [23,24]. The isomers of the three model complexes having a positive rotational strength for the lowest energy CD band ($A \rightarrow A$ transition) have assigned the same (Λ) absolute configuration as $(-)_{546}$-[Co(edta)]$^-$. This assignment of configuration is also compatible with the solubility rule [91] and X-ray structure analysis data [87].

The preparation of Na[Cr(1,3-pdta)]$\cdot$3H_2O was reported by Weyh and Hamm [92]. It was later improved by Ogino et al. [93] who gave a new method [94] for the preparation of chromium(III) complexes. The fast formation of [Cr^{II}(1,3-pdta)]$^{2-}$ and the subsequent electron-transfer reaction between [Cr^{II}(1,3-pdta)]$^{2-}$ and chromium(III) leads to the formation of the monomeric [Cr(1,3-pdta)]$^-$ complex. The same method has also been used for the preparation of sodium(tetramethylenediaminetetraacetato)chromate(III) tetrahydrate, Na[Cr(tdta)]$\cdot$4H_2O. The electronic absorption spectra of complexes follow the expected trend with regard to the crystal field strength of ligands. All attempts at resolution of the [Cr(1,3-pdta)]$^-$ complex were fruitless, but a crystallographic study undertaken by Herak et al. [88] indicates the spontaneous resolution of this complex.

Radanović and co-workers [95,96] reported the preparation of a hexadentate [Rh(1,3-pdta)]$^-$ complex using the "sealed-tube" technique employed by

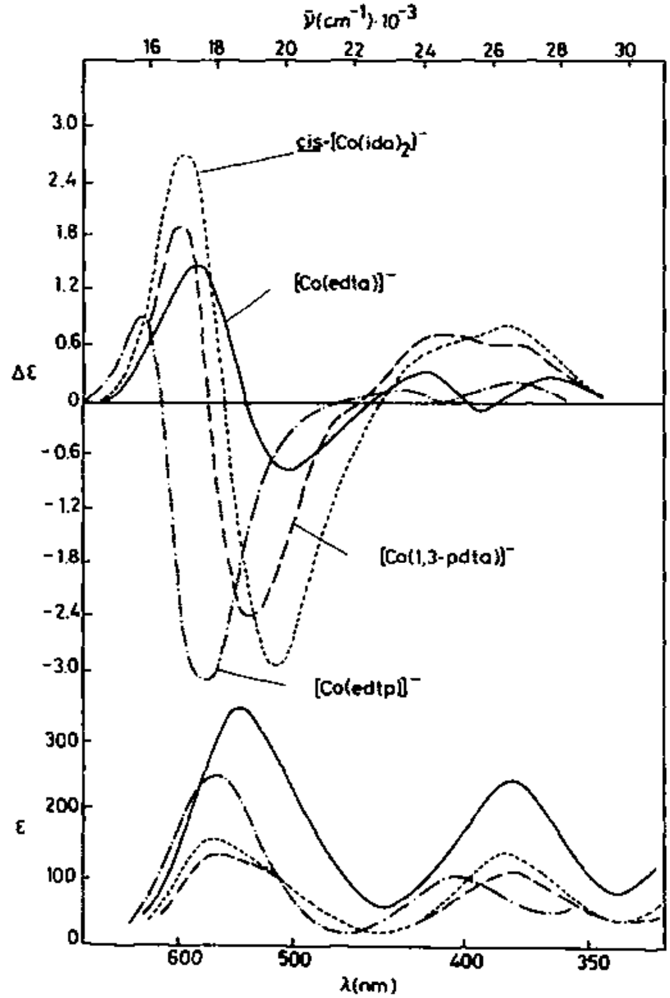


Fig. 13. CD and absorption spectra for Λ-(−)$_{546}$-[Co(edta)]$^-$ and corresponding isomers of [Co(1,3-pdta)]$^-$, *cis*-[Co(ida)$_2$]$^-$ and [Co(edtp)]$^-$. (Reproduced with permission from ref. 83; copyright 1969 American Chemical Society.)

Dwyer and Garvan [97]. Structural assignments were made on the basis of PMR, ^{13}C NMR and IR spectra [95] and also electronic absorption and CD spectra [96]. The two *AB* patterns (J_{AB} = 15.8 Hz and J_{AB} = 18.2 Hz) appear in the PMR spectrum of this complex, associated with in-plane (G) and out-of-plane (R) rings and its ^{13}C NMR spectrum was interpreted easily. The resolution of the complex was achieved using (−)$_D$-oxalatobis(ethylenediamine)cobalt(*III*) bromide. The electronic absorption and CD spectra [96] were assigned in accordance with a D_{4h} model (see Table 5, Fig. 14). The

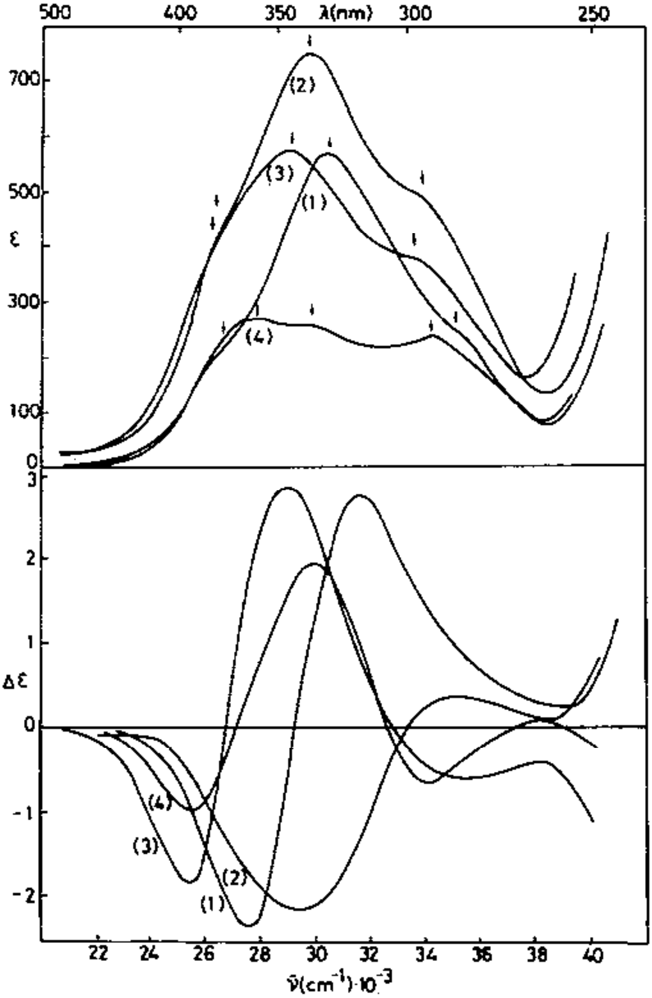


Fig. 14. CD and absorption spectra for $[Rh(edta\text{-}type)]^-$ complexes: (1) *trans*(O_5)-Λ-$(+)_D$-$[Rh(SS\text{-}edds)]^-$; (2) *trans*(O_5)-Λ-$(-)_D$-$[Rh(eddda)]^-$; (3) *trans*(O_5O_6)-Λ-$(-)_D$-$[Rh(eddda)]^-$ and (4) Λ-$(-)_D$-$[Rh(1,3\text{-}pdta)]^-$.

$(-)_D$-$[Rh(1,3\text{-}pdta)]^-$ having a negative CD peak in the lowest energy region was assigned the Λ configuration by comparison with the CD spectrum of the *trans*(O_5)-$[Rh(SS\text{-}edds)]^-$ isomer of known Λ configuration [98]. By analogy to $[Co(edta)]^-$ type complexes (assigned as Λ for a positive CD peak in the lowest energy region), the $(-)_D$-$[Rh(1,3\text{-}pdta)]^-$ would be assigned the Δ configuration if no reversal of order of the E and A_2 energies occurs. However, the results of a crystallographic study of the $(-)_D$-$[Rh(1,3\text{-}pdta)]^-$ complex [88] confirm the Λ configuration.

Some complexes of cobalt(III)-containing derivatives of 1,3-pdta ligand have also been studied. The [Co(1,3-mpdta)]$^-$ complex, having a methyl group attached to a terminal carbon of the six-membered backbone ring, has been prepared by Chang and Douglas [61] to aid spectral assignments and to be used as a source of detailed stereochemical information in a series of hexadentate complexes.

Fujita and co-workers [99] examined cobalt(III) complexes of the 2,4-pentanediaminetetraacetate (2,4-ptnta) ligand which has two methyl groups on the α-carbon atoms adjacent to the amino nitrogen and discussed the relationship between the structure of these complexes and the optical isomerism of 2,4-pentanediamine, from which the 2,4-pentanediaminetetraacetate ligand is derived. Molecular models show that *RR*- and *SS*-2,4-pentanediaminetetraacetate could form only configurational isomers ($\Delta(\lambda)$ for *RR*-2,4-ptnta and $\Lambda(\delta)$ for *SS*-2,4-ptnta) having both methyl groups in equatorial positions. The racemic pair, Δ-[Co(*RR*-2,4-ptnta)]$^-$ and Λ-(Co(*SS*-2,4-ptnta)]$^-$ exhibits an absorption spectrum very similar to that of [Co(1,3-pdta)]$^-$. The IR and PMR spectra of this racemic complex also provide useful information. The $(+)_D$-[Co(2,4-ptnta)]$^-$ isomer exhibits a CD pattern (see Table 5) very similar to that of Δ-[Co(1,3-pdta)]$^-$ in the region of the first absorption band, indicating that the complexes have the same Δ configuration. $(-)_D$-2,4-Pentanediaminetetraacetate coordinates stereospecifically producing only the $(+)_D$-Δ-[Co(*RR*-2,4-ptnta)]$^-$ complex from which the absolute configuration of the carbon atoms was assigned *RR*. The *meso*-2,4-pentanediaminetetraacetate (*RS*) coordinates to the metal ion as a quinquedentate ligand with a free acetate branch. The stereospecific formation of such complexes has been attributed to the steric regulation coming from the methyl groups on the α-carbon atoms.

Recently, Kaizaki and Mori [100] have reported a new chiral Cr(III) complex containing (*SS*)-ptnta which was found to be formed stereospecifically with a Λ ($\Lambda\Delta\Lambda$) absolute configuration as has been revealed for the corresponding Co(III) complex [99]. The CD data in the spin-forbidden transitions as well as in the spin-allowed transitions of the $(+)_{589}$-[Cr(*SS*-ptnta)]$^-$ complex (CD data for spin-allowed transitions are given in Table 5) are examined together with those in the spin-forbidden transitions of chiral *trans*(O$_5$) isomers of $(-)_{589}$-[Cr(eddda)]$^-$ and $(+)_{589}$-[Cr(*SS*-edds)]$^-$, of which the CD spectra in the spin-allowed transitions have been previously reported by Radanović and Douglas [101]. Their CD spectra in the whole region of the $d \rightarrow d$ transitions were compared with one another and discussed on the basis of both trigonal and tetragonal symmetry assumptions. In the assumption of effective C_2 symmetry for the complexes of this type, the lowest-frequency CD component in the first band region was assigned to the $^4B(C_2)$ state, for which the CD signs are considered to be the same as those for the $^4B(C_2)$ state with $^4E(^4T_{2g})$ trigonal parentage or with $^4E(^4T_{2g})$

tetragonal parentage as in the case of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions for Co(III) complexes [14b,101–103].

(b) Analogues of ethylenediaminetetraacetate forming seven-membered diamine rings

In 1970, Ogino et al. [93a] synthesized potassium (tetramethylenediaminetetraacetato)cobaltate(III) trihydrate, K[Co(tdta)]·3H_2O. The IR and PMR spectra indicated that a quadrivalent tdta anion is hexadentate in this complex. Later, Ogino et al. [93b] reported the preparation and isolation of Na[Cr(tdta)]·4H_2O, using a new method [94] proposed for the preparation of chromium(III) complexes. Assignments of complexes were made by means of the electronic absorption and IR spectra. There is no evidence for the resolution of these complexes.

Soma and Mizukami [104] prepared a cobalt(III) complex containing the *cis*-2-butene-1,4-diaminetetraacetate ligand (see structural formula of the ligand in Table 3). *cis*-2-Butene-1,4-diaminetetraacetate (dcbta) has been prepared from *cis*-2-butene-1,4-diamine (dcb) having two amino groups and one double bond. Sodium (*cis*-2-butene-1,4-diaminetetraacetato)cobaltate(III) dihydrate, Na[Co(dcbta)]·2H_2O was prepared and resolved. In the region 15,000–40,000 cm^{-1}, the electronic absorption and CD spectra of $(+)_D$-[Co(dcbta)]$^-$ are very similar to those of Δ-$(+)_D$-[Co(1,3-pdta)]$^-$. It was concluded that the *cis*-2-butene-1,4-diaminetetraacetate ligand is hexadentate and that $(+)_D$-[Co(dcbta)]$^-$ has the Δ(λ) structure. This Δ(λ) structure was also supported by the PMR spectrum of this complex.

Finally, Douglas and co-workers [85] prepared and resolved the (xylylenediaminetetraacetato)cobaltate(III) ion, [Co(xdta)]$^-$, which has a benzene ring incorporated into the ethylenediamine backbone, producing a seven-membered ring when coordinated. They studied the effect of the benzene ring which may exert a large influence on CD spectra. Although studies indicated that the complex may be somewhat labile, resolution by fractional recrystallization of the diastereoisomer formed with $(+)_D$-[Co(en)$_2$(ox)]$^+$ was successful. A model of [Co(xdta)]$^-$ shows that the seven-membered ring is locked into a fairly rigid conformation, but there appears to be much less strain in the G rings than for [Co(edta)]$^-$. The absorption and CD spectra of [Co(xdta)]$^-$ are similar in some respects to the spectra of the less strained model compounds. Its CD spectrum (see Table 5) exhibits two bands of opposite sign in the $^1T_{1g}$ region but, unlike the bands for [Co(edta)]$^-$ or the model compounds, they are of approximately equal intensity. The most significant feature of the CD spectrum of the [Co(xdta)]$^-$ complex is the unusually large Δε value (+6.42 and −6.32). The first absorption band is unsymmetrical with a shoulder on the higher energy side, indicating greater splitting of the components than for [Co(edta)]$^-$. The isomer of [Co(xdta)]$^-$, having a positive lowest energy CD peak has been related to $(-)_{546}$-$[Co(edta)]^-$ and assigned the same (Λ) configuration. The PMR and ^{13}C NMR spectra of the $[Co(xdta)]^-$ complex were also reported and compared to those of other cobalt(III) hexadentate complexes.

(iii) Analogues of ethylenediaminetetraacetate with structural changes in carboxylate arms

Complexes with several ligands structurally similar to ethylenediaminetetraacetate, but having various structural changes in carboxylate arms have been prepared and are now discussed.

(a) S,S-Ethylenediamine-N,N′-disuccinate (SS-edds) and other hexadentate ligands containing the aspartic acid unit (see Table 3)

Neal and Rose [105] reported the synthesis and characterization of a novel ligand, *S,S*-ethylenediamine-*N,N′*-disuccinate (*SS*-edds) and discussed its complexes with cobalt(III), rhodium(III) and nickel(II). Two isomers (I and II in Fig. 2(b)) are possible, but only one (isomer I) has been prepared. The *S,S*-ethylenediamine-*N,N′*-disuccinate ligand, because of its ability to form five- and six-membered chelate rings and because of its two asymmetric carbon atoms imposes stereospecificity upon chelation. The ligand reacts with sodium tris(carbonato)cobaltate(III) to produce the sodium salt of $[Co(SS\text{-edds})]^-$ of one absolute configuration in at least 75% yield. The optical rotatory dispersion curve of this complex exhibits the strongest rotations at 17.360 cm^{-1} ($[M] = -4300$) and 19,530 cm^{-1} ($[M] = +800$). The complex exhibits a visible spectrum similar to that of $[Co(edta)]^-$ but it was suggested that *SS*-edds imposes a stronger crystal field on the metal ion. One isomer of $[Rh(SS\text{-edds})]^-$ complex also has been prepared. The authors concluded that the *SS*-edds ligand coordinates in a stereospecific hexadentate fashion to metal ions with the carboxylate moieties in the six-membered chelate rings providing donor atoms in the equatorial positions. This was supported by pH and IR studies and by a detailed analysis of the PMR spectra. IR spectra of solutions of the complexes exhibit two separate bands in the 1560–1640 cm^{-1} spectral region associated with the six- and five-membered chelate rings of coordinated *SS*-edds. Finally, the proposed structure of complexes has been confirmed by an X-ray crystal structure determination [106a,b] (isomer I, trans(O_5) configuration, Fig. 2(b)) *.

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* The similar ligand, *S,S*-6,9-diaza-2,13-dithiatetradecane-5,10-dicarboxylate, *SS*-ebm (*SS*-$[CH_3SCH_2CH_2CH(COO^-)NHCH_2-]_2$) was prepared [106c] from *S*-methionine and 1,2-dibromoethane according to a method given for *SS*-edds. The *SS*-ebm is also a stereospecific hexadentate agent for Co(III) (the donor atom sets being $N_2O_2S_2$) forming the preferred *trans*(O_5) Λ-$(-)_{589}$-$[Co(SS\text{-ebm})]^-$ complex [106d] with six-membered chelate rings in the G plane (the N and S atoms are present in the *R* configurational arrangement).

Legg and Neal [107] considered the correlation between hexadentate complexes of known configurations and closely related bis-tridentate amino acid complexes and suggested that some of the assignments made earlier were incorrect. In support of this argument they prepared the (S)-ethylenediamine-N,N-diacetate-N'-monosuccinate (S-eddams) ligand of known absolute configuration and used it in preparation of the hexadentatecobalt(III) complex. This ligand exhibits stereospecificity on coordination to cobalt(III) to give a complex of known absolute configuration (see Fig. 15, "O_6-eq" isomer) which has been characterized by visible, IR, PMR and CD spectroscopy. The spectral behavior of this complex supports its proposed absolute configuration in relation to the $(-)_{546}$-[Co(edta)]$^-$ and [Co(SS-edds)]$^-$ complexes (Fig. 15). These complexes having approximately mirror image CD spectra (dominant CD peak of $(-)_{546}$-[Co(edta)]$^-$ of opposite sign to dominant peaks of the other two complexes, see Fig. 16, Table 6) were assigned the same configuration. It was postulated that the contribution of the chelate rings to optical activity for these complexes strongly depends on their relative size. In addition, they made a correlation scheme for the relationship of the complexes of known absolute configurations (left column) to closely related bis-tridentate amino acid complexes.

$[\mathrm{Co(edta)}]^- \leftrightarrow [\mathrm{Co(ida)_2}]^-$

$[\mathrm{Co(eddams)}]^- \leftrightarrow [\mathrm{Co(ida)(asp)}]^-$

$[\mathrm{Co(}SS\text{-edds)}]^- \leftrightarrow [\mathrm{Co(asp)_2}]^-$

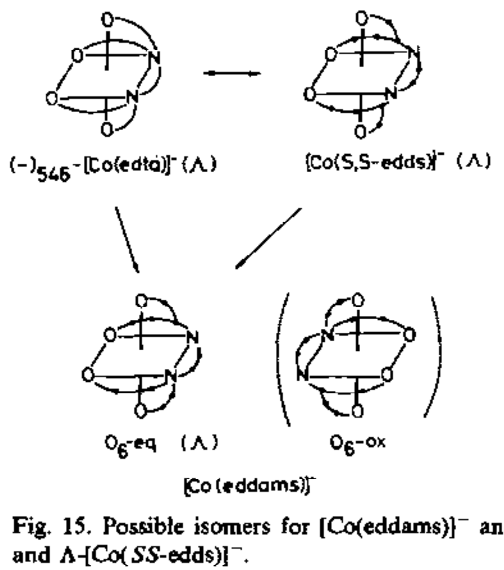

Fig. 15. Possible isomers for [Co(eddams)]$^-$ and their relationship to Λ-$(-)_{546}$-[Co(edta)]$^-$ and Λ-[Co(SS-edds)]$^-$.

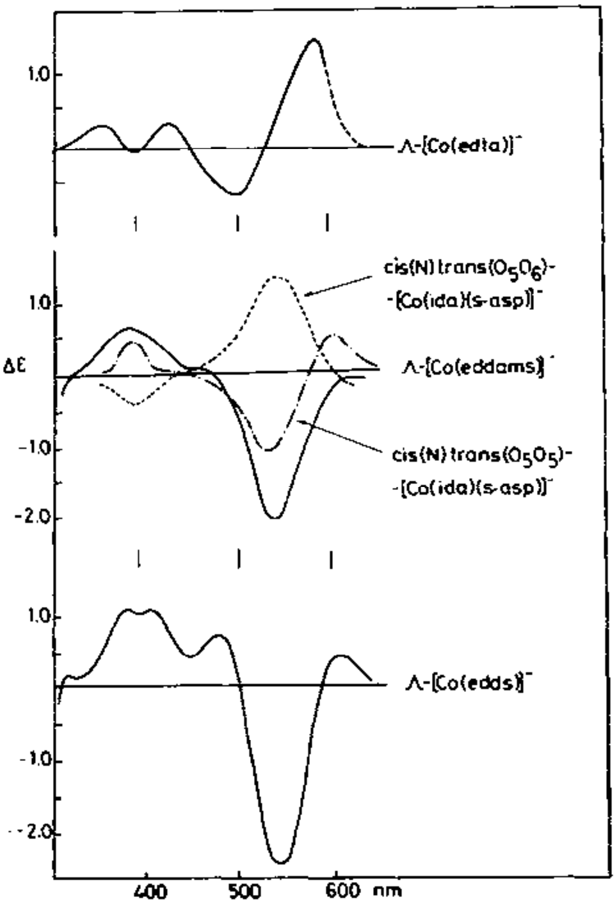

Fig. 16. CD spectra of $[Co(eddams)]^-$ and related complexes. (Reproduced with permission from ref. 107; copyright 1973 American Chemical Society.)

From a comparison of the CD spectrum of $[Co(S\text{-eddams})]^-$ to the spectra obtained for the two isomers of $[Co(ida)(asp)]^-$ the absolute configurations of these isomers have been assigned tentatively as shown in Fig. 16. An analogous comparison between $[Co(SS\text{-edds})]^-$ and the two isomers of $[Co(asp)_2]^-$ was used to assign their absolute configurations. It was suggested that comparison with complexes having the same number of aspartic acid and iminodiacetate acid units permits a reasonably safe correlation of absolute configurations on the basis of CD.

In order to evaluate the contribution due to the asymmetric nitrogens in the $[Co(SS\text{-edds})]^-$ system, Jordan and Legg [108] prepared the *N*-methyl (medds) and *N,N'*-dimethyl (dmedds) derivatives of that complex which also exhibit absolute stereospecificity like *SS*-edds. The fact that $[Co(medds)]^-$ and $[Co(dmedds)]^-$ complexes have the same absolute configuration as

TABLE 6

Absorption (AB) and circular dichroism (CD) data for [M(*SS*-edds)]$^-$, [M(eddda)]$^-$ and related complexes

Complex	AB		CD		Ref.
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	$\Delta\epsilon$	
Λ-(+)-*trans*(O$_5$)-*RR*-[Co(*SS*-edds)]$^-$	19.40	300 [a]	16.47	+0.39	105,108
			18.25	−2.31	
	26.24	115 [a]	25.64	+0.95	
Λ-(+)-*trans*(O$_5$)-*RR*-[Co(*SS*-medds)]$^-$	19.10 [a]	320 [a]	16.55	+0.39	108
			18.45	−2.17	
	26.10 [a]	110 [a]	26.31	+0.83	
Λ-(+)-*trans*(O$_5$)-*RR*-[Co(*SS*-dmedds)]$^-$	18.80 [a]	310 [a]	16.55	+0.18	108
			18.52	−1.88	
	25.80 [a]	110 [a]	26.31	+0.56	
Λ-(−)-*trans*(O$_5$)-*R*-[Co(*S*-eddams)]$^-$	19.36	260	18.40	−1.98	107
	26.35	150	26.30	+0.58	
Λ-(−)$_{589}$-*trans*(O$_5$)-*RR*-[Co(eddda)]$^-$	18.50	342	16.20	+0.40	103
			18.30	−2.78	
	25.70	186	24.20	+0.29	
			26.30	+0.36	
Λ-(−)$_{589}$-*trans*(O$_5$O$_6$)-*SR*-[Co(eddda)]$^-$	18.60	253	16.50	+2.25	103
			18.40	−3.12	
	25.80	142	24.40	+0.31	
			26.60	+0.56	
Λ-(+)$_{589}$-*trans*(O$_5$)-*RR*-[Cr(*SS*-edds)]$^-$	19.60	175	17.50	+0.40	101
			19.30	−0.39	
			21.70	+0.44	
	26.00	57	23.50 sh	+0.34	
			26.90	+0.37	
Λ-(−)$_{589}$-*trans*(O$_5$)-*RR*-[Cr(eddda)]$^-$	18.90	214	16.50	+0.20	101
			18.70	−0.78	
			20.60 sh	−0.20	
	25.30	107	24.30	−0.08	
			26.70	+0.22	

TABLE 6 (continued)

Complex	AB		CD		Ref.
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	$\Delta\epsilon$	
Λ-$(+)_{589}$-*trans*(O_5)-*RR*-[Rh(*SS*-edds)]$^-$	26.66 sh	215	27.54	−2.29	98
	30.48	565	31.54	+2.74	
	35.08 sh	245			
Λ-$(-)_{589}$-*trans*(O_5)-*RR*-[Rh(eddda)]$^-$	26.45 sh	405	29.41	−2.10	98
	29.85	745			
	33.89 sh	480	34.96	+0.36	
Λ-$(-)_{589}$-*trans*(O_5O_6)-*SR*-[Rh(eddda)]$^-$	26.31 sh	390	25.44	−1.80	98
	29.07	565	28.98	+2.84	
	33.55 sh	380	35.71	−0.55	

[a] Values estimated from spectra.

[Co(*SS*-edds)]$^-$ is apparent from the similarity of their CD spectra (see Table 6). Because of only slight changes in the CD spectra among the cobalt(III) complexes, they concluded that there is only a very small contribution to rotational strength due to the asymmetric nitrogen atoms in the *SS*-edds system. Having eliminated the N-vicinal, C-vicinal and conformational effects as structural sources responsible for the major differences between the CD spectra of [Co(edta)]$^-$ and [Co(*SS*-edds)]$^-$, the contribution of the chelate rings to optical activity for these complexes, then, as concluded, strongly depends on both their relative size, as postulated by Legg and Neal [107] and their distribution about an octahedron.

The [M(*SS*-edds)]$^-$ complexes have recently been employed [96,98,101] as references for assigning the absolute configuration of complexes containing the structurally similar ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate ligand.

*(b) Ethylenediamine-*N,N′*-diacetate-*N,N′*-di-3-propionate (eddda)*

Byers and Douglas [102] prepared and resolved the *trans*(O_5) isomer of [Co(eddda)]$^-$ (three isomers are possible: *trans*(O_5), *trans*(O_5O_6) and *trans*(O_6), see Fig. 2(c)). The IR, PMR, absorption and CD spectra were used to characterize the complex. The *J* value obtained (18.4 Hz) is typical for an *AB* pattern of out-of-plane glycinate rings. Absorption and CD data were correlated with those of $(-)_{546}$-$[Co(edta)]^-$ [77] and $[Co(SS\text{-edds})]^-$ [105] complexes of known Λ configuration. The spectral data for $[Co(eddda)]^-$ (see Table 6) are more similar to those of $[Co(SS\text{-edds})]^-$ than to those of $[Co(edta)]^-$. The positive lowest energy CD peak was treated as the $A(C_2)$ component and the isomer, obtained from the less soluble diastereoisomer with $(-)_D$-$[Co(en)_2ox]^+$, was assigned the Λ configuration. The signs and relative intensities of the two low-energy CD peaks are similar for $[Co(eddda)]^-$ and $[Co(SS\text{-edds})]^-$ complexes (see Table 6) indicating the same Λ configuration.

Later, Radanović and Douglas [103] reported the preparation and resolution of a second (*trans*(O_5O_6)) isomer of $[Co(eddda)]^-$ complex. Because of the strain of G rings [2a], as expected, the *trans*(O_5) isomer was formed preferentially, as reported for similar $[Co(SS\text{-edds})]^-$ [105] and $[Co(S\text{-eddams})]^-$ [107] complexes. More complete resolution of the reported [102] *trans*(O_5) isomer has been achieved. Two *AB* patterns ($J_{AB} = 18.4$ Hz and $J_{AB} = 16.4$ Hz) associated with R and G glycinate rings were identified for the expected *trans*(O_5O_6) geometry. The electronic absorption and CD data were related to those of other model compounds [77,83,105,107] (see Tables 4–6) and both $(-)_D$ isomers having a positive lowest energy $A(C_2)$ CD peaks have been tentatively assigned the Λ configuration. On the basis of overall comparisons with $[Co(SS\text{-edds})]^-$ [105] and $[Co(S\text{-eddams})]^-$ [107] complexes of known configuration, $(-)_D$ isomers of $[Co(eddda)]^-$ were also assigned the Λ configuration. The possible contributions to the CD intensities due to the asymmetric nitrogen atoms (*RR* for *trans*(O_5) and *SR* for *trans*(O_5O_6) isomers of the Λ configuration) were also considered. Because of the similarity in shape of CD curves of the $[Co(edtp)]^-$ complex [83] (in which case there is no contribution due to asymmetric nitrogens) and those of the *trans*(O_5) isomer of the $[Co(eddda)]^-$ complex and the relative intensities of their lowest energy CD components (see Tables 5 and 6) it was concluded that the contribution due to the asymmetric nitrogens is not very great in this system.

The preparation and stereochemistry for the hexadentate complexes $[Cr(eddda)]^-$ and $[Cr(SS\text{-edds})]^-$ were reported by Radanović and Douglas [101]. With both ligands only *trans*(O_5) geometrical isomers have been prepared. IR spectra for $[M(eddda)]^-$ and $[M(SS\text{-edds})]^-$ complexes (M = Co or Cr) in the asymmetric stretch carboxylate region were assigned and compared to those of other hexadentate complexes. The two well-resolved bands associated with the six-membered and five-membered chelate rings were found and assigned for complexes having *trans*(O_5) geometry. The expected four bands for the reported [103] *trans*(O_5O_6) isomer of $[Co(eddda)]^-$ complex were also obtained and assigned. Complexes with each metal ion were presumed to have the same splitting and sign patterns in the spin-allowed $d \rightarrow d$ transition region (see Table 6) and the lowest energy positive CD peak for the *trans*(O_5)-[Cr(*SS*-edds)]$^-$ (of known configuration from the stereospecificity of *SS*-edds, Fig. 2(b), isomer I) was presumed to be the $A(C_2)$ component. The $(-)_D$ isomer of the *trans*(O_5)-[Cr(eddda)]$^-$ complex, having a positive CD peak at lowest energy in the first spin-allowed band region was tentatively assigned the Λ configuration, by comparison of its CD spectrum to the CD spectra of the corresponding *trans*(O_5)-[Co(eddda)]$^-$ [102,103] and *trans*(O_5)-[Cr(*SS*-edds)]$^-$ complexes of known configuration. The $(-)_D$ isomers of the *trans*(O_5)-[M(eddda)]$^-$ were isolated from the less soluble diastereoisomers using $(-)_D$-[Co(en)$_2$(ox)]$^+$, which lends support to the assignment of the same absolute configuration for these complexes [91]. It was shown that the CD peaks are less than one half as intense for the chromium(III) complexes. As concluded, the CD intensities of these chromium(III) complexes are due mainly to configurational effects, with only small contributions [108] to the CD of the asymmetric nitrogens (*RR*) for the Λ configuration. Assignment of the Λ absolute configuration to the $(-)_D$ isomer of *trans*(O_5)-[Cr(eddda)]$^-$ complex was later confirmed by a single-crystal X-ray diffraction study [109].

Radanović and co-workers [95,98] have studied optical activity in [Rh(eddda)]$^-$ and the previously reported [105] [Rh(*SS*-edds)]$^-$ complex. The pure complexes were isolated using ion-exchange chromatography (QAE Sephadex, A-25) and gel filtration (G-10 Sephadex) techniques. PMR, ^{13}C NMR and IR spectra [95] and also electronic absorption and CD spectra [98] were used for characterizing the complexes. As expected, one *AB* pattern (J_{AB} = 18.8 Hz) and two *AB* patterns (J_{AB} = 16.0 Hz and 17.5 Hz) were found in the glycinate region of the spectrum of the *trans*(O_5) and *trans*(O_5O_6) isomers, respectively. Selective decoupling and deuterium exchange studies of *trans*(O_5)-[Co(eddda)]$^-$ [110] allowed the assignments of the ^{13}C NMR spectra of rhodium(III) complexes. In the spectrum of the *trans*(O_5O_6) isomer (lower symmetry) two peaks were found for every one in the spectrum of the *trans*(O_5) isomer in both (methylene and carbonyl) regions. The isomers of [Rh(eddda)]$^-$ complex were resolved using the $(-)_D$-[Co(en)$_2$(ox)]$^+$ and a very clean high-yield resolution resulted ($[\alpha]_D = \pm 13°$ or $[\alpha]_{436} = \pm 148°$ for *trans*(O_5) and $[\alpha]_D = \pm 83°$ or $[\alpha]_{436} = \pm 455°$ for the *trans*(O_5O_6) isomer). The absorption and CD data of the rhodium(III) complexes (Fig. 14, Table 6), were correlated with those of the corresponding cobalt(III) [103,105] and chromium(III) [101] complexes, which, according to Neal and Rose [105], have also been interpreted and assigned using the D_{4h} model. While the lowest energy, $A(C_2)$, components of the [M(edta)]$^-$ type complexes [77,83,101,103] (M = Co or Cr) have been correlated with both the $E_g^a(D_{4h})$ and $E_a(D_3)$ states and interpreted best in terms of C_2 symmetry, for the [Rh(eddda)]$^-$ and [Rh(*SS*-edds)]$^-$ complexes the D_{4h} model is appropriate and peaks at lower and higher energy were assigned to belong to the $E_g^a(D_{4h})$ and $A_{2g}(D_{4h})$ components respectively. The $(+)_D$-*trans*(O_5)-[Rh(*SS*-edds)]$^-$ complex of known Λ configuration [105,106] (see Fig. 2(b), isomer I) has a negative sign for the lowest energy $E(D_{4h})$ CD peak. The assignment of the absolute configuration of this complex would be reversed based on the correlation with [Co(edta)]$^-$ type complexes (the peak assigned as $E(D_{4h})$ for [Co(edta)]$^-$ type complexes [77,83,103] is positive for the $\Lambda(\Lambda\Delta\Lambda)$ configuration). The authors chose to use the stereospecificity of the *SS*-edds ligand as the basis for the tentative assignment of the absolute configurations of the $(-)_D$ isomers of [Rh(eddda)]$^-$ and *trans*(O_5)-[Rh(*SS*-edds)]$^-$, both having negative lowest energy CD peaks. Because of the similarity of the CD intensities of all three rhodium(III) complexes it was assumed that the optical activity in each case is due mainly to configurational effects.

(c) Complexes with other ligands

Williams et al. [111] reported a hexadentate complex of cobalt(III) with ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-di-α-propionate (edpa) ligand. Like eddda (see Fig. 2(c)) the edpa ligand was expected to form three geometrical isomers with cobalt(III) and with the optically active ligand, the number of isomers possible is 20. The structure of the isolated complex has been deduced from the PMR spectrum and resolution of both the ligand and its cobalt(III) complex. Both *meso* and enantiomeric forms of the ligand have been synthesized but only one was used for complexation. It was demonstrated clearly that this bulky analog of edta coordinates with geometric specificity, the bulkier linkages attaching to the out-of-plane sites. The complex is a racemic mixture, its ORD showing only a vicinal effect.

Van Saun and Douglas [83] reported the preparation and resolution of a complex of cobalt(III) with ethylenediaminetetrapropionate (edtp) ion in which four carboxylate groups are lengthened (each by one atom) with respect to the edta ligand. This complex was resolved using $(-)_D$-[Co(en)$_2$(ox)]$^+$ and its CD spectrum (taken from a solution of the complex without isolating the solid) has been included in a series of model complexes for [Co(edta)]$^-$ where the strain in the chelate ring system was varied. An increase in net rotational strength for the less strained complexes has been demonstrated (see Fig. 13, Table 5).

*(iv) Triethylenetetraamine-*N^2,N^3*-diacetate (ttda) and its analogues*

This section includes triethylenetetraamine-N^2,N^3-diacetate (ttda), 1,9-diamino-3,7-diazanonane-3,7-diacetate (ddda) and 1,9-diamino-4-methyl-3,7-diazanonane-3,7-diacetate (mddda) ligands which have been prepared by

TABLE 7

Absorption (AB) and circular dichroism (CD) data for hexadentate *trans*(O)-$[Co(N)_4(O)_2]$ type complexes

Complex	AB		CD		Ref.
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	$\Delta\epsilon$	
Λ-$(+)_{589}$-*trans*(O)-*RR*-$[Co(ttda)]^+$	18.83	161	18.05	+3.75	112,114
	22.00 sh	sh	20.16	−1.78	
	27.89	183			
Λ-$(+)_{589}$-*trans*(O)-*RR*-$[Co(ddda)]^+$	18.66	99	17.89	+4.54	113,115
	21.88 sh	sh	19.92	−2.23	
	27.62	119	28.82	+1.00	
Λ-$(+)_{589}$-*trans*(O)-*SS*-$[Co(edma)_2]^+$	18.90	85	18.35	+2.62	112,113
"Model complex"	22.30 sh	sh	22.27	−1.80	
	28.01	125	28.17	+0.92	

joining two molecules of piperazinone by an alkylene linkage [61,112,113]. These ligands can form three geometrical isomers (Fig. 2(a)). The tertiary nitrogen donor atoms (see structure of ttda in Fig. 5) are asymmetric.

Douglas and co-workers [114,115] studied cobalt(III) complexes with triethylenetetraamine-N^2,N^3-diacetate and 1,9-diamino-3,7-diazanonane-3,7-diacetate ligands. Fujii et al. [116] reported the preparation of the less strained *trans*(O)-$[Co(edma)_2]^+$ "model complex" containing two tridentate ethylenediaminemonoacetate (edma) ligands. The optical resolution of the complexes was carried out using disilver-*d*-tartrate and *d*-tartaric acid. Structural assignments were made in accordance with a D_{4h} model using the electronic absorption and CD spectra (see Table 7). All complexes show an obvious shoulder on the shorter wavelength side on the first absorption band indicating *trans*(O) type geometry. This geometry has also been found by detailed assignments of the ^{13}C NMR spectra for a series of a hexadentate $[Co(N)_4(O)_2]$ type complexes [61].

The absolute configuration of the $(+)_{589}$-$[Co(edma)_2]^+$ complex has tentatively been assigned as $\Lambda\Lambda\Delta$ [17] or a net Λ configuration [10] according to the sign of the $E(D_{4h})$ transition. Based on the comparison with this complex and on the basis of a dominant positive rotational strength in the first absorption band region [27c], $(+)_{589}$-isomers of $[Co(ttda)]^+$ and $[Co(ddda)]^+$ complexes have also been assigned the net Λ configuration (Table 7). As was postulated by Douglas and co-workers, the difference in the CD splitting patterns between $[Co(edma)_2]^+$ and the two hexadentate complexes might be due to the difference in the contribution of asymmetric nitrogens. The *trans*(O)-$[Co(edma)_2]^+$ complex is the least strained in the series and has the lowest intensity and lowest energy CD peak, opposite to the results obtained for a series of a hexadentate $[Co(N)_2(O)_4]$ type complexes [83]. They reasoned that a significant contribution of the *SS* nitrogens in the Λ isomer of $[Co(edma)_2]^+$ complex (the corresponding isomers of $[Co(ttda)]^+$ and $[Co(ddda)]^+$ complexes have asymmetric nitrogens of *R* configuration) could affect the apparent splitting pattern, masking the third component and causing a less intense low-energy peak.

D. QUINQUEDENTATE COMPLEXES WITH ED3A-TYPE LIGANDS

The study of $[MYX]^{n-}$ chelates (Y = ed3a-type or the singly protonated edta-type ligands; X = unidentate ligand; *n* = the charge on X) has yielded a wealth of stereochemical information. Table 8 summarizes the ligands based on or related to ethylenediamine-*N,N,N'*-triacetate (ed3a) which have been investigated. The ed3a moiety was expected to form three octahedral geomet-

TABLE 8

Quinquedentate ed3a-type ligands

Ligand	Abbreviation
Ethylenediamine-*N,N,N'*-triacetate $(^{-}OOCCH_2)_2NCH_2CH_2NH(CH_2COO^{-})$	ed3a
N-Methylethylenediamine-*N,N',N'*-triacetate $(^{-}OOCCH_2)N(CH_3)CH_2CH_2N(CH_2COO^{-})_2$	med3a
N-Hydroxyethylethylenediamine-*N,N',N'*-triacetate $(^{-}OOCCH_2)N(HOCH_2CH_2)CH_2CH_2N(CH_2COO^{-})_2$	hed3a
N-Benzylethylenediamine-*N,N',N'*-triacetate $(^{-}OOCCH_2)N(C_6H_5CH_2)CH_2CH_2N(CH_2COO^{-})_2$	bed3a
N-(Acetoxyethyl)-ethylenediamine-*N,N',N'*-triacetate $(^{-}OOCCH_2)N(CH_3COOCH_2CH_2)CH_2CH_2N(CH_2COO^{-})_2$	aeed3a
1,2-Propanediamine-*N,N',N'*-triacetate (1,2-propylenediaminetriacetate) $(^{-}OOCCH_2)NHCH(CH_3)CH_2N(CH_2COO^{-})_2$	pd3a
2-Methyl-1,2-propanediamine-*N,N',N'*-triacetate (1,2-diamino-2-methylpropanetriacetate) $(^{-}OOCCH_2)NHC(CH_3)_2CH_2N(CH_2COO^{-})_2$	dmp3a
1,3-Propanediamine-*N,N,N'*-triacetate (trimethylenediamine-*N,N,N'*-triacetate) $(^{-}OOCCH_2)_2NCH_2CH_2CH_2NH(CH_2COO^{-})$	1,3-pd3a (trdtra)
N-Methyl-1,3-propanediamine-*N,N',N'*-triacetate (*N*-methyl-trimethylenediamine-*N,N',N'*-triacetate) $(^{-}OOCCH_2)N(CH_3)CH_2CH_2CH_2N(CH_2COO^{-})_2$	1,3-mpd3a (*N*-Me-trdtra)

ric isomers: *cis*-equatorial, *trans*-equatorial and *cis*-polar (see Fig. 3(b)). The studies of $[MYX]^{n-}$ complexes are mostly limited to the *cis*-equatorial configuration [38,57–60,129–131] and this structure has been confirmed crystallographically [117–119].

These complexes have no net octant sign [16] and no net chirality according to the ring-pair method [17], but their distributions of chelate rings are not achiral. This emphasizes one of the weaknesses of the present methods for determining chirality. The configuration of the complexes is related to the corresponding hexadentate complex as shown (Fig. 17) for the favored *cis*-equatorial configuration.

(i) *Ethylenediaminetetraacetate and related ligands acting as quinquedentate ligands*

(a) *Complexes with cobalt(III)*

Complexes of the type $[Co(Hedta)X]^{n-}$ (Hedta = the singly protonated form of ethylenediaminetetraacetic acid; X = Cl^-, Br^-, NO_2^- or H_2O) are known to yield a single isomer, but there were conflicting reports as to the geometry of the complex isolated [48,57–60,120–130]. In general, these complexes have been assigned the *cis*-equatorial structure on the basis of absorption [38,128], CD [131], PMR [129] and ^{13}C NMR spectra [57–60,130].

Schwarzenbach [48] prepared the first quinquedentate cobalt(III) complexes using ethylenediaminetetraacetic acid. He reported compounds with the general formula $[Co(Hedta)X]^-$ (X = Br^- and NO_2^-). Morris and Busch [120] carried out a rather extensive IR investigation of quinquedentate complexes containing chloro, bromo or nitro unidentate ligands. They showed the applicability of IR spectroscopy for distinguishing between complexed

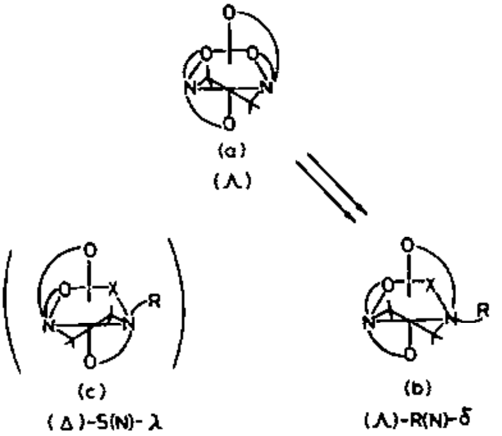

Fig. 17. Configuration relationship between Λ-(−)$_{546}$-$[Co(edta)]^-$ and *cis*-eq ed3a-type complexes (Λ configuration).

carboxyl groups and free carboxylic acid groups in the presence of each other.

The chloro and bromo complexes were synthesized either via reaction (1) or (2)'

$$2[\mathrm{Co(edta)}]^{2-} + \mathrm{X}_2 \rightarrow 2[\mathrm{Co(edta)X}]^{2-} \tag{1}$$

$$[\mathrm{Co(edta)}]^{-} + \mathrm{HX(conc)} \rightarrow [\mathrm{Co(Hedta)X}]^{-} \tag{2}$$

The bromo complex was reported to consist of two geometric isomers by studies of the ring-closure reaction [120–127] and ^{13}C NMR [130], although Schwarzenbach [48] described his complex as a single species. However, recent studies by Ohba and Fujita [130] have shown that one of the reported two isomers was not the bromo complex but the chloro complex. The bromo complex was assigned the *cis*-equatorial structure on the basis of its electronic absorption and ^{13}C NMR spectra.

Complexes, represented by the general formula $[\mathrm{Co(Hedta)X}]^{n-}$ were found to be unstable [120–127] with respect to the reaction (3)

$$[\mathrm{Co(Hedta)X}]^{n} \rightarrow [\mathrm{Co(edta)}]^{-} + \mathrm{X}^{n} + \mathrm{H}^{+} \tag{3}$$

and the pK_a for this proton was found to be about 3 and nearly independent of X [48,122]. The kinetics of this reaction were investigated and when the $\mathrm{pH} \leqslant 7$, a first-order reaction was indicated [122–126].

Dwyer and Garvan [121] reported the resolution of the quinquedentate cobalt(III) complexes of ethylenediaminetetraacetic acid with nitro, chloro and bromo groups occupying the sixth coordination position. The complete resolution of these complexes was effected conveniently and rapidly with optically active *cis*-dinitrobis(ethylenediamine)cobalt(III) chloride ($[\alpha]_{546} = \pm 800°$ for the isomers of $\mathrm{K[Co(Hedta)Cl]\cdot H_2O}$, $\mathrm{K[Co(Hedta)Br]}$ and $\mathrm{Na[Co(Hedta)NO_2]}$). Treatment of the active bromo and chloro complexes with mercury(II) nitrate or freshly precipitated silver oxide caused a quantitative transformation to the hexadentate complex with complete retention of configuration. When the optically active hexadentate complex was treated with concentrated hydrochloric acid, it was converted to the quinquedentate complex with some retention of configuration. In the reaction with ethylenediamine, all of the complexes exchanged to give tris(ethylenediamine)-cobalt(III) ion.

Dwyer and Garvan [69] also reported the preparation of a single optical isomer of the quinquedentate cobalt(III) complexes of optically active propylenediaminetetraacetic acid with chloro or nitro groups. The resolution of *DL*-$\mathrm{K[Co(}$*dl*-$\mathrm{Hpdta)Cl]}$ with *cis*-$[\mathrm{Co(en)_2(NO_2)_2}]^+$ ion yielded only two isomers, $\Lambda(Dd)$ and $\Delta(Ll)$ (D,L refer to the sign of rotation of the complexes, see footnote on p. 178), identical with the isomers prepared from the optically active complexing agent ($[\alpha]_{546} = \pm 800°$ for the isomers of $K[Co(Hpdta)Cl] \cdot 2H_2O$). Both isomers were transformed with complete retention of configuration to the pure hexadentate complexes. Similarly, the chloro complex was prepared from the hexadentate complex with complete retention. The changes in sign in these reactions, e.g. $\Delta(Dl)$ hexadentate → $\Delta(Ll)$ quinquedentate, have been attributed to rotatory dispersion phenomena [121]. The corresponding nitro complex has also been resolved and two isomers, Λ and Δ, were isolated ($[\alpha]_{546} = \pm 850°$ for the isomers of $Na[Co(Hpdta)(NO_2)] \cdot 2H_2O$). The quinquedentate chloro complex of cyclohexanediaminetetraacetic acid was obtained in solution in hydrochloric acid, but the solid could not be isolated, and the hexadentate complex reformed rapidly on dilution. Similarly, attempts to prepare the nitro complex were fruitless.

Haines and Douglas [131] discussed the absorption, ORD and CD spectra for complexes of the type $[Co(edta)X]^{2-}$ ($X = Br^-$, Cl^- or NO_2^-). The absorption and CD data obtained for these complexes are summarized in Table 9. The relative positions of the long wavelength band are consistent with what would be predicted from the spectrochemical series and splitting is observed for one band only for the nitro compound. Although the ORD curves give some information regarding the absolute configuration, the CD data were used to confirm the assignments of the complexes. The isomers of the quinquedentate complexes have been related to that of the $(-)_{546}$-$[Co(edta)]^-$ complex. The *A* component of $(-)_{546}$-$[Co(edta)]^-$ having the Λ configuration, was related to one of the three *A* components of the quinquedentate complexes. On the basis of the similarity of the ORD and CD curves the Λ configuration was assigned to the $(+)_{546}$ isomers of $[Co(edta)Br]^{2-}$, $[Co(edta)Cl]^{2-}$ and the $(-)_{546}$ isomer of $[Co(edta)(NO_2)]^{2-}$. This was supported by the fact that $(-)_{546}$-$[Co(edta)]^-$ is converted into $(+)_{546}$-$[Co(edta)Cl]^{2-}$ with complete retention of configuration [121]. For all the complexes studied the CD spectra were interpreted assuming three CD bands in the region of the first absorption band, as for the $[Co(edta)]^-$ complex, indicating rhombic symmetry and suggesting that the X group is *trans* to a nitrogen (later assigned *cis*-equatorial).

Optically active aqua(hydrogenethylenediaminetetraacetato)cobalt(III), $[Co(Hedta)(H_2O)]$ was prepared and its CD data presented [132]. By using the reported equilibrium constants the concentrations of $[Co(Hedta)(H_2O)]$ and $[Co(edta)]^-$ were calculated and used to interpret the CD spectrum obtained for this equilibrium solution. It was suggested that the similarity of the CD spectra of $[Co(Hedta)(H_2O)]$ and $[Co(edta)Cl]^{2-}$ in 0.1 M HCl may be due to the formation of a pseudo-chelate ring with a preferred conformation.

Fujita and co-workers [99] showed that the *meso*-2,4-pentanediaminetetraacetate (*RS*-2,4-ptnta) ligand coordinates to the metal ion as a quinquedentate ligand, forming the [Co(*RS*-2,4-Hptnta)Cl]$^-$ complex for which the electronic absorption spectrum was presented. The stereospecific formation of the quinquedentate complex from the *meso*-2,4-ptnta was attributed to the steric regulation coming from the methyl groups.

Gailey and Douglas [110] reported the preparation and characterization of

TABLE 9

Absorption (AB) and circular dichroism (CD) data for complexes of cobalt(III) containing edta-type ligands acting as quinquedentate

Complex	AB		CD		Ref.
	$\tilde{\nu} \times 10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu} \times 10^{-3}$ (cm^{-1})	$\Delta\epsilon$	
Λ-(+)$_{546}$-*cis*-eq-[Co(edta)Cl]$^{2-}$	17.10	250	15.45	+0.05	131
			17.70	−1.48	
	24.75	221	22.35	+0.07	
			24.65	−0.30	
Λ-(+)$_{546}$-*cis*-eq-[Co(edta)Br]$^{2-}$	17.05	293	17.50	−1.44	131
	25.05	282	22.10	+0.08	
			24.30	−0.27	
Λ-(−)$_{546}$-*cis*-eq-[Co(edta)(NO$_2$)]$^{2-}$	17.10 sh	116	17.15	+1.01	131
	20.05	236	19.45	−1.13	
			21.75 sh	−0.42	
	29.40	3410	24.45	+0.25	
			28.25	−0.90	
Λ-(−)$_{546}$-*cis*-eq-[Co(Hedta)(H$_2$O)]			17.10	+0.23	132
			18.90	−1.02	
cis-polar-[Co(*RS*-2,4-Hptnta)Cl]$^-$	17.24	144.5			99
	25.71	162.2			
	42.55	19952.6			
Λ-(+)-*cis*-eq-[Co(eddda)(NO$_2$)]$^{2-}$ (derived from *trans*(O$_5$)	16.80 [a] sh	sh	16.80	+0.46	110
	19.80 [a]	205 [a]	19.68	−1.61	
			24.50 [a]	+0.31 [a]	
Λ-(+)-*trans*-eq-[Co(eddda)(NO$_2$)]$^{2-}$ (derived from *trans*(O$_6$))	17.00 [a] sh	sh	16.89	+1.99	110
	19.60 [a]	145 [a]	20.0	−0.44	
Λ-(+)-*cis*-polar-[Co(eddda)(H$_2$O)]$^-$ (derived from *trans*(O$_5$))	18.00 [a]	310 [a]	16.18	+0.24	110
			18.45	−1.92	
	25.70 [a]	188 [a]	26.00 [a]	+0.20 [a]	
Λ-(+)-*cis*-eq-[Co(eddda)(H$_2$O)]$^-$ (derived from *trans*(O$_5$O$_6$)	18.00 [a]	215 [a]	16.39	+1.48	110
			18.28	−2.66	
	25.60 [a]	135 [a]	24.00 [a]	+0.30 [a]	

[a] Values estimated from spectra.

quinquedentate complexes with the ethylenediamine-*N*,*N'*-diacetate-*N*,*N'*-di-3-propionate (eddda) ligand. While only three isomers are possible for corresponding complexes involving edta, there are ten structures possible with eddda derived from the geometric isomers of a hexadentate $[Co(eddda)]^-$ complex (Fig. 2(c)). Those of the quinquedentate complexes are quite complicated and difficult to interpret. PMR (at 250 MHz) and ^{13}C NMR spectra were used for the study of the stereochemistry of the isolated complexes. The four quinquedentate complexes of eddda (two nitro and two aqua) were resolved optically and their electronic absorption and CD spectra measured. The numerical data for the nitro and aqua isomers having a positive sign of the lowest energy CD peaks are given in Table 9. By correlation of these spectra with the CD spectra of the hexadentate species [102,103] all complexes giving rise to spectra shown are assigned the Λ absolute configuration with the single exception of one (second isolated) nitro complex which has no net chirality (Λ or Δ ring pairs) if the rings are considered equivalent. In addition, the isolated dinitro complex was also characterized and only the more "symmetrical" quadridentate structure (*trans*(O_5)) was considered possible. Reaction pathways for conversion of quadridentate to hexadentate $[Co(eddda)]^-$ species were suggested.

(b) Complexes with chromium(III) and rhodium(III)

Absorption and optical activity data for complexes of chromium(III) and rhodium(III) are summarized in Table 10.

Aqua(hydrogenethylenediaminetetraacetato)chromium(III), $[Cr(Hedta)(H_2O)]$ was obtained by Brintzinger et al. [51] and the kinetics of its complexation reaction were studied spectrophotometrically by Hamm [133]. Stability constants of chromium(II) and chromium(III) with edta ligand have been determined by Pecsok et al. [134].

Schwartzenbach and Biedermann [135] showed that $[Cr(Hedta)(H_2O)]$ contains one coordinated water molecule. Later, the *cis*-equatorial structure of this complex was confirmed crystallographically [117].

Dwyer and Garvan [97] prepared the $[Cr(Hedta)(H_2O)]$ complex by the method of Hamm [133] and showed that its IR spectrum in the solid gave two expected peaks in the carboxyl region (at 1739 and 1639 cm^{-1}). The $[Cr(edta)(H_2O)]^-$ anion could not be resolved under a variety of conditions with a range of resolving cations. The formula $[Cr(edta)(H_2O)]^-$ also was assigned in solution by absorption spectra for the pH range 3.6 to 5.3 using acetate buffer solutions [94].

Ogino et al. studied the equilibrium and kinetics of the reactions of $[CrY(H_2O)]^- + X \rightleftharpoons [CrYX]^{2-} + H_2O$ (Y = edta and its analogs; X = an anion such as OAc^- [136], N_3^- [137], ONO^- and NCS^- [138]). They found that anation proceeds quite rapidly and the equilibrium constant is large because

TABLE 10

Absorption (AB) and circular dichroism (CD) data for Cr(III) and Rh(III) complexes with edta-type ligands acting as quinquedentate[a]

Complex	AB		CD		Ref[b]
	$\tilde{\nu} \times 10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu} \times 10^{-3}$ (cm^{-1})	$\Delta\epsilon$	
cis-eq-[Cr(Hedta)(H_2O)]	18.38	146			*138*,133
(*dl*)	26.04	110			
[Cr(edta)(H_2O)]$^-$	18.55	228			*138*,133
(*dl*)	25.51	115			
[Cr(edta)(NCS)]$^{2-}$	18.65	208			*138*,140
(*dl*)	25.64	120			
[Cr(edta)(OAc)]$^{2-}$	17.70	147			138
(*dl*)	25.38	119			
Δ-(+)$_{546}$-[Cr(*S*-pdta)(H_2O)]$^-$	18.69	102.3	17.54	−0.7	80a
			19.49	+1.2	
	25.91	70.8	24.75	−0.2	
			27.47	+0.3	
cis-eq-[Rh(Hedta)(H_2O)]	28.33				*97*,145
(*dl*)					147
[Rh(edta)(H_2O)]$^-$	28.90	602.5			97,145
(*d* and *l*)	34.13	389.0			147
[Rh(Hedta)Cl]$^-$	26.83	549.5			145,*147*
(*d* and *l*)	32.93	445.6			
[Rh(Hedta)Br]$^-$	26.07	562.3			147
(*dl*)	32.18	549.5			
[Rh(Hedta)I]$^-$	24.93	588.8			147

(*dl*)	34.13				
$[Rh(H_2edta)Cl_2]^-$	24.87	400			*80a*,97
(*dl*)	29.85	200			145
	38.46	18000			
$[Rh(Hedta)Cl_2]^{2-}$	–				97
(*dl*)					
$[Rh(edta)Cl_2]^{3-}$	33.30	14000			97,*148*
(*d*)	34.00	11000			
	38.00	8000			
	39.20	12000			
$[Rh(H_2edta)Br_2]^-$	23.92	460			*80a*,97
(*dl*)	29.41	250			
	38.46	20000			
$[Rh(Hedta)Br_2]^{2-}$	–				97
(*dl*)					
$[Rh(edta)Br_2]^{3-}$	–				97
(*l*)					
$[Rh(edta)(OH)_2]^{3-}$	31.50	5000			*148*
(*dl*)	32.60	4000			
	36.50	4000			
	38.00	3000			
Δ-$(+)_{546}$-$[Rh(S\text{-}Hpdta)(H_2O)]$	28.73	490	23.70	+0.3	*80a*
	33.78	301	–		
	43.47	15000	–		
$(-)_{546}$-$[Rh(R\text{-}Hpdta)(H_2O)]$	–				69
$(-)_{546}$-$[Rh(R\text{-}pdta)(H_2O)]^-$	–				69

[a] Some quadridentate Rh(III) complexes are also included. [b] References to numerical data are italicized.

the free carboxymethyl group assists in expelling the water molecule from the coordination sphere, but in the case of X = NCS, the equilibrium constant was very small [138]. Attempts to prepare $[Cr(edta)X]^-$ ($X = Cl^-$ or Br^-) by treating $[Cr(Hedta)(H_2O)]$ with concentrated hydrochloric acid or hydrobromic acid resulted in the formation of other species such as $[CrCl_2(H_3edta)(H_2O)]$ or $[CrBr_2(H_3edta)(H_2O]$ [139a].

Tsuchiya et al. [140] investigated the thermal reactions of the complexes in the solid phase. They prepared $[Cr(NH_3)_5NCS][Ca(edta)] \cdot 5H_2O$ and showed that this complex was finally converted into Ca[Cr(edta)NCS] upon heating in the solid phase. The complex was isolated from water as the hexahydrate and characterized by IR and absorption spectra. The authors proposed this as a general method for the production of other new chromium(III) complexes of the series $[Cr(\text{edta or its analog})X]^{2-}$ (X = unidentate anions).

In a recent study Ogino et al. [141] made kinetic measurements of the cleavage of the Cr–C bond in (ethylenediaminetetraacetato)(hydroxyalkyl)-chromium(III) complexes, $[Cr(CR_1R_2OH)(edta)]^{2-}$ (R_1, R_2 = H or CH_3), to give $[Cr(edta)(H_2O)]^-$. The activation parameters of these reactions were also determined. Comparison of the kinetic parameters with those of the corresponding (hydroxyalkyl) quinqueaqua complexes indicates that the uncoordinated carboxylic acid group of the coordinated edta acts as an internal electrophile to the chromium-bound carbon atom.

Dwyer and Garvan [69] prepared aqua(hydrogen-*l*-propanediaminetetra-acetato)chromium(III) from the optically active complexing agent. The specific rotation ($[\alpha]_{546} = -800°$) was the same as the laevo isomer prepared by the resolution of the racemic complex with either optically active $[Co(en)_2(NO_2)_2]^+$ or $[Co(en)_2(ox)]^+$.

Gillard [80a] has prepared the $(+)_{546}$-$[Cr(S\text{-pdta})(H_2O)]^-$ complex and studied its absorption and CD spectra. The absolute configuration of $(+)_{546}$-$[Cr(S\text{-pdta})(H_2O)]^-$ is known from the stereospecific requirement of the methyl group [69] and this configuration was described as Δ (the notation given in the paper is $S(C_2)$).

Rhodium(III) was shown to form quinquedentates with edta (in which case some quadridentate complexes were also described) and pdta ligands and the complexes were studied by a variety of physicochemical techniques.

Dwyer and Garvan [97] prepared the aqua(hydrogenethylenediaminetetra-acetato)rhodium(III) complex from rhodium(III) hydroxide and aqueous ethylenediaminetetraacetic acid at 145–150°C. The IR spectrum showed a free carboxylic group, and by analysis the presence of a molecule of water was deduced, as expected for $[Rh(Hedta)(H_2O)]$. From pH titrations, for the reactions

$$[Rh(Hedta)(H_2O)] \rightleftharpoons H^+ + [Rh(edta)(H_2O)]^- \rightleftharpoons H^+ + [Rh(edta)(OH)]^{2-}$$

the authors obtained pK_1 and pK_2 values ($pK_1 = 2.32 \pm 0.08$ and $pK_2 = 9.12 \pm 0.02$). The potassium and ammonium salts were prepared by neutralization of the complex acid. Resolution was effected through the active *cis*-$[Co(en)_2(NO_2)_2]^+$ ($[\alpha]_D = \pm 140°$; $[\alpha]_{546} = \pm 180°$ for the isomers of $K[Rh(edta)(H_2O)] \cdot H_2O$). Solutions of the active potassium salts retained their rotations unchanged for three months in the dark, but $[\alpha]_{546}$ had decreased from -180 to $-100°$ in a year. The half-life at 96°C in the dark was calculated to be 163 min from the mean value of the rate constant, $k = 4.2 \times 10^{-3}$ min^{-1} (where k is the rate of racemization). The more rapid racemization might occur through the photoracemization of $[Rh(edta)(H_2O)]^-$. Treatment of $K[Rh(edta)(H_2O)]$ with concentrated hydrochloric and hydrobromic acids at 90°C gave the dichloro and dibromo complexes $K[Rh(H_2edta)Cl_2]$ and $K[Rh(H_2edta)Br_2]$. The active dihalo quadridentate complexes, prepared from active $K[Rh(edta)(H_2O)] \cdot H_2O$, did not undergo photoracemization in aqueous solution, but, in the dark, the halogen atoms slowly dissociated, and at the end of two months the original aqueous complex was obtained with complete retention of configuration.

Later, the same authors [69] prepared one isomer laevo-aqua(hydrogen-*l*-propanediaminetetraacetato)rhodium(III) monohydrate, $(-)_{546}$-[Rh(*R*-Hpdta)$(H_2O)]H_2O$ ($[\alpha]_{546} = -158°$). No isomer with a positive rotation could be detected even after transformation to the barium salt, Ba[Rh(*R*-Hpdta)$(H_2O)]_2$ and resolution through the *cis*-$[Co(en)_2(NO_2)_2]^+$ cation. The IR spectrum of the complex showed two expected peaks in the carboxyl region (at 1732 and 1620 cm^{-1}). No rotational change occurred when solutions of $(-)_{546}$-Ba[Rh(*R*-Hpdta)$(H_2O)]_2$ were heated in the dark at 96°C for 6 h. The solutions of [Rh(*R*-Hpdta)$(H_2O)]^-$ slowly lost their activity at 20°C in diffuse laboratory light. The observed mutarotation of $(-)_{546}$-[Rh(*R*-Hpdta)$(H_2O)]$ was interpreted to be due to the photoaquation of the complex in which a water molecule is substituted for one of the carboxylate ligands.

However, Blackmer et al. [142] have investigated the systems involving optically active $[Rh(edta)]^-$ and [Rh(*R*-pdta)$]^-$ complexes by PMR and CD in neutral solution (pH = ca. 6.5, the ligands being hexadentate [55]) and reached a different conclusion as to the nature of the photolysis product. They reproduced Dwyer and Garvan's results in all respects under these conditions. For the $(-)_{546}$-[Rh(III)(*R*-pdta)$]^-$ complex $[\alpha]_{546}$ was found to decrease from $-159.7°$ to $-49.5°$ after photolysis. No significant changes in the acetate portion of the PMR spectrum of [Rh(*R*-pdta)$]^-$ were observed upon photolysis of the sample indicating the hexadentate character of the ligand was retained and both expected diastereoisomers were identified. This photoracemization model was tested by irradiating a partially resolved $[Rh(edta)]^-$ sample at pH ~ 6.5 in which case the racemized enantiomers would be of equal energy; thus no dark recovery of optical activity would be expected. As concluded, the details of the photochemical processes and the explanation of the photostationary state must await further investigation.

Based on powder photographs Dwyer and Garvan [97] found that [Rh(Hedta)(H_2O)] was isomorphous with [Cr(Hedta)(H_2O)]. Both complexes of rhodium(III), [Rh(Hedta)(H_2O)] [97] and [Rh(*R*-Hpdta)(H_2O)]·H_2O [69] were thought to have the same (equatorial) structure and the favored *cis*-equatorial isomer (Fig. 3(b)) of the [Rh(Hedta)(H_2O)] complex has recently been confirmed by X-ray analysis [119].

Recipes given for the analytical use [143] have given rise to mixtures, and early values [144] for electronic absorption spectra of complexes of edta with rhodium(III) also refer to a mixture. More recently the spectra of properly characterized compounds have been studied [80a,145–147].

Ezerskaya and Filimonova [145] studied the composition of rhodium(III) complexes formed in solution at different pH values and chloride ion concentrations. The solution studies involved polarography, spectrophotometry, potentiometry and ion exchange, but also some compounds were isolated and analyzed. They established that the reaction of sodium hexachlororhodate with edta (pH = 4.5–5) gives Na[Rh(edta)(H_2O)], but in the region of pH = 5–8, the aquahydroxorhodium cation and probably a polymerized $[Rh(edta)(OH)]_n^{2-}$ are also formed. When treated with HCl, Na[Rh(edta)(H_2O)] is converted into the monochloro and dichloro complexes, Na[Rh(Hedta)Cl]·$2H_2O$ and Na[Rh(H_2edta)Cl_2]·$2H_2O$, which were isolated.

Gillard [80a] collected absorption data for several known [97,145,146] complexes of rhodium(III). For this purpose, he also repeated the preparation of quadridentate $[Rh(H_2edta)Cl_2]^-$ and $[Rh(H_2edta)Br_2]^-$ complexes and prepared optically active $(+)_{546}$-[Rh(*S*-Hpdta)(H_2O)] for which absorption and CD data were presented. The $(+)_{546}$-[Rh(*S*-Hpdta)(H_2O)] complex, which has approximately C_2 symmetry, shows a splitting of band I similar to that of the $(-)_{546}$-$[Co(S\text{-pdta})]^-$ isomer of known configuration [69], and its absolute configuration has been described as Δ (assigned in the paper as $S(C_2)$).

Yamasaki and Sugiura [146] reported the compound formulated as Na[Rh(edta)]·H_2O which was shown [80a] to be the same as that prepared by Dwyer and Garvan [97], and studied in solution by Russian workers [145]. This compound has been shown [80b] by IR spectroscopy to contain quinquedentate edta, and so is correctly formulated as Na[Rh(edta)(H_2O)].

Later, Sugiura and Yamasaki [147] prepared the following compounds of rhodium(III): Na[Rh(Hedta)Cl]·$2H_2O$, H[Rh(Hedta)Cl]·$2H_2O$, Na[Rh(edta)(H_2O)]·H_2O, [Rh(Hedta)(H_2O)]·$2H_2O$, Na[Rh(Hedta)Br]·$2H_2O$ and K[Rh(Hedta)I]·$2H_2O$. The complexes have been characterized from their chemical properties and electronic absorption and IR spectra. Of these, the complexes $Na[Rh(Hedta)Cl] \cdot 2H_2O$ and $Na[Rh(edta)(H_2O)] \cdot H_2O$ have been resolved through their diastereoisomeric salts with strychnine or $(-)_D$-$[Co(en)_2(NO_2)_2]^+$ and the values of optical rotation for the latter complex were different from that obtained by Dwyer and Garvan [97] ($[\alpha]_D = -25.2°$ and $+25.8°$ for the isomers of K[Rh(Hedta)Cl] and $[\alpha]_D$ $-25.2°$ and $+31.8°$ for the isomers of $K[Rh(edta)(H_2O)]$). From ORD curves of the $(+)_D$-$[Rh(Hedta)Cl]^-$ and $(-)_D$-$[Rh(edta)(H_2O)]^-$ complexes it was suggested that these complexes have opposite absolute configurations.

Smith and Sawyer [55] investigated the PMR spectra of several complexes of edta with rhodium(III) and determined the stereochemistry of the complexes in aqueous solution. The work is believed to include the first evidence for the formation of various species in solution in a limited pH range (pH 0–10). For the monoaqua and monochloro edta complexes the spectra indicate that edta acts as a quinquedentate ligand at low pH (ca. 1) and that complexes probably have the *cis*-equatorial structure (Fig. 3(b)). At higher pH values (ca. 4–8) the spectra of the monoaqua complex indicate that ionization of the unbound carboxylic acid proton is accompanied by coordination to form the hexadentate complex. The data obtained for the dichloro and dibromo complexes confirm that edta functions as quadridentate and that the complexes should have the *trans*(O) configuration (Fig. 3(c), isomer **I**).

Finally, Russian workers [148] have recently studied the formation (in solution) of $[Rh(edta)Cl_2]^{3-}$ and $[Rh(edta)(OH)_2]^{3-}$ complexes in which edta also functions as a quadridentate ligand.

*(ii) Ethylenediamine-*N,N,N′*-triacetate (ed3a) and its substituted derivatives*

The quinquedentate ligand system most completely studied to date has been ethylenediamine-*N*,*N*,*N*′-triacetate (ed3a) and N-substituted analogs (Table 8). Numerous studies indicated the existence of only one geometric isomer, but prior to the determination of the crystal structure [118] of $[Co(ed3a)(NO_2)]^-$, there were conflicting reports on which isomer is formed [129,149–152].

In a PMR study, Blackmer and Sudmeier [129] found the geminal coupling constants for the glycinate *AB* splitting patterns. These results, a series of stereospecific acid- and base-catalyzed deuteration experiments, and chemical shift correlations could all be interpreted as support for the presence of the *cis*-equatorial isomer alone. These results were in contrast with previous PMR and kinetic studies [150,151] which favored the existence of the polar isomer, based largely on the slow rate of base-catalyzed deuterium exchange.

Van Saun and Douglas [149] prepared and resolved the series of complexes $[Co(hed3a)X]^-$ and $[Co(med3a)X]^-$ where hed3a is the anion of *N*-hydroxyethylethylenediamine-*N*,*N'*,*N'*-triacetic acid, med3a is the anion of *N*-methylethylenediamine-*N*,*N'*,*N'*-triacetic acid, and X is Cl^-, Br^- or NO_2^-. Previous studies [121,131] with edta and this work with the optical isomers of these complexes found no evidence for geometrical isomerism. The least strained isomer (later assigned as *cis*-equatorial, Fig. 3(b)) was assumed to be present in the studies. The authors also repeated the resolution of $[Co(edta)Cl]^{2-}$ and found an error in the CD data earlier reported [131] for $(+)_{546}$-$[Co(edta)Cl]^{2-}$. This confusion resulted from the fact that the CD curve reported [131] was for a mixture of the protonated and deprotonated species. The absorption and CD data for the complexes studied (Table 11) were compared with those for the related series of complexes $[Co(edta)X]^{2-}$ [131] (Table 9). The CD splitting patterns are similar for complexes containing the same unidentate ligand, but significant variations were observed in the intensities of some CD bands, particularly for the NO_2^- complexes. The great similarities of the CD curves for $[Co(hed3a)X]^-$, $[Co(med3a)X]^-$ and $[Co(edta)X]^{2-}$ ($X = Cl^-$ or Br^-) indicate that the free acetate group in $[Co(edta)X]^{2-}$ does not make a significant contribution to the optical activity of the complex. The CD data for the isomers of $(+)_{546}$-$[Co(hed3a)(NO_2)]^-$ and $(+)_{546}$-$[Co(med3a)(NO_2)]^-$ (Table 11) were related to those of $(+)_{546}$-$[Co(edta)(NO_2)]^{2-}$ [131] (Table 9) and these complexes were assigned the same (Δ) configurations. The $(-)_{546}$ isomers of chloro and bromo complexes with hed3a and med3a were assigned the same (Δ) configuration as for $(-)_{546}$-$[Co(edta)Cl]^{2-}$, on the basis of the similar sign patterns of their CD curves.

A series of complex compounds of cobalt(III) involving quinquedentate ethylenediamine-*N*,*N*,*N'*-triacetic acid as the chelating agent were prepared and characterized by Legg and co-workers [152]. The structures of these complexes, with the general formula $[Co(ed3a)X]^-$ ($X = Cl^-$, NO_2^- or ONO^-) *, were inferred from their chemistries and spectral data. Chromatography revealed the presence of only one isomer in all cases. No complexity in the IR spectral bands was noted, also suggesting the presence of only one isomer (later assigned as *cis*-equatorial [154]). The absorption spectra of the complexes were compared with those for the related series of complexes $[Co(edta)X]^{2-}$, $[Co(Hedta)X]^-$ and $[Co(med3a)X]^-$. The PMR spectra of the complexes indicate that ed3a acts as a quinquedentate ligand, exhibiting three different *AB* patterns occurring in the region 4.3 to 3.2 p.p.m. (vs. sodium 3-(trimethylsilyl)-1-propanesulfonate). The spectrum in

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* The complex believed to be a nitrito isomer was later found [153, 154] to correspond to the *trans*-equatorial isomer of the nitro complex (see Fig. 3(b)).

TABLE 11

Absorption (AB) and circular dichroism (CD) data for [M(ed3a)X]^{n} type complexes

Complex	AB		CD		Ref.
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ε	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	Δε	
Δ-$(-)_{546}$-*cis*-eq-[Co(edta)Cl]$^{2-}$	17.10	220	15.50	−0.05	149
in 0.1 M HCl			17.70	+1.33	
	24.75	190	22.80	−0.10	
			24.40	+0.20	
Δ-$(-)_{546}$-*cis*-eq-[Co(hed3a)(Cl)]$^{-}$	17.10	278	17.60	+1.45	149
	24.80	251	22.50	−0.03	
			24.60	+0.31	
Δ-$(-)_{546}$-*cis*-eq-[Co(med3a)(Cl)]$^{-}$	17.30	210	17.50	+1.50	149
	24.80	188	22.40	−0.04	
			24.60	+0.14	
Δ-$(-)_{546}$-*cis*-eq-[Co(hed3a)(Br)]$^{-}$	17.00	241	17.35	+1.41	149
	25.00 sh	243	22.20	−0.05	
			24.10	+0.28	
Δ-$(-)_{546}$-*cis*-eq-[Co(med3a)(Br)]$^{-}$	17.10	215	17.42	+1.38	149
	24.90	216	22.30	−0.04	
			24.10	+0.18	
Δ-$(+)_{546}$-*cis*-eq-[Co(hed3a)(NO$_2$)]$^{-}$	17.10 sh	110	17.30	−0.69	149
	20.20	232	19.20	+0.82	
			21.80 sh	+0.35	
	29.20	3470	24.20	−0.26	
Δ-$(+)_{546}$-*cis*-eq-[Co(med3a)(NO$_2$)]$^{-}$	17.10 sh	90	17.40	−0.33	149
	20.30	182	19.30	+0.40	
			21.80	+0.32	
	29.40	3100	24.60	−0.21	
Δ-$(-)_{546}$-*cis*-eq-[Co(ed3a)(NO$_2$)]$^{-}$	17.10 sh	90	17.18	+0.72	156
	20.40	193	21.05	−1.21	
Δ-$(+)_{546}$-*cis*-eq-[Co(bed3a)(NO$_2$)]$^{-}$	16.80 [a] sh	sh	17.24	−0.66	156
	20.20 [a]	240 [a]	19.41	+1.10	
			22.00 [a] sh	+0.40 [a]	
			24.20 [a]	−0.30 [a]	
Δ-$(-)_{546}$-*cis*-eq-*R*-[Co(*R*-pd3a)-	17.20 sh	93	17.03	+0.77	154,156
(NO$_2$)]$^{-}$			18.80 [a]	+0.50	
	20.30	191	21.18	−1.04	
Λ-$(+)_{546}$-*trans*-eq-*S*-[Co(*R*-pd3a)-	17.80	181	17.80 [a]	−1.25	154
(NO$_2$)]$^{-}$	20.90	174	21.30 [a]	+1.60	
Λ-$(-)_{546}$-*cis*-eq-[Co(ed3a)(H$_2$O)] [b]	18.35	230	17.92	−1.76	158
			20.75	+0.25	
	26.45	175			

TABLE 11 (continued)

Complex	AB		CD		Ref.
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	$\Delta\epsilon$	
Λ-(−)$_{546}$-*cis*-eq-[Co(hed3a)(H$_2$O)][b]	18.08	248	18.69	−1.40	158
			23.25	+0.15	
	25.90	208	25.60[a]	−0.35[a]	
Λ-(−)$_{546}$-*cis*-eq-[Co(med3a)(H$_2$O)][b]	18.10	165	18.20	−0.90	158
	25.90	139	25.60	−0.07	
Λ-(−)$_{546}$-*cis*-eq-[Co(med3a)(CN)]$^-$ [b]	17.20	73	17.50	+0.38	132
	20.90	148	19.60	−0.45	
			22.20	+0.26	
	27.60	185	25.60	+0.95	
Λ-(−)$_{546}$-*cis*-eq-[Co(hed3a)(CN)]$^-$ [b]	17.30	71	17.20	+1.05	132
	20.60	160	19.80	−0.99	
	27.60	195	25.40	+1.32	
[Cr(ed3a)(H$_2$O)]	18.48	133			136
	25.90	107			
[Cr(med3a)(H$_2$O)]	18.55	143			136
	25.90	113			
[Cr(hed3a)(H$_2$O)]	18.35	151			136
	25.97	118			
[Cr(ed3a)(NCS)]$^-$	18.72	166			138
	25.54	102			
[Cr(hed3a)(NCS)]$^-$	18.69	187			138
	25.54	110			
[Cr(hed3a)(N$_3$)]$^-$	18.11	207			138
	24.57	130			
[Cr(ed3a)(OAc)]$^-$	18.34	147			136
	25.44	108			
[Cr(med3a)(OAc)]$^-$	18.21	154			136
	25.38	112			
[Cr(hed3a)(OAc)]$^-$	17.98	162			136
	25.38	113			
[Cr(hed3a)(Cl)]$^-$	17.69	128			139a,b
	25.18	109			
[Cr(hed3a)(Br)]$^-$	17.39	127			139a,b
	24.51	145			

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[a] Values estimated from spectra. [b] Unpublished data from theses.

acid solution confirms the existence of the ed3a ligand by the amine proton absorption and its coupling with the low-field acetate protons. Partial resolution of the complexes was accomplished by the cellulose ion-exchange method given by Legg and Douglas [155].

Maricondi and Maricondi [156] studied the contribution to the rotatory strength from the asymmetric nitrogen donor atom in the nitro complexes of cobalt(III) containing unsubstituted ethylenediamine-*N*,*N*,*N'*-triacetate and its *N*-benzyl derivative (bed3a). These structures were established by preparation of the nitro complexes with a quinquedentate *R*-propanediamine-*N*,*N*,*N'*-triacetate (*R*-pd3a) and *R*-pdta ligands which react stereospecifically [69] with cobalt(III) to give complexes of known structure. Spectral data for the one isomer of the nitro complex obtained with *R*-pd3a [154] (Table 11) and data for $(-)_{546}$-$[Co(ed3a)(NO_2)]^-$ (R = H) indicated that both isomers have the structure shown in Fig. 18. On the other hand, Dwyer and Garvan's work [69] with the nitro complex with quinquedentate *R*-pdta

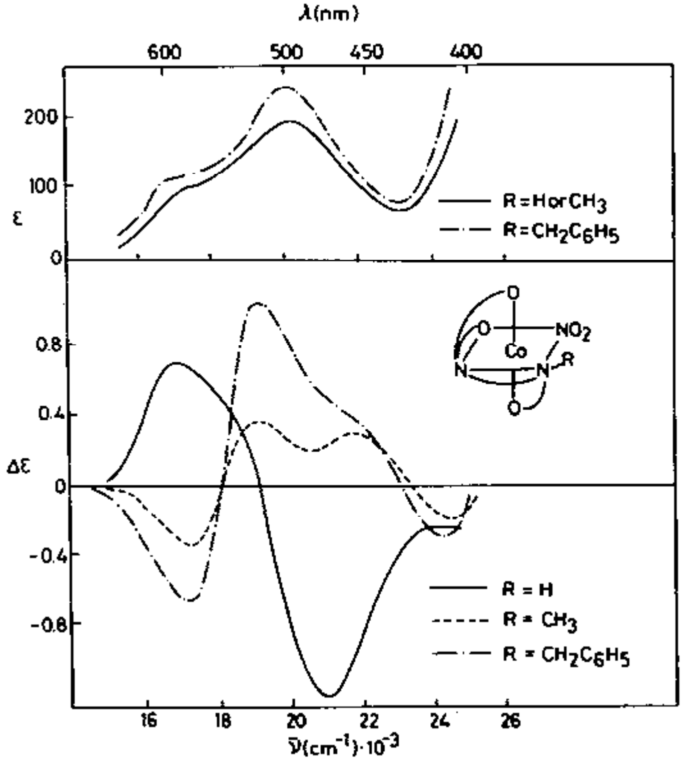


Fig. 18. CD and absorption spectra and Δ absolute configuration of the $(-)_{546}$-$[Co(ed3a)(NO_2)]^-$ (——), $(+)_{546}$-$[Co(bed3a)(NO_2)]^-$ (·–·–·), and $(+)_{546}$-$[Co(med3a)(NO_2)]^-$ (— — —). (Reproduced with permission of ACS from ref. 156.)

indicates that $(+)_{546}$-[Co(pdta)(NO_2)]$^-$ also has the structure shown in Fig. 18. Since the CD curves of the complexes with R = CH_2COO^-, CH_3 or $CH_2C_6H_5$ are so similar in general shape and sign pattern, it was assumed that the $(+)_{546}$ isomers of the methyl and benzyl complexes have the same structure as $(-)_{546}$-[Co(ed3a)(NO_2)]$^-$ (see Fig. 18). The isomers of [Co(ed3a)(NO_2)]$^-$ and [Co(bed3a)(NO_2)]$^-$ with comparable structures give CD curves which have opposite signs over most of the region of the octahedral $A_{1g} \rightarrow T_{1g}$ cobalt(III) absorption. Thus the compounds reported give clear evidence for a change in sign of CD bands due to replacement of H by another substituent on an asymmetric nitrogen donor atom. Also, although the asymmetric donor nitrogens make significant contributions to the intensity of individual CD bands, their contribution to the net rotatory strength of the compounds reported is quite small. In addition, the same authors [154] isolated and characterized two isomers of the [Co(*R*-pd3a)(NO_2)]$^-$ complex. The red isomer has the same visible absorption spectrum as the nitro complexes formed with several *N*-substituted ed3a ligands and was designated as *cis*-equatorial. The purple isomer was shown by IR, visible absorption, CD and PMR spectra to have *trans*-equatorial geometry (see Fig. 3(b)). The CD spectra for these complexes (Table 11) provided the first evidence that they were not linkage isomers of the nitro group and curves are readily explained by the opposite configurations of the asymmetric nitrogens resulting from the two different arrangements of the coordinated quinquedentate ligand. Because the asymmetric nitrogen in the *cis*-equatorial isomer is necessarily in an *R* configuration [11] and that in the *trans*-equatorial is necessarily in an *S* configuration, one would expect the two CD curves to have opposite signs. The change in the position of the acetate ring attached to the secondary nitrogen in the two isomers results in significant changes in the CD and PMR spectra. The CD data obtained support previous work [156] that the asymmetric nitrogen donor atom is the major source of optical activity in complexes of this type. The *trans*-equatorial isomer formed with unsubstituted ed3a (reported as "nitrito" complex) [152] was found to be converted readily to the *cis*-equatorial form. This requires a flip in the conformation of the puckered backbone ring which is hindered in *R*-pd3a by the preference of the methyl group for an equatorial position. In general, it was thought that for ed3a-type ligands without bulky backbone groups, one would expect to form *cis*-equatorial as the only stable isomer.

Bernhard [157] studied the hydrolysis of the optically active [Co(ed3a)Cl]$^-$, [Co(med3a)Cl]$^-$, [Co(hed3a)Cl]$^-$ and [Co(hed3a)Br]$^-$ complexes. The kinetics of these reactions were investigated over a range of pH values and thermodynamic parameters were calculated. Bernhard [157] discussed the configurations of complexes obtained as a product of the hydrolysis and

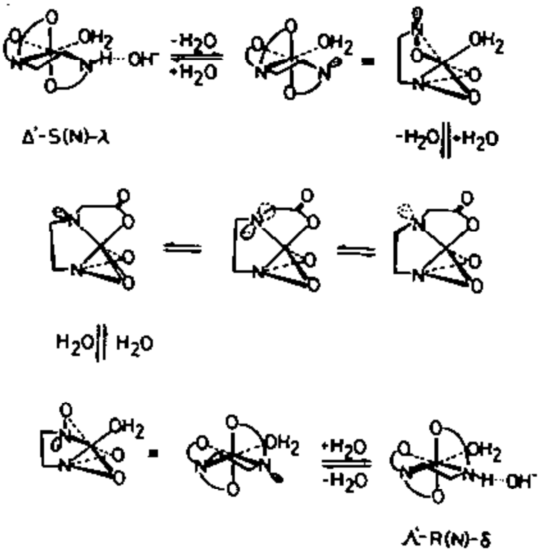


Fig. 19. Proposed mechanism of racemization for the [Co(ed3a)(H_2O)] complex going from Δ to Λ configuration.

correlated the absolute configurations of the initial and final complexes. A mechanism of racemization for the [Co(ed3a)(H_2O)] complex (Fig. 19) was proposed.

Bausę [158] studied the conversion of ed3a-type nitro complexes to the aqua species and prepared [Co(ed3a)(H_2O)], [Co(hed3a)(H_2O)], [Co(med3a)(H_2O)] and [Co(dmp3a)(H_2O)] complexes (dmp3a = 2-methyl-1,2-propanediamine-*N*,*N*′,*N*′-triacetate). The complexes were characterized from their IR, PMR, ^{13}C NMR and CD spectra. The enantiomers of the aqua complexes were generated from resolved nitro complexes by the addition of acid. The optically active [Co(ed3a)(H_2O)] was not isolated in the solid state, but the enantiomeric forms of the nitro complex yielded mirror image CD curves for the aqua isomers. The CD spectra of $(-)_{546}$-[Co(ed3a)(H_2O)], $(-)_{546}$-[Co(hed3a)(H_2O)] and $(-)_{546}$-[Co(med3a)(H_2O)] were compared (Table 11) and all of these complexes were assigned to have Λ configuration. The assignments are based partially on the assumption that the interconversion of these ed3a-type complexes with nitro, aqua, etc., proceeds with retention of configuration and was supported by the previous CD work done on related complexes [131,149,154,156]. The contribution to the CD spectra is determined mainly by the nature of the asymmetric donor nitrogen atom and the phenomenon observed for the nitro complexes [154,156] was not noticed for the aqua complexes.

Russell [132] reported absorption and CD spectra for [Co(med3a)CN]$^-$,

$[Co(hed3a)CN]^-$, $[Co(med3a)(H_2O)]$ and $[Co(Hedta)(H_2O)]$ complexes. It was suggested that the following series of reactions occurred with complete retention of configuration in aqueous solution

$$(+)_{546}\text{-}[Co(med3a)Br]^- \xrightarrow{AgClO_4} (+)_{546}\text{-}[Co(med3a)(H_2O)]$$

$$\xrightarrow{KNO_2} (+)_{546}\text{-}[Co(med3a)(NO_2)]$$

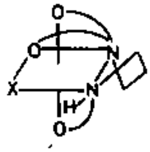
The CD spectra for $[Co(med3a)CN]^-$ and $[Co(hed3a)CN]^-$ complexes, prepared from the corresponding bromo complexes, were found to resemble the corresponding nitro quinquedentate spectra. On this basis, $(-)_{546}$-$[Co(med3a)CN]^-$ and $(-)_{546}$-$[Co(hed3a)CN]^-$ were assigned the same absolute configuration as $(-)_{546}$-$[Co(edta)]^-$ (see Table 11). It was suggested that the *N*-hydroxyethyl group interacts with the coordinated cyanide molecule to account for the intensity differences between the med3a and hed3a complexes. The possibility of a preferred ring conformation for the *N*-hydroxyethyl group was also considered. The change in sign of the third band in the $T_{1g}(O_h)$ region for $[Co(med3a)CN]^-$ relative to $[Co(med3a)(NO_2)]^-$ was discussed; however the reason for the sign change is unknown. The absorption and CD spectra of $[Co(med3a)(H_2O)]$ and $[Co(hed3a)(H_2O)]$ were also given. It was suggested that the similarity of the CD spectra of $[Co(hed3a)(H_2O)]$ and $[Co(edta)Cl]^{2-}$ in 0.1 M HCl may be due to the formation of a pseudo-chelate ring with a preferred conformation. The interaction of this type should not exist for $[Co(med3a)(H_2O)]$ and $[Co(edta)Cl]^{2-}$ in water, which is consistent with the single CD band observed in the $T_{1g}(O_h)$ region.

The series of aqua and nitro cobalt(III) complexes with various quinquedentate ligands (ed3a, med3a, hed3a, dmp3a and *R*-pd3a) has been studied recently using ^{13}C magnetic resonance by Douglas et al. [153]. The peak assignments were made using noise-decoupling, off-resonance decoupling, acid-catalyzed deuteration, methyl substitution on the backbone ring and structural comparison. The stereochemical studies of these complexes using ^{13}C chemical shift provide a means of detecting the change of structural parameters in solution.

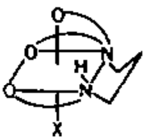
The reactions $[Cr(Y)(H_2O)]^- + X \rightleftharpoons [Cr(Y)(X)]^{2-} + H_2O$ were investigated by Ogino et al. [136,138,139b] (Y = edta and its quinquedentate analogs; X = an anion with −1 charge). The authors calculated rate constants and equilibrium constants of the reactions and presented electronic absorption spectra for complexes studied. The formation constants of $[(Cr(Y)(X)]^{2-}$ increase in the following order with the nature of the X^-: Br^-, $Cl^- < ONO^- < NCS^- \sim OAc^- < N_3^-$. The order seems not to be related directly to that of the basicity of the X^-.

*(iii) 1,3-Propanediamine-*N,N,N′*-triacetate (1,3-pd3a) and its substituted derivatives*

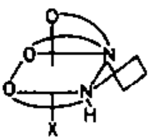
Cobalt(III) complexes with ligands directly related to ed3a, but with lengthened diamine chains have been prepared [159–161]. Such ligands are given in Table 8 (1,3-propanediamine-N,N,N'-triacetate, (1,3-pd3a or trdtra) and N-methyl-1,3-propanediamine-N,N',N'-triacetate, (1,3-mpd3a or N-Me-trdtra)). Since these ligands form six-membered diamine rings, the complexes of the $[M(1,3\text{-pd3a})(X)]^n$ type can form three possible geometric isomers (derived from basic isomerism, Fig. 3(b)) designated as equatorial-skew, polar-chair and polar-skew



equatorial-skew



polar-chair



polar-skew

Fujita and co-workers [160] prepared and characterized two isomers (equatorial-skew and polar-chair) of $[Co(1,3\text{-mpd3a})(X)]^n$ ($X = H_2O$, NH_3 and Cl^-) and only one (polar-chair) isomer of $[Co(1,3\text{-mpd3a})(CN)]^-$. The structures of the complexes were assigned from their PMR and absorption spectra and from the results of kinetic studies. The isomers with PMR signals corresponding to two in-plane and one out-of-plane acetate arms were assigned to the polar-chair. On the other hand, the isomers showing PMR signals corresponding to two out-of-plane and one in-plane acetate arms were assigned to the equatorial-skew. The absorption spectra showed that maximum frequencies of the first and the second bands depend on the kind of unidentate ligand and shift in accordance with the spectrochemical series. The first absorption bands of the equatorial-skew isomers are broader than those of the polar-chair isomers. The equatorial-skew isomer of the chloro complex shows the first absorption band split apparently into two components. The origin of the difference in the band shapes between the two geometric isomers could not be explained.

Later, Fujita and co-workers [161] prepared and characterized three geometric isomers (equatorial-skew, polar-chair and polar-skew) of $[Co(1,3\text{-pd3a})(X)]^n$ type complexes ($X = H_2O$, NH_3 and Cl^-) and only one isomer (polar-chair) of $[Co(1,3\text{-pd3a})(CN)]^-$. The structures were assigned mainly by comparing their electronic spectra with those of the equatorial-skew and polar-chair isomers of $[Co(1,3\text{-mpd3a})(X)]^n$ complexes reported previously. The first absorption bands of the skew isomers are broader than those of the chair isomers and for the corresponding aqua and chloro complexes the first absorption band is split into two components. When the type of unidentate ligand is changed, the lower frequency components shift to a greater extent than the higher frequency components, although all the bands shift in accordance with the spectrochemical series.

Chang and Douglas [159] prepared $[Co(1,3\text{-pd3a})(NO_2)]^-$ from equatorial-skew-$[Co(1,3\text{-pd3a})(H_2O)]$. The absorption spectrum and the ^{13}C NMR spectrum show the nitro product to be a polar isomer for which the diamine backbone ring is believed to have the chair conformation. Since NO_2^- and CN^- are both strong field ligands the very sharp band observed for the NO_2^- complex is very similar to that reported [161] for the polar-chair $[Co(1,3\text{-pd3a})(CN)]^-$ complex. The similarity between CN^- and NO_2^- as ligands leads one to expect the equatorial-skew polar isomerization observed here on substitution of NO_2^- for H_2O. The observation of only two peaks in the carbonyl region (^{13}C NMR: 182.21 and 184.03 p.p.m.) is consistent with the assignment as a polar isomer with the two in-plane carbonyl carbons equivalent.

E. COMPLEXES WITH LINEAR EDDA-TYPE LIGANDS

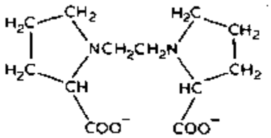
The study of M(III) chelates of ethylenediamine-*N*,*N*′-diacetate (edda) and related quadridentate ligands (see Table 12) has yielded a wealth of stereochemical information. The preparative chemistry is similar to that for the quinquedentate ed3a-type complexes. Octahedral complexes of the general type $[M(\text{edda-type})(L)]^n$ (L = two unidentate or one bidentate ligands) have been prepared mostly by metathetical interaction of $[M(\text{edda-type})Cl_2]^-$ or $[M(\text{edda-type})(H_2O)_2]^+$ with the corresponding unidentate or bidentate ligands. The edda-type moiety is expected to form three geometric isomers: s-*cis*, uns-*cis*, and *trans* (Fig. 4(a)) and most of the complexes investigated have been limited to edda or tmdda ligands (tmdda = trimethylenediamine-*N*,*N*′-diacetate) in the s-*cis* and uns-*cis* configuration, respectively. The structures of isolated complexes (mostly with cobalt(III)) have been deduced from their PMR, ^{13}C NMR, electronic absorption, IR and CD or ORD measurements.

(i) Ethylenediaminetetraacetate (edta) and other ligands of this type and ed3a-type acting as quadridentate

The edta or ed3a-type ligands can occupy four of the six available coordination sites of the M(III) ion to form one or all five of the possible geometric isomers shown in Fig. 3(c) (*trans*(O)(**I**), *trans*(O)(**II**), *cis*(O)(**I**), *cis*(O)(**II**), *cis*(O)(**III**)). Such complexes have been investigated with cobalt(III).

TABLE 12

Quadridentate edda-type ligands

Ligand	Abbreviation
Ethylenediamine-*N*,*N*′-diacetate ($^-OOCCH_2)NHCH_2CH_2NH(CH_2COO^-$)	edda
N,*N*′-Dimethylethylenediamine-*N*,*N*′-diacetate ($^-OOCCH_2)N(CH_3)CH_2CH_2(CH_3)N(CH_2COO^-$)	dmedda
N,*N*′-Diethylethylenediamine-*N*,*N*′-diacetate ($^-OOCCH_2)N(C_2H_5)CH_2CH_2(C_2H_5)N(CH_2COO^-$)	deedda
N,*N*′-Dibenzylethylenediamine-*N*,*N*′-diacetate ($^-OOCCH_2)N(C_6H_5CH_2)CH_2CH_2(C_6H_5CH_2)N(CH_2COO^-$)	dbedda
l-Stilbenediamine-*N*,*N*′-diacetate ($^-OOCCH_2)NHCH(C_6H_5)CH(C_6H_5)NH(CH_2COO^-$)	*l*-sdda
Ethylenediamine-*N*,*N*′-di-*S*-α-propionate [$^-OOC(CH_3)CH]NHCH_2CH_2NH[CH(CH_3)COO^-$]	*SS*-eddp
1,3-Propanediamine-*N*,*N*′-diacetate (trimethylenediamine-*N*,*N*′-diacetate) ($^-OOCCH_2)NHCH_2CH_2CH_2NH(CH_2COO^-$)	tmdda
(2*S*,2′*S*)-1,1′-(ethane-1,2-diyl)bis(pyrrolidine-2-carboxylate) 	pren
Ethylenediamine-*N*,*N*′-di-*S*-α-isovalerate $^-OOC[(CH_3)_2CH]CHNHCH_2CH_2NHCH[CH(CH_3)_2]COO^-$	*SS*-eddiv
1-Diethylenetriamineacetate $H_2NCH_2CH_2NHCH_2CH_2NH(CH_2COO^-)$	dtma
N,*N*-bis(2-aminoethyl)glycinate $(H_2NCH_2CH_2)_2NCH_2COO^-$	i-dtma
N-(2-aminoethyl)iminodiacetate (β-aminoethyliminodiacetate) $H_2NCH_2CH_2N(CH_2COO^-)_2$	aeida

Ogino and co-workers [162a,b] prepared mixed ligand cobalt(III) complexes containing ethylenediamine (or *R*-propanediamine) tetra- (or tri-) acetate and ethylenediamine by the reactions of [Co(edta)]$^-$ and [Co(*R*-pdta)]$^-$ complexes with ethylenediamine. The following complexes were isolated and characterized: *trans*(O)(I)-[Co(H$_2$edta)(en)]$^+$, *trans*(O)(I)-[Co(Hed3a)(en)]$^+$, *trans*(O)(I)-[Co(*R*-H$_2$pdta)(en)]$^+$, *trans*(O)(I)-[Co(*R*-Hpd3a)(en)]$^+$, *trans*(O)(II)-[Co(*R*-H$_2$pdta)(en)]$^+$ and two quinquedentate complexes (*cis*-eq-[Co(*R*-Hpdta)(enH)]$^+$ and *cis*-eq-[Co(*R*-pd3a)(enH)]$^+$. The structures of the complexes were assigned on the basis of pH titration, optical resolution and IR, electronic absorption, and PMR spectroscopy. The CD data of $(-)_{589}$-[Co(H$_2$edta)(en)]$^+$ and $(-)_{589}$-[Co(Hed3a)(en)]$^+$ (see Table 13) were compared with that of the known Δ-*s*-*cis*-[Co(edda)(en)]$^+$

TABLE 13

Absorption (AB) and circular dichroism (CD) data for cobalt(III) complexes containing ethylenediamine (or *R*-propanediamine) tetra (or tri)acetate and ethylenediamine[a]

Complex	AB		CD	
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	$\Delta\epsilon$
Δ-$(-)_{589}$-*trans*(O)(I)-[Co(H$_2$edta)(en)]$^+$	18.60	89.1	18.02	−1.25
	26.38	120.2	20.90	−0.56
	43.48	15848.9	41.67	+17.12
Δ-$(-)_{589}$-*trans*(O)(I)-[Co(Hed3a)(en)]$^+$	18.69	95.5	18.40	−2.78
	27.40	117.4	21.98	+0.35
	44.25	21379.6	43.48	+21.74
Λ-$(+)_{589}$-*trans*(O)(I)-[Co(*R*-H$_2$pdta)(en)]$^+$	18.60	83.1	18.00	+1.14
	26.38	128.8	20.88	+0.48
	43.46	13182.5	41.67	−16.20
Λ-$(+)_{589}$-*trans*(O)(I)-[Co(*R*-Hpd3a)(en)]$^+$	18.69	95.5	18.40	+2.41
	27.40	120.2	21.96	−0.28
	44.25	19952.6	43.00	−20.86
Λ-$(-)_{589}$-*trans*(O)(II)-[Co(*R*-H$_2$pdta)(en)]$^+$	18.22	117.4	17.10	+1.07
	26.12	114.8	19.00	−1.67
	43.48	14454.3	37.88	+15.33
$(+)_{589}$-*cis*-eq-[Co(*R*-Hpdta)(enH)]$^+$	19.08	190.5	16.81	−0.28
	26.98	229.0	18.69	+1.24
	43.86	7585.7	40.00	−10.02
$(+)_{589}$-*cis*-eq-[Co(*R*-pd3a)(enH)]$^+$	17.70 sh	144.5	17.30	−0.86
	19.80	141.2	20.49	+1.07
	26.67	204.1	27.19	+0.32
	44.54	19952.6	42.02	−23.13

[a] Data from ref. 162a,b.

[163]. These data, including PMR results, led to the conclusion that the complexes have the *trans*(O)(I) geometry (see Fig. 3(c)). The $(+)_{589}$-[Co(*R*-H$_2$pdta)(en)]$^+$ shows absorption spectrum identical with that of the $(-)_{589}$-[Co(H$_2$edta)(en)]$^+$ indicating the same geometry (*trans*(O)(I)), but the CD curves of complexes suggested the opposite configuration. Since the $(+)_{589}$-[Co(*R*-H$_2$pdta)(en)]$^+$ complex has the Λ-configuration owing to the stereospecificity coming from the equatorial orientation of the methyl group, the absolute configuration of the $(-)_{589}$-[Co(H$_2$edta)(en)]$^+$ was assigned as Δ. Also, the $(-)_{589}$-[Co(*R*-H$_2$pdta)(en)]$^+$ complex (Table 13) was assigned the *trans*(O)(II) structure by analogy to that of the *trans*-equatorial isomer of [Co(*R*-pd3a)(NO$_2$)]$^-$ complex prepared by Maricondi and Maricondi [154]. The two isolated quinquedentate complexes have been assigned the *cis*-equatorial structure by analogy with other investigated quinquedentate complexes

[129]. The authors also concluded that the reactivity of these mixed complexes with ethylenediamine contradicts the mechanism of the reactions of $[Co(edta)]^-$ and $[Co(pdta)]^-$, with ethylenediamine proposed by Busch et al. [47b].

*(ii) Ethylenediamine-*N,N′*-diacetate (edda) and its substituted derivatives*

Geometric isomerism and optical activity studies of complexes with flexible linear ethylenediamine-*N,N′*-diacetate (edda) or its N- or C-substituted analogues have been carried out extensively in the last two decades. Most of the data obtained for complexes of $[Co(edda\text{-}type)\,(L)]^n$ prior to 1971 have been reviewed by Brubaker et al. [164]. The present review includes the foregoing discussion and data which have appeared in the last decade.

Mori et al. [165] were the first to report the synthesis of cobalt(III) complexes of edda. They prepared the carbonato, diaqua and dinitro complexes. The isomers appear to have been characterized incorrectly but the authors postulated the s-*cis* configuration from a comparative analysis of absorption spectra.

Legg and Cooke [6] prepared $[Co(edda)(am)]^+$, (am = en, $2NH_3$), and the *N*-alkyl substituted analogues (dmedda and deedda, see Table 12) with ethylenediamine. They isolated the s-*cis* and uns-*cis* isomers for the edda complexes, although the latter isomers were obtained in trace quantities only. It was postulated that non-bonding interactions between the sterically restricted amine protons and edda prevented the formation of substantial amounts of the uns-*cis* isomers. They reported a comprehensive study of the stereochemistry of these complexes based on PMR and absorption spectra. A comparison of the PMR spectra obtained for the s-*cis* isomer of edda and the N-substituted analogues enabled these investigators tentatively to assign the individual methylene proton resonances on the basis of bond anisotropies. The authors also assigned the PMR spectrum of the uns-*cis*-$[Co(edda)(en)]^+$ complex. They supported their assignments by showing that the chemical shift differences (attributed to bond anisotropy differences) between s-*cis*-$[Co(edda)(en)]^+$ and its *N*-alkylated analogues (dmedda and deedda) were comparable to those between uns-*cis*-$[Co(edda)(en)]^+$ and $[Co(edta)]^-$.

Sudmeier and Occupati [56e] demonstrated that the less sterically hindered proton in s-*cis*-$[Co(edda)(en)]^+$ (H_A proton) exchanged with deuterium in D_2O approximately ten times more rapidly then H_B. The reaction was acid- or base-catalyzed and, when the ethylenediamine was replaced by the bulkier ligands *N,N′*-dimethyl- or *N,N′*-diethylethylenediamine, the rate of isotopic exchange was found to increase.

Later, Legg and co-workers [56f,166] showed that, when "steric interaction between the ligands" postulated for the diamine analogs in the uns-*cis* isomers [6] was eliminated by employing bidentate ligands (carbonate, oxalate, malonate) or unidentate ligands (H_2O, Cl^-), substantial quantities of the uns-*cis* isomers were obtained. They prepared $[Co(edda)(L)]^{\mp}$ complexes ($L = CO_3^{2-}$, ox^{2-}, mal^{2-}, $2H_2O$, $2Cl^-$) and substantial yields of both the s-*cis* and uns-*cis* isomers were isolated through a series of chromatographic steps and fractional crystallizations, with no evidence for the *trans* configuration of edda *. A study of the PMR spectra [56f] of the uns-*cis*-isomers of edda complexes, using selective deuterium exchange, showed the original assignment of H_B by Legg and Cooke [6] to be incorrect. The new data obtained for the edda chelate system were compared with PMR data previously reported for cobalt(III) complexes of related ligands. This permitted a systematic classification of the glycine ring methylene resonances (an *AB* spectrum) into four categories. The assignment was significantly different from the original assignment [6], thus casting some doubt on the explanation of chemical shift differences based only on bond anisotropies.

Good preparative methods for diamine uns-*cis* edda-Co(III) complexes were developed later on Kuroda's assumption [168a,b,c] that the coordination mode of edda depends on the temperature. Kuroda and Watanabe [168a] prepared and examined a series of edda cobalt(III) complexes containing chloride, water, ammonia, ethylenediamine, 1,10-phenanthroline and 2,2′-bipyridine (bipy) as the additional ligands. Two isomers were isolated in the cases of the phenanthroline (phen) and 2,2′-bipyridine (bipy) complexes which have been inferred to be the s-*cis* and the uns-*cis* isomers on the basis of their electronic absorption spectra. A new convenient route for the preparation of the series, which passes through the dichloro, chloroaqua and diaqua complexes, has been presented. In addition Kuroda [168b,c] prepared and examined a group of edda cobalt(III) complexes with ammonia, pyridine or alkylamines derived from $[Co(edda)(H_2O)_2]ClO_4$. Three different series among the complexes: (1) the aqua(amine) series, $[Co(edda)(H_2O)(am)]^+$, (2) the s-*cis*-bis(amine) series, $[Co(edda)(am)_2]^+$, and (3) uns-*cis*-$[Co(edda)(NH_3)_2]^+$ as well as uns-*cis*-$[Co(edda)(en)]^+$, have been prepared depending on the conditions of the reaction between the starting diaqua complex and the amines (see Scheme II).

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* The only known *trans* edda isomer (Fig. 4(a)) is *trans*-$[Pt(edda)Cl_2]$ formed by oxidation of square-planar [Pt(edda)] by Cl_2 [167].

$$\text{s-}\mathit{cis}\text{-}[\mathrm{Co(edda)(H_2O)_2}]\mathrm{ClO_4}\;\begin{cases}\xrightarrow[45^\circ\mathrm{C}]{\text{amine}} \text{s-}\mathit{cis}\text{-}[\mathrm{Co(edda)(H_2O)(am)}]\mathrm{ClO_4}\\ \xrightarrow[50^\circ\mathrm{C}]{\text{amine,C}} \text{s-}\mathit{cis}\text{-}[\mathrm{Co(edda)(am)_2}]\mathrm{ClO_4}\\ \xrightarrow[50^\circ\mathrm{C}]{\text{elam}} \text{s-}\mathit{cis}\text{-}[\mathrm{Co(edda)(elam)}]\mathrm{ClO_4}\\ \xrightarrow[100^\circ\mathrm{C}]{\mathrm{NH_3}\text{ or en}} \text{uns-}\mathit{cis}\text{-}[\mathrm{Co(edda)(NH_3)_2}]\mathrm{ClO_4}\\ \qquad\text{or uns-}\mathit{cis}\text{-}[\mathrm{Co(edda)(en)}]\mathrm{ClO_4}\\ \qquad(\text{the s-}\mathit{cis}\text{ isomer included})\end{cases}$$

Scheme II. Preparation of $[\mathrm{Co(edda)(amine)}]^+$ complexes [168b].

The coordination tendency of edda and amines has also been discussed. Structural assignments of complexes were made on the basis of electronic absorption and PMR spectra.

Legg et al. [163] first reported the resolution of an edda-Co(III) complex when they resolved s-*cis*-[Co(edda)(L)], (L = en, *R*-pn, *S*-ala, gly). The CD data of complexes studied are tabulated in Table 14. The ethylenediamine complex was resolved using the hydrogen tartrate anion to form diastereoisomers. The two complexes with the optically active ligands were resolved directly by fractional crystallization of the diastereoisomers, and the glycine complex was partially resolved chromatographically on starch. The coordinated *R*-1,2-propanediamine and *S*-alanine exhibit vicinal effects which were subtracted to obtain the configurational contribution to the CD. It was suggested that all $(+)_{589}$-isomers of s-*cis*-[Co(edda)(L)], which have a dominant positive low-energy component should have the same (Λ) absolute configuration as $(+)_{589}$-$[\mathrm{Co(en)_3}]^{3+}$. An additional check on the assignment of absolute configuration to the s-*cis* complexes was found by comparing the PMR spectra obtained for the two diastereoisomers of $[\mathrm{Co(edda)(\mathit{R}\text{-}pn)}]^+$ where *R*-pn is of known absolute configuration [71,72]. In one of the isomers the "outside" proton ($\mathrm{H_A}$) was split into a doublet. This was explained in terms of the close non-bonding proton–proton interactions between $\mathrm{H_A}$ and the *R*-pn amine protons in one of the isomers.

Legg [169] demonstrated the high sensitivity of ion-exchange chromatography by completely separating the four isomers of uns-*cis*-$[\mathrm{Co(edda)(\mathit{R}\text{-}pn)}]^+$. These consist of two sets of diastereoisomers where the two sets of isomers result from the two possible orientations (with respect to the methyl group) of *R*-pn in the uns-*cis* isomer (see Fig. 4(a)). Legg and Douglas [155] also demonstrated the utility of ion-exchange cellulose to achieve rapid resolution of ionic complexes by partially resolving s-*cis*-$[\mathrm{Co(dmedda)(en)}]^+$, s-*cis*-$[\mathrm{Co(deedda)(en)}]^+$, s-*cis*-$[\mathrm{Co(edda)(am)}]^+$ (am = *N*-methyl-, *N*-ethyl-, *N*,*N*′-dimethyl-, and *N*,*N*′-diethylethylenediamine (men, een, dmen and deen, respectively)) in various combinations, as well as [Co(edta)]$^-$ and related anionic complexes.

Later, Halloran and Legg [170] prepared and characterized uns-*cis* isomers of [Co(edda)(L)] (L = *R*-pn, *S*-ala, en). The uncommon uns-*cis* geometry for

TABLE 14

Absorption (AB) and circular dichroism (CD) data for [Co(edda)(L)] complexes (L = en, *R*-pn, *S*-ala, gly)

Complex	AB		CD		Ref.
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	$\Delta\epsilon$	
Λ-(+)-s-*cis*-*SS*-[Co(edda)(en)]$^+$	18.90	87.3	18.80	+4.46	163
	22.30 sh		22.40	−1.75	
	27.60 [a]	120 [a]	26.50 [a]	+0.40 [a]	
Λ-(+)-s-*cis*-*SS*-[Co(edda)(*R*-pn)]$^+$	18.90	94.5	18.80	+4.63	163
	22.02 sh		22.50	−1.71	
	27.60 [a]	116 [a]	26.50 [a]	+0.32 [a]	
Λ-(+)-s-*cis*-*SS*-[Co(edda)(gly)] [b]	18.40	90	18.50	+2.63	163
	21.30 sh		21.70	−1.22	
	26.80 [a]	110 [a]	–	–	
Λ-(+)-s-*cis*-*SS*-[Co(edda)(*S*-ala)]	18.40	95	18.40	+4.00	163
	21.50 sh		21.60	−1.92	
	26.80 [a]	125 [a]	26.30 [a]	+0.40 [a]	
Λ-(+)-uns-*cis*-[Co(edda)(en)]$^+$	20.28	170	20.66	+2.24	170
	27.86	169	28.01	−0.89	
Λ-(+)-uns$_1$-*cis*-[Co(edda)(*S*-ala)]	19.23	250	19.01	+1.22	170
(facial)	26.74	184	27.03	−0.83	
uns$_2$-*cis*-[Co(edda)(*S*-ala)]	17.24 sh				170
(meridional)	20.28	163			
	27.03	189			
uns-*cis*-[Co(edda)(*R*-pn)]$^+$					
Δ-(−)-*cis,cis*(N–O) Isomer 1	20.24	167	20.32	−1.90	170
	27.93	170	28.01	+0.74	
Λ-(+)-*cis,cis*(N–O) Isomer 2	20.28	171	20.79	+2.56	170
	27.93	170	27.85	−0.91	
Δ-(−)-*cis,trans*(N–O) Isomer 3	20.24	167	20.28	−1.70	170
	27.93	172	27.93	+0.77	
Λ-(+)-*cis,trans*(N–O) Isomer 4	20.20	178	20.74	+2.40	170
	27.93	177	27.85	−0.90	

[a] Values estimated from spectra. [b] Partially resolved complex.

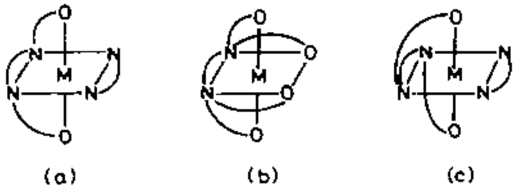

Fig. 20. Configurational comparison between: (a) Λ-(+)-s-*cis*-$[Co(edda)(en)]^+$; (b) Δ-$(+)_{546}$-$[Co(edta)]^-$; and (c) Δ-(−)-s-*cis*-$[Co(edda)(en)]^+$.

the edda was produced by displacement of carbonate from uns-*cis*-$[Co(edda)CO_3]^-$, the preferred isomer for this complex. The *R*-pn and *S*-ala diastereoisomers were separated by chromatography while the ethylenediamine optical isomers were resolved using *d*-α-bromocamphor-π-sulfonate. The four uns-*cis* *R*-pn isomers were identified as the diastereoisomeric pairs of *cis*,*cis*(N–O) and *cis*,*trans*(N–O) isomers. The facial and meridional uns-*cis* isomers (Fig. 4(b)) of [Co(edda)(*S*-ala)] were assigned on the basis of their visible absorption spectra. The uns-*cis* facial diastereoisomers were retained more effectively by the resin while complete separation of the two uns-*cis* meridional diastereoisomers from each other was not achieved. The methyl PMR resonances of these two distinctly different isomers were correlated with the corresponding resonances in the *R*-pn system and, in conjunction with CD spectra, were used to make tentative absolute configuration assignments to the four closely related uns-*cis*-$[Co(edda)(R\text{-pn})]^+$ isomers. Isomers (1) and (3) (see Table 14) of uns-*cis*-$[Co(edda)(R\text{-pn})]^+$ which have negative dominant peaks were assigned as net Δ [17] (Δ, Δ, Δ, Λ) [10] and isomers (2) and (4) with positive peaks were assigned as net Λ (Λ, Λ, Λ, Δ). These assignments have also been confirmed by a crystal and molecular structure determination of the Δ-*cis*,*trans*(N–O) isomer of uns-*cis*-$[Co(edda)(R\text{-pn})]^+$ [171].

It was tempting to relate the s-*cis*-$[Co(edda)(en)]^+$ complex to $[Co(edta)]^-$ which is of known absolute configuration through the common "backbone" as shown in Fig. 20 (a, b) [163]. This configurational relationship is consistent with the chiralities defined by the "ring pairing" method [17]. However, detailed structural analyses of edda-Co(III) complexes have resulted from PMR studies by Cooke and co-workers [172]. They prepared a series of cobalt(III) complexes containing the asymmetric quadridentate ethylenediamine-*N*,*N*′-di-*S*-α-propionate (*SS*-eddp) or -*R*-α-propionate (*RR*-eddp) which are of known absolute configuration and ethylenediamine or *R*-propanediamine. The absolute configurations of the diastereoisomers were assigned by considering the PMR spectra and the known configuration of the ligand. Optical activity data of the complexes (see Table 15) confirm the PMR assignments. Comparison of CD and ORD data of the *SS*-eddp and edda analogs provided a check on the assignment of absolute configuration to the edda complexes. The results obtained required that configurations (b) and (c) (see Fig. 20), of [Co(edta)]$^-$ and s-*cis*-[Co(edda)(en)]$^+$ must be configurationally related.

Dabrowiak and Cooke [173] used steric compression to explain the chemical shifts and to assign absolute configurations to several new amino

TABLE 15

Absorption (AB) and optical activity data for [Co(*SS*- or *RR*-eddp)(L)]$^+$ complexes (L = en, *R*-pn) [a]

Complex	AB		ORD	CD	
	$\bar{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$[M]_{589}$ (cm^{-1})	$\bar{\nu}\times10^{-3}$	$\Delta\epsilon$
Δ-(−)-s-*cis*-*RR*-[Co(*SS*-eddp)(en)]$^+$	18.76	97.0	−6408	18.80	−3.54
	22.27 sh			22.20	+1.15
	27.25	115.9			
Λ-(+)-s-*cis*-*SS*-[Co(*SS*-eddp)(en)]$^+$	19.05	97.6	+6026	18.90	+4.01
	22.42 sh			22.40	−1.41
	27.62	122.7			
Δ-(−)-uns-*cis*-[Co(*SS*-eddp)(en)]$^+$	18.15 sh		−1076 [b]	21.30	−4.01 [b]
	20.24	177.4 [b]		24.10	−0.41 [b]
	27.86	175.7 [b]			
Δ-(−)-s-*cis*-*RR*-[Co(*SS*-eddp)(*R*-pn)]$^+$	18.76	73.1	−6305	18.70	−3.69
	21.88 sh			22.20	+1.16
	27.25	92.9			
Λ-(+)-s-*cis*-*SS*-[Co(*SS*-eddp)(*R*-pn)]$^+$	19.01	84.1	+6487	18.90	+4.02
	22.27 sh			22.30	−1.36
	27.55	113.0			
Δ-(−)-uns-*cis*-[Co(*SS*,eddp)(*R*-pn)]$^+$	18.45 sh		−981		–
	20.37	125.8 [b]			
	27.78	146.2 [b]			
Δ-(−)-s-*cis*-*RR*-[Co(*RR*-eddp)(*R*-pn)]$^+$	18.98	95.6	−6403	18.90	−3.85
	22.27 sh			22.40	+1.42
	27.47	111.4			
Λ-(+)-s-*cis*-*SS*-[Co(*RR*-eddp)(*R*-pn)]$^+$	18.73				+
	21.69 sh				
	27.25				
Λ-(+)-uns-*cis*-[Co(*RR*-eddp)(*R*-pn)]$^+$	18.42 sh				+
	20.33				
	27.78				

[a] Data from ref. 172. [b] Estimated value.

acid complexes as well as to confirm the absolute configuration assigned by other means to related cobalt(III) diastereoisomers.

Van Saun and Douglas [174] reported the preparation and resolution of s-*cis*-[Co(edda)(L)]$^-$, (L = CO_3^{2-}, ox, mal), using optically active [Co(en)$_2$(ox)]$^+$ as a resolving agent. The CD data of these complexes are given in Table 16. PMR spectra were used to establish the s-*cis* configuration of edda in the isomers studied. The authors tentatively assigned the Λ absolute configuration to the isomers for which the CD bands of lowest energy (related to $A_1 \rightarrow E$ in the tetragonal approximation) were positive as that of $(+)_{589}$-s-*cis*-[Co(edda)(en)]$^+$ of known configuration [163,172]. They noted that the ring size of the bidentate chelate had little effect on the rotational strengths of the $d \rightarrow d$ transitions.

The complexes uns-*cis*-[Co(edda)(L)]$^-$ (L = CO_3^{2-}, ox, mal) have been prepared by Jordan and Legg [175] and their resolution was achieved using optically active [Co(en)$_2$(ox)]$^+$. The CD spectra of uns-*cis* complexes (see Table 16) have been compared with the spectra of the corresponding s-*cis* isomers to assess the relative contributions of configurational and vicinal effects as well as chelate ring size to rotatory strengths. The dominant CD band intensities of the uns-*cis*-[Co(edda)(L)]$^-$ complexes are much smaller than those reported [174] for the s-*cis* analogs. The changes observed in the CD spectra are consistent with the changes known to occur in two important structural sources of dissymmetry in these complexes: the arrangement of chelate rings and the configurations about the asymmetric nitrogen atoms and were found to have marked and systematic effects on the CD spectra. The two ring pairs of like chirality for the uns-*cis* isomers were thought to make a smaller configurational contribution to the rotatory strength than the (net) three pairs of s-*cis* geometry. A comparison of the CD data of the uns-*cis* complexes reveals that the net d–d rotatory strengths, as well as the dominant peak intensities, decrease in the order $CO_3^{2-} > \text{ox} > \text{mal}$ with increasing chelate ring size. An additional factor which could affect the relative rotatory strengths of uns-*cis* complexes would be expected by any variation in the vicinal effect. According to the interpretation of the vicinal contribution the authors noted that the *SR* (*RS*) isomer should give rise to a more intense dominant CD band than the *SS* (*RR*) isomer. The isomers having positive dominant peaks at ca. 18.20×10^3 cm^{-1} were assigned tentatively the ΛΛΛΔ or net Λ configuration.

Garnett and Watts [176] reported the preparation and resolution of the following series of cobalt(III) complexes of edda in both the s-*cis* and uns-*cis* configurations: [Co(edda)CO$_3$]$^-$, [Co(edda)(H$_2$O)$_2$]$^+$, [Co(edda)(NO$_2$)$_2$]$^-$, [Co(edda)Cl$_2$]$^-$, [Co(edda)(H$_2$O)Cl], [Co(edda)(mal)]$^-$. The stereochemistry of the complexes was established by analysis, PMR, IR and visible spectroscopy. The possible existence of two uns-*cis* isomers arising from the mode of

TABLE 16

Absorption (AB) and optical activity data for [M(edda)(L)] complexes (L = CO_3^{2-}, ox, mal, $(NO_2)_2$, $(H_2O)_2$, Cl_2, $(H_2O)Cl$, $(OH)_2$)

Complex	AB		CD		Ref.
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	$\Delta\epsilon$	
Λ-(+)$_{589}$-s-*cis*-*SS*-[Co(edda)CO_3]$^-$	17.69	114	17.50[a]	+5.10[a]	174–176
			20.60[a]	−1.40[a]	
	26.17	128	25.20[a]	+0.60[a]	
Λ-(+)$_{589}$-uns-*cis*-[Co(edda)CO_3]$^-$	18.76	234	18.18	+2.80	175,176
	25.64	182	26.11	−0.67	
Λ-(+)$_{589}$-s-*cis*-*SS*-[Co(edda)(ox)]$^-$	17.92	128	17.85	+5.20	174,175
			20.60[a]	−1.60[a]	
	26.00[a]	139[a]	25.20	+0.50[a]	
Λ-(+)$_{589}$-uns-*cis*-[Co(edda)(ox)]$^-$	18.93	200	18.38	+2.05	175
	25.80[a]	196[a]	26.40[a]	−0.90[a]	
Λ-(+)$_{589}$-s-*cis*-*SS*-[Co(edda)(mal)]$^-$	17.85	134	17.69	+4.70	174–176
			20.20[a]	−2.10[a]	
	25.90	110	25.20[a]	+0.40[a]	
Λ-(+)$_{589}$-uns-*cis*-[Co(edda)(mal)]$^-$	19.01	202	16.50[a]	−0.70[a]	175,176
			18.30[a]	+1.80[a]	
			21.00[a]	−0.10[a]	
	26.11	172	26.50[a]	−0.60[a]	
Λ-(+)$_{589}$-s-*cis*-*SS*-[Co(edda)$(NO_2)_2$]$^-$	19.60	153	ORD		176
Λ(−)$_{589}$-uns-*cis*-[Co(edda)$(NO_2)_2$]$^-$	21.36	238	ORD		176
Λ-(+)$_{589}$-s-*cis*-*SS*-[Co(edda)$(H_2O)_2$]$^+$	18.62	136	ORD		176
	25.84	75			
Λ-(−)$_{589}$-uns-*cis*-[Co(edda)$(H_2O)_2$]$^+$	19.41	180	ORD		176
	26.11	137			
Λ-(−)$_{589}$-s-*cis*-*SS*-[Co(edda)Cl_2]$^-$	17.00	184	ORD		176
	24.03	134			
Λ-(+)$_{589}$-uns-*cis*-[Co(edda)Cl_2]$^-$	17.39	171	ORD		176
	24.03	170			
s-*cis*-[Co(edda)(H_2O)Cl]	17.73	150			176
	24.87	100			
uns-*cis*-[Co(edda)(H_2O)Cl]	18.45	157			176
	25.00	165			
s-*cis*-[Cr(edda)(ox)]$^-$	18.72	88.6			177b
	25.44	73.7			

TABLE 16 (continued)

Complex	AB		CD		Ref.
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	$\Delta\epsilon$	
s-*cis*-[Cr(edda)(mal)]$^-$	18.53	68.9			177b
	25.06	53.2			
s-*cis*-[Cr(edda)(H_2O)$_2$]$^+$	18.83	78.9			177a,b
	25.00	48.0			
s-*cis*-[Cr(edda)(OH)]$_2$·4H_2O	18.08	89.5			177b,c
	25.25	71.8			

[a] Estimated from spectra.

coordination of the planar sec-*N* atom was discussed. Absolute configurations of complexes (see Table 16) were established from ORD measurements and X-ray diffraction study. The isomers of s-*cis* and uns-*cis* geometry exhibiting a dominant positive Cotton effect for the low energy visible absorption band were assigned the Λ configuration. Further evidence for the assignment was provided by the observation of a negative Cotton effect for Δ-uns-*cis*-[Co(*SS*-eddp)(en)]$^+$, the absolute configuration of which was established from a PMR study together with a knowledge of the absolute configuration of the ligand [172]. Moreover, the evidence for the assignment of a common absolute configuration to complexes with similar ORD curves was provided by a series of experiments based on reactions normally observed to occur with retention of configuration

$$[\mathrm{Co(edda)Cl_2}]^- \xrightarrow{\mathrm{Hg^{2+},H_3O^+}} [\mathrm{Co(edda)(H_2O)_2}]^+$$

$$[\mathrm{Co(edda)(H_2O)_2}]^+ \xrightarrow{\mathrm{HCO_3^-}} [\mathrm{Co(edda)CO_3}]^-$$

$$[\mathrm{Co(edda)(H_2O)_2}]^+ \xrightarrow{\mathrm{NO_2^-}} [\mathrm{Co(edda)(NO_2)_2}]^-$$

$$[\mathrm{Co(edda)(CO_3)}]^- \xrightarrow{\mathrm{H_3O^+}} [\mathrm{Co(edda)(H_2O)_2}]^+$$

Finally, the X-ray structural investigation showed the uns-*cis*-[Co(edda)(H_2O)$_2$]ClO_4 to be the racemate consisting of Λ-uns-*cis*-(*SR*) and Δ-uns-*cis*-(*RS*) and the same structure was predicted for the solid uns-*cis* carbonato and dichloro complexes.

Weyh and Pierce [177a] were the first to report the synthesis of a chromium(III) complex of edda. They assigned both (the *s-cis* and uns-*cis*) isomers of $[Cr(edda)(H_2O)_2]^+$ on the basis of ion-exchange study and comparative analysis of absorption spectra. Recently, Radanović et al. [177b] have prepared edda-Cr(III) complexes with water or hydroxide, oxalate and malonate ions as the additional ligands. Structural assignments of complexes were made on the basis of their IR and electronic absorption spectra and *s-cis* geometry for all complexes was proposed. The *s-cis* configuration of chelated edda has been confirmed by a crystallographic study of the hydroxo-dimer complex, $[Cr(edda)(OH)]_2 \cdot 4H_2O$ [177c]. Radanović [177d] claims that the complete resolution of $[Cr(edda)(ox)]^-$ and $[Cr(edda)(mal)]^-$ could be achieved by using $(-)_D$-$[Co(en)_2(ox)]^+$ as a resolving agent.

Most of the edda-type complexes investigated had N- or C-substituted edda analogs with various additional ligands. The CD spectra obtained for these complexes are summarized in Table 17.

In order to assess the importance of the asymmetric nitrogen centers of coordinated edda in determining the rotational strengths of complexes, Maricondi and Douglas [178] resolved four cobalt(III) complexes containing *N*-alkyl-substituted edda. The four *s-cis* complexes in the series contained *N*,*N'*-dimethylethylenediamine-*N*,*N'*-diacetate ion (dmedda) or *N*,*N'*-diethylethylenediamine-*N*,*N'*-diacetate ion (deedda) and ethylenediamine or oxalate ion. Two of the complexes with ethylenediamine have been prepared before [6] and partially resolved [155]. Both ethylenediamine complexes give very similar absorption and CD spectra, as do the two oxalate complexes (see Table 17). The dominant lowest energy CD band was assumed to be related to the $A \rightarrow E(D_{4h})$ transition for all the complexes. This band is positive for the isomers assigned the Λ configuration. The CD peak intensities of all the complexes, however, are less than half those of the corresponding unsubstituted edda complexes (see Tables 14, 16 and 17). This reduction in intensities was attributed to a lower contribution to the asymmetry of the complexes from nitrogens in the *N*-alkyl-substituted edda's as compared to unsubstituted edda.

Trimethylenediamine-, diammine- and dinitro-cobalt(III) complexes with either ethylenediamine-*N*,*N'*-diacetate, or the *N*,*N'*-dimethyl (dmedda) or *N*,*N'*-diethyl (deedda) derivative coordinated in the *s-cis* geometry have been reported by Jordan and Douglas [179]. This was a continuation of efforts to clarify the relationship between rotatory strength and structure in the edda–Co(III) system. The resolution of these complexes was achieved using *d*-tartaric acid and silver *d*-tartrate or optically active cation ($[Co(en)_2(ox)]^+$ or $[Co(en)_2(NO_2)_2]^+$) in the case of the dinitro complexes. Comparisons of their CD spectra were made to examine the effects of chelate ring size, configuration of chelate rings, and crystal field due to the ligand(s) at the

TABLE 17

Absorption (AB) and circular dichroism (CD) data for s-*cis*-[Co(edda)(L)]$^{\pm}$ and substituted analogs (L = ox, $(NH_3)_2$, en, tn, $(NO_2)_2$)

Complex	AB		CD		Ref.
	$\bar{\nu}\times10^{-3}$ (cm^{-1})	ε	$\bar{\nu}\times10^{-3}$ (cm^{-1})	Δε	
Λ-(+)-s-*cis*-*SS*-[Co(dmedda)(ox)]$^-$	17.60[a]	110[a]	17.92	+2.72	178
			20.90[a]	−0.20[a]	
	25.60[a]	150[a]	23.00[a]	+0.10[a]	
Λ-(+)-s-*cis*-*SS*-[Co(deedda)(ox)]$^-$	17.70[a]	98[a]	17.73	+2.42	178
	25.70[a]	140[a]	23.00[a]	+0.10[a]	
			25.00[a]	−0.20[a]	
			27.30[a]	+0.20[a]	
Λ-(+)-s-*cis*-*SS*-[Co(dmedda)(en)]$^+$	18.80	77.7	18.24	+2.15	6,178
	21.74 sh				
	27.10	110.0	27.00	−0.15	
Λ-(+)-s-*cis*-*SS*-[Co(deedda)(en)]$^+$	18.69	77.7	17.92	+1.80	6,178
	21.62 sh		21.40[a]	+0.40[a]	
	26.81	106.0	27.30[a]	+0.08[a]	
Λ-(+)-s-*cis*-*SS*-[Co(edda)$(NH_3)_2]^+$	18.66	92.6	18.86	+4.05	6,179
	21.69 sh		21.88	−2.00	
	27.47	118.0	26.17	+0.21	
Λ-(+)s-*cis*-*SS*-[Co(edda)(tn)]$^+$	18.60	96.0	18.90	+4.62	163,179
	21.60 sh		21.97	−2.00	
	27.60	149	26.17	+0.13	
			28.90	−0.09	
Λ-(+)-s-*cis*-*SS*-[Co(dmedda)$(NH_3)_2]^+$	18.50	83.5	18.83	+1.76	163,179
	20.90 sh				
	26.90	111	27.10	−0.25	
Λ-(+)-s-*cis*-*SS*-[Co(dmedda)(tn)]$^+$	18.20	93.2	16.58	−0.18	163,179
	20.90 sh		18.65	+3.05	
			21.88	−0.16	
	26.90	135.2	26.81	−0.50	
Λ-(+)-s-*cis*-*SS*-[Co(deedda)$(NH_3)_2]^+$	18.50[a]	86[a]	18.72	+1.20	179
	26.60[a]	112[a]	27.32	−0.20	
Λ-(+)-s-*cis*-*SS*-[Co(deedda)(tn)]$^+$	18.00[a]	88[a]	16.60[a]	−0.20[a]	179
			18.79	+2.52	
	26.70[a]	125[a]	26.59	−0.44	
Λ-(+)-s-*cis*-*SS*-[Co(edda)$(NO_2)_2]^-$	19.30	151	16.70	−0.17	163,179
			20.16	+2.50	
	23.30 sh		24.21	−0.73	

TABLE 17 (continued)

Complex	AB		CD		Ref.
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	$\Delta\epsilon$	
Λ-(+)-s-*cis*-*SS*-$[\mathrm{Co(dmedda)(NO_2)_2}]^-$	19.20 [a]	124	18.58	−0.90	163,179
	23.30 sh		22.93	+2.41	
Λ-(+)-s-*cis*-*SS*-$[\mathrm{Co(deedda)(NO_2)_2}]^-$	19.10	136	18.51	−1.09	163,179
	23.10 sh		22.47	+2.50	
Λ-(+)-s-*cis*-*SS*-[Co(edda)(*l*-stien)]$^+$	18.87	102	18.69	+5.10	180
	22.22 sh	49	22.32	−1.97	
	27.93	158	26.67	+0.43	
Δ-(−)-s-*cis*-*RR*-[Co(edda)(*l*-stien)]$^+$	18.87	102	18.69	−5.97	180
	22.22 sh	49	22.47	+0.69	
	27.93	158	26.67	−0.40	
Δ(Λ)-(+)-s-*cis*-*SS*-[Co(*l*-sdda)(en)]$^+$	18.42	89	18.94	+3.22	180
	21.74 sh	37	22.12	−0.64	
	27.40	117	27.40	−0.23	
Λ-(+)-s-*cis*-*RR*-[Co(dmbedda)(en)]$^+$	18.69	115	17.92	+1.81	180
	21.28 sh	52	21.55	+0.68	
	26.32	139	25.00	+0.29	
Λ-(+)-s-*cis*-*RR*-$[\mathrm{Co(dNO_2bedda)(en)}]^+$	18.69	97	17.92	+1.32	180
	21.28 sh	61	21.50	+1.12	
			24.69	+0.49	
Λ-(+)-s-*cis*-*RR*-[Co(dClbedda)(en)]$^+$	18.69	107	17.92	+1.79	180
	21.28 sh	52	21.50	+0.75	
	26.32	132	25.00	+0.36	
Λ-(+)-s-*cis*-*RR*-[Co(dbedda)(en)]$^+$	18.45	116	17.95	+1.70	156,180
	21.10 sh	58	21.15	+0.65	
	26.85	150	24.55	+0.21	

[a] Estimated from spectra.

octahedral sites not occupied by the quadridentate ligand, as well as the effect of the edda asymmetric nitrogens, on the rotatory strengths. That only small differences are observed between the CD spectra of s-*cis*-[Co(edda)(L)]$^+$ (L = $(\mathrm{NH_3})_2$, en, tn) (see Table 17) was consistent with the fact that a chelate ring due to a bidentate ligand L (en or tn) has little effect on the rotatory strengths of these complexes. For the CD spectra of [Co(dmedda)(L)]$^+$ and [Co(deedda)(L)]$^+$ (see Table 17) the dominant peak appears to be related to the dominant peak in the spectrum of the corresponding edda complex, though the intensities are substantially diminished. The absolute configurations were, therefore, assigned in the same manner as for the edda complexes, a positive dominant peak indicating a Λ configuration [10,163,172].

For all of the edda and dialkyl-edda complexes with diamine ligands the frequencies of the absorption maxima decrease in the order en > diammine > tn corresponding to decreasing ligand field strength. At the same time, the dominant CD peak frequencies decrease in just the opposite order tn > diammine > en, and the frequency difference between absorption maximum and dominant CD peak frequency increases in the order edda < dmedda < deedda or with diminishing vicinal effect. The inverted order for the dominant CD peaks suggests significant differences in the degree of splitting of the A_2 and B_2 components of the E transition for the three different diamine ligand systems. For the dialkyl-edda-tn complexes (see Table 17), the splitting is sufficiently large that both components of E parentage are observed with three CD peaks in the first absorption band region. The authors also suggested that the components of the E transition change energy order on going from tn and diammine to en. The vicinal effect due to the asymmetric nitrogens of the *s-cis*-coordinated edda was approximated by subtracting the CD curves of the deedda complexes from those of the corresponding edda complexes (see Fig. 21). The difference curves are very nearly identical

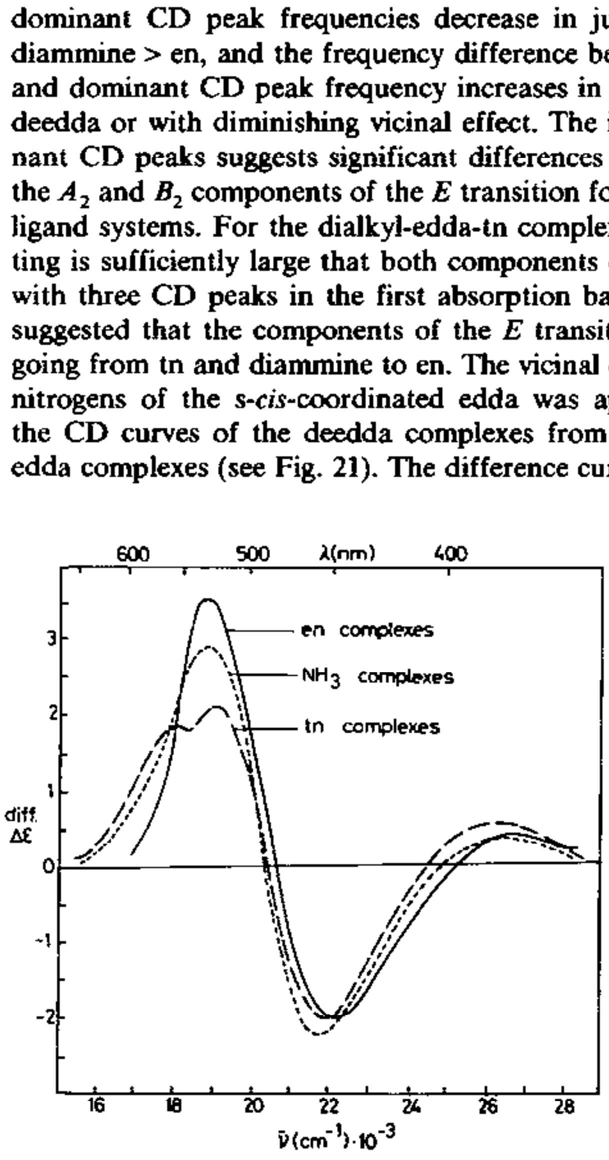

Fig. 21. Difference curves: $\Delta\epsilon[Co(edda)(L)]^+ - \Delta\epsilon[Co(deedda)(L)]^+$ (L = tn, en and $(NH_3)_2$).

in the region of the $A_2(D_{4h})$ and $T_2(O_h)$ transitions. In the region of the $E(D_{4h})$ transition the intensities diminish in the order en > diammine > tn with simultaneous curve broadening indicative of increasingly large splittings of the A_2 and B_2 components of the $E(D_{4h})$ transition.

The two D_{4h} components of the first absorption band are well-separated in the absorption spectra of $[Co(edda)(NO_2)_2]^-$ and the dimethyl and diethyl analogs. The CD spectrum of *s-cis*-$[Co(edda)(NO_2)_2]^-$ also exhibits pronounced splitting of the first absorption band and three CD peaks (see Table 17) are observed in this region with the same sign pattern seen in the spectrum of *s-cis*-$[Co(deedda)(tn)]^+$, indicating that the complexes have the same (Λ) absolute configuration. On the other hand, the CD curves of $[Co(deedda)(NO_2)_2]^-$ and $[Co(dmedda)(NO_2)_2]^-$ are quite unlike those of the dicarboxylato and diamine analogs. Two CD peaks ($-$, $+$) are observed for the dialkyl complexes for which they suggested the Λ configuration because the complexes had a positive dominant peak at ca. 22.50×10^3 cm^{-1} by comparing the difference curves $\Delta\epsilon[Co(edda)(L)]$–$\Delta\epsilon[Co(deedda)(L)]$ for the dinitro, ethylenediamine [178] and oxalato [178] complexes (see Fig. 22). Since the configuration about the asymmetric nitrogens is fixed by the arrangement of chelate rings, the complexes with the same absolute configuration give rise to very similar vicinal effect (difference) curves with peaks

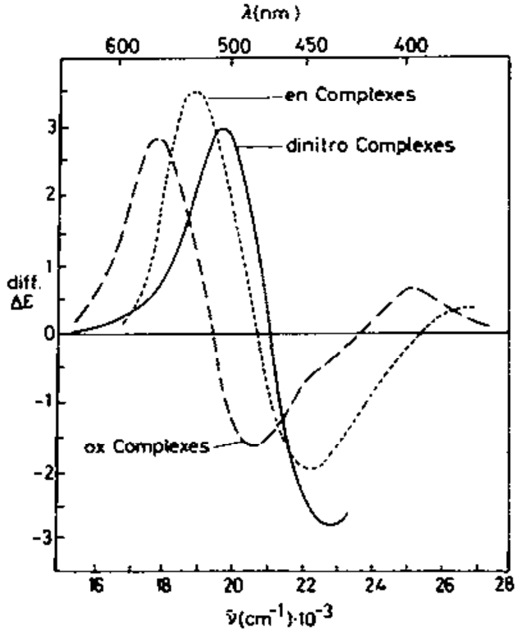

Fig. 22. Difference curves: $\Delta\epsilon[Co(edda)(L)]$–$\Delta\epsilon[Co(deedda)(L)]$ (L = ox, en and $(NO_2)_2$). (Reproduced with permission of ACS from ref. 179.)

shifted according to the field strengths of the ligands. It was noted that this assignment of configuration contradicts that based on the solubility rule [91].

Maricondi and Maricondi [156] prepared and resolved the cobalt(III) complex with ethylenediamine and *N*,*N*′-dibenzylethylenediamine-*N*,*N*′-diacetate (dbedda) coordinated in the s-*cis* geometry. The resolution of this complex was achieved using $(-)_{546}$-[Co(edta)]$^-$ and the isomer $(+)_{546}$-[Co(dbedda)(en)]Cl·4H_2O ($\Delta\epsilon = -1.7$ and $[\alpha]_{546} = +260°$) was isolated from the less soluble diastereoisomer. The CD spectrum of this complex ($(-)_{546}$ isomer) was compared with the CD spectra of the corresponding complexes with ethylenediamine-*N*,*N*′-diacetate and *N*,*N*′-dimethyl derivative (dmedda) which have been reported previously [163,178]. This comparison (see Table 17 and Fig. 23 (top)) indicated that the asymmetric nitrogen donor atoms make opposite contributions to the rotatory strength of the complexes when R = H as compared with R = benzyl. An approximation of the contribution of the asymmetric nitrogens to the CD of the edda and dbedda complexes was obtained by subtracting the curve of the dmedda complex from each. The resulting difference curves (see Fig. 23 (bottom) show the first band positive for the unsubstituted edda (R = H) and negative for the dibenzyl complex but the intensity of the individual bands is much larger for the edda complex. The vicinal effect of the edda-type complexes was discussed in terms of a regional rule proposed by Mason [39] for tetragonal complexes. For the $(-)_{546}$ isomer of the [Co(dbedda)(en)]$^+$ complex having a positive dominant peak the Λ absolute configuration was predicted [32e].

In order to assess the contributions from asymmetric nitrogens depending upon the homogeneity of the chemical environment about the nitrogen atom Douglas and co-workers [180] studied the cobalt(III) complexes containing phenyl-substituted ethylenediamine-*N*,*N*′-diacetate analogs. They prepared [Co(*l*-sdda)(en)]$^+$ (*l*-sdda = *l*-stilbenediamine-*N*,*N*′-diacetate), [Co(edda)(*l*-stien)]$^+$ (*l*-stien = *l*-stilbenediamine) and several para-substituted *N*,*N*′-dibenzylethylenediamine-*N*,*N*′-diacetate cobalt(III) complexes. The ^{13}C NMR spectra for the first two complexes verified their s-*cis* geometry. The [Co(edda)(*l*-stien)]$^+$ was prepared to estimate the contribution from the asymmetric carbons in *l*-stien having δ(*SS*) absolute configuration [86]. The formation of the complex was stereoselective, with the (−)-isomer favored by the ratio (7 : 3). Based on the CD data (see Table 17) and steric considerations the (−)-isomer of this complex was assigned the Δ configuration. It was calculated that *l*-stien makes a negative contribution to the rotational strength in the visible region but the edda portion of the complex is still dominant in determining the overall shape and intensity of the curve. The one isomer of [Co(*l*-sdda)(en)]$^+$ contains asymmetric nitrogens bonded to a hydrogen and a benzyl group, two substituents known to make opposite contributions to the rotational strength. Its positive dominant CD peak suggests the Λ configuration, which would require the *l*-stilbenediamine backbone to have λ conformation forcing the large substituents into unfavorable axial positions. Since only one isomer was obtained, the favored δ conformation was expected, indicating that the isomer of $[Co(\textit{l}\text{-sdda})(en)]^+$ has the Δ configuration (see Table 17). The latter choice was preferred but the authors noted that only an X-ray structure determination could settle the question with certainty.

The formal designations of absolute configurations for nitrogens with the same overall arrangement of substituents, *RR* for the *s-cis* isomers of

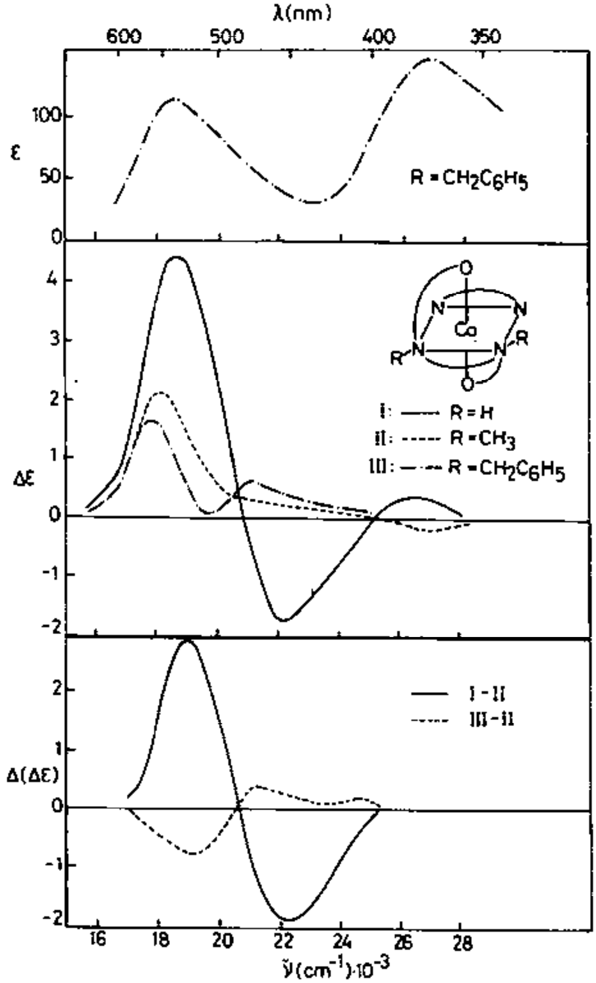

Fig. 23. CD spectra of the (+)-*s-cis* isomers of $[Co(edda)(en)]^+$ (I), $[Co(dmedda)(en)]^+$ (II), and $[Co(dbedda)(en)]^+$ (III) having Λ absolute configuration (top) and difference curves: I − II and III − II (bottom).

Δ-$[Co(edda)(en)]^+$ and *SS* for Δ-$[Co(dbedda)(en)]^+$ and Δ-$[Co(l\text{-sdda})(en)]^+$ resulted from changes in priorities of substituents on N. Both complexes, $[Co(edda)(l\text{-stien})]^+$ and $[Co(l\text{-sdda})(en)]^+$ contain a nitrogen bonded to a hydrogen and carbons bonded to benzene rings. Neither the signs nor the magnitudes of these particular substituents are known or readily predictable.

Finally, a series of *para*-substituted dbedda analogs was prepared [180] to study any possible electronic effects on asymmetric nitrogens which might be manifested in the CD spectra. The substituted dbedda complexes which were prepared were the *para*-methyl, chloro and nitro derivatives and their resolution was achieved using dibenzyl-*d*-tartaric acid and disilver dibenzyl-*d*-tartrate. The isomers of these complexes were compared to the dbedda complex [179] which contains a hydrogen in the *para* position (see Table 17). As shown, substitution of different groups in the *para* position of the benzene ring has no effect on the position of the maxima for the low-energy (^1E) component and very little effect on the intensities.

*(iii) 1,3-Propanediamine-*N,N′*-diacetate (tmdda or 1,3-pdda)*

Numerous mixed ligand complexes with 1,3-propanediamine-*N*,*N′*-diacetate, as an edda-type ligand containing a larger diamine backbone, have been reported [181–185]. The CD spectra of these complexes are given in Tables 18–20.

The synthesis and resolution of uns-*cis*-$[Co(tmdda)(L)]^+$ complexes (L = ammonia, ethylenediamine (en), trimethylenediamine (tn), 2,2′-bipyridine (bipy), or 1,10-phenanthroline (phen) has recently been described [181]. For comparison, uns-*cis*-$[Co(edda)(L)]^+$ (L = $(NH_3)_2$, tn) were also prepared and resolved to determine the effects of changes in the diamine ligands. The resolution of complexes was carried out using *d*-tartaric acid and silver *d*-tartrate except for the $[Co(tmdda)(phen)]^+$ complex for which the $(-)_{546}$-$[Co(edta)]^-$ was used as a resolving agent. The structures of isolated complexes have been deduced from the electronic absorption and CD spectra and the assignments were made using effective D_{4h} symmetry. The first absorption band of each of these complexes is nearly symmetrical, as was expected for uns-*cis* complexes. However, when L = ammonia or tn, two well resolved CD components have been recognized. These two CD peaks (−, +; see Table 18) in the first absorption band assigned as A_2 (lower energy) and E (higher energy), are opposite to the order for s-*cis*-$[Co(edda)(diamine)]^+$ complexes [6,163]. In the CD spectra of these complexes, the A_2 component is reduced gradually in the order diammine to trimethylenediamine, and it disappears completely for the ethylenediamine complex. The net rotatory strength (T_{1g},O_h) is decreased in the order ethylenediamine, trimethylenediamine, and diammine complexes. It was noted that the tmdda complexes prefer the uns-*cis* configuration (the edda complexes prefer the s-*cis* configuration) suggesting that the size of the diamine chelate ring has a profound effect on the distribution of geometric isomers. It was also found that the central chelate ring size of edda and tmdda and the ring size of the bidentate ligands affect the shape of CD spectra in the same fashion. The complexes with positive major CD peaks were confidently assigned the ΛΛΛΔ configuration [10]. The same assignments resulted from the sign of the net rotational strength in the $T_{1g}(O_h)$ band region as proposed by Richardson [27c] and as related to $[Co(en)_3]^{3+}$.

In order to extend the investigation of the effect of chelate ring size on CD spectra, Igi and Douglas [182] resolved the uns-*cis*-[Co(tmdda)(L)]$^-$ complexes (L = CO_3^{2-}, ox, mal) using optically active $[Co(en)_2(ox)]^+$ to form diastereoisomers. The assignments of complexes were made using tetragonal (D_{4h}) symmetry, (the $A_2(D_{4h})$ level being higher in energy than the $E(D_{4h})$ level). The CD spectrum of the malonato complex (see Table 19) shows three peaks in the first absorption band region (reflecting the true lower symmetry), while those of the oxalato and carbonato complexes show only one

TABLE 18

Absorption (AB) and circular dichroism (CD) data for uns-*cis*-[Co(edda-type)(amine)]$^+$ complexes [a]

Complex	AB		CD	
	$\tilde{\nu} \times 10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu} \times 10^{-3}$ (cm^{-1})	$\Delta\epsilon$
Λ-(+)-uns-*cis*-[Co(tmdda)(en)]$^+$	20.04	127	20.00	+1.48
	27.78	132	27.55	−0.48
Λ-(+)-uns-*cis*-[Co(tmdda)(tn)]$^+$	19.69	112	18.02	−0.53
			20.16	+1.94
	27.70	142	27.78	−0.56
Λ-(+)-uns-*cis*-[Co(tmdda)$(NH_3)_2$]$^+$	19.76	112	18.22	−0.89
			20.58	+1.28
	27.78	126	27.78	−0.48
Λ-(+)-uns-*cis*-[Co(tmdda)(bipy)]$^+$	19.72	128	19.65	+2.58
	26.67 sh	218	27.03	−0.54
Λ-(+)-uns-*cis*-[Co(tmdda)(phen)]$^+$	19.69	120	19.31	+2.89
	25.64 sh	135	26.60	−0.63
Λ-(+)-uns-*cis*-[Co(edda)$(NH_3)_2$]$^+$	20.04	154	18.05	−0.64
			20.70	+1.87
	27.93	157	27.93	−0.72
Λ-(+)-uns-*cis*-[Co(edda)(tn)]$^+$	19.90	160	17.30	−0.029
			20.41	+2.00
	27.93	187	28.09	−0.77

[a] Data are from ref. 181.

TABLE 19

Absorption (AB) and circular dichroism (CD) data for uns-*cis*-[M(tmdda)(L)]$^-$ complexes (M = Co, or Cr; L = carbonate, oxalate, malonate)

Complex	AB		CD		Ref.
	$\tilde{\nu} \times 10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu} \times 10^{-3}$ (cm^{-1})	$\Delta\epsilon$	
Λ-(+)-uns-*cis*-[Co(tmdda)(CO_3)]$^-$	18.18	170	17.70	+2.11	182
	25.64	180	23.00	+0.12	
			25.97	−0.45	
Λ-(+)-uns-*cis*-[Co(tmdda)(ox)]$^-$	18.35	131	17.73	+1.25	182
	25.81	171	23.59	+0.05	
			25.71	−0.34	
			28.57	+0.12	
Λ-(+)-uns-*cis*-[Co(tmdda)(mal)]$^-$	18.66	108	16.26	−0.09	182
			17.83	+0.70	
			19.84	−0.38	
	25.81	125	23.81	+0.09	
			25.64	−0.13	
			28.17	+0.14	
Δ-(−)-uns-*cis*-[Cr(tmdda)(ox)]$^-$	19.30	108	17.12 sh	+0.62	184
			17.76	+0.90	
			20.00	−2.93	
	25.57	93	24.63	+0.75	
			25.77	+0.81	
Δ-(−)-uns-*cis*-[Cr(tmdda)(mal)]$^-$	19.34	94	17.06 sh	+0.52	184
			17.67	+0.76	
			19.84	−1.76	
	25.70	68	25.19	+0.56	
			25.77	+0.50	

peak, as reported for the corresponding uns-*cis*-edda complexes [175]. It was also found that the CD intensities expressed in terms of major peaks or net rotational strengths, decrease in the order of CO_3^{2-} > ox > mal, with increasing size of the dicarboxylato chelate ring. Based on CD spectral correlation [14b], the (+)-uns-*cis*-[Co(tmdda) (L)]$^-$ complexes were tentatively assigned the ΛΛΛΔ [10] or net Λ configuration [17]. The assignments made for the uns-*cis* complexes are supported by the assignments made of the absolute configurations of complexes of *SS*-eddp acid from PMR studies [172]. The results obtained do not permit a choice between the two possible configurations of the asymmetric nitrogen atoms (e.g. *RR* or *RS*) for the Λ-uns-*cis* isomers.

In order to investigate the utility of the ^{13}C NMR technique for the study

TABLE 20

Absorption (AB) and circular dichroism (CD) data for uns-*cis*-[Co(tmdda)(*S*-am)] complexes [a]

Complex	AB		CD	
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu}\times10^{-3}$ cm^{-1})	$\Delta\epsilon$
Λ-(+)-*mer*-[Co(tmdda)(*S*-aspH)]	18.69	97.7	19.34	+1.95
	26.67	154.8	26.81	−0.76
Δ-(−)-*mer*-[Co(tmdda)(*S*-aspH)]	18.69	100.0	16.67	+0.05
			19.69	−2.08
	26.53	154.8	26.60	+0.99
Λ-(+)-*fac*-[Co(tmdda)(*S*-aspH)]	19.08	204.1	18.52	+1.61
			21.28	−0.13
	26.46	169.8	24.63	+0.14
			26.88	+0.39
			29.41	+0.04
Δ-(−)-*fac*-[Co(tmdda)(*S*-aspH)]	19.19	177.8	18.73	−1.52
			21.93	+0.03
	26.53	141.2	24.81	−0.15
			27.10	+0.40
			29.76	−0.05
Λ-(+)-*mer*-[Co(tmdda)(*S*-gluH)]	18.80	97.7	16.86	−0.23
			19.19	+2.37
	26.60	158.4	26.74	−0.88
Δ-(−)-*mer*-[Co(tmdda)(*S*-gluH)]	18.83	102.3	19.69	−2.13
	26.60	158.4	26.60	+0.95
Λ-(+)-*fac*-[Co(tmdda)(*S*-gluH)]	19.16	177.8	18.52	+1.50
			21.05	−0.15
	26.39	147.9	24.69	+0.12
			26.88	−0.36
			29.50	+0.06
Δ-(−)-*fac*-[Co(tmdda)(*S*-gluH)]	19.16	177.8	18.62	−1.80
			22.12	+0.03
	26.39	147.9	24.69	−0.15
			26.88	+0.41
			29.76	−0.05
Λ-(+)-*mer*-[Co(tmdda)(*S*-ala)]	18.94	95.4	16.89	−0.24
			19.23	+2.14
	26.67	151.3	26.88	−0.73
Δ-(−)-*mer*-[Co(tmdda)(*S*-ala)]	18.80	100.0	16.72	+0.05
			19.61	−2.18
	26.60	147.9	26.67	+0.96

TABLE 20 (continued)

Complex	AB		CD	
	$\bar{\nu} \times 10^{-3}$ (cm^{-1})	ϵ	$\bar{\nu} \times 10^{-3}$ cm^{-1})	$\Delta\epsilon$
Λ-(+)-*mer*-[Co(tmdda)(*S*-val)]	18.90	97.7	16.89	−0.73
			19.08	+2.54
	26.60	158.4	26.74	−0.94
Λ-(−)-*mer*-[Co(tmdda)(*S*-val)]	18.73	102.3	19.88	−2.26
	26.60	154.8	26.60	+0.93
Λ-(+)-*mer*-[Co(tmdda)(*S*-pro)]	19.08	120.2	16.78	−0.39
			19.01	+3.24
	26.39	194.9	26.53	−0.98
Δ-(−)-*mer*-[Co(tmdda)(*S*-pro)]	18.66	107.1	16.92	+0.22
			20.12	−1.46
	26.32	158.4	26.39	+1.01

[a] Data are from ref. 185.

of stereochemistry, Douglas and co-workers [183] performed ^{13}C NMR measurements on nine uns-*cis* complexes (the dinitro complex was newly prepared), one newly prepared (ethylenediamine) s-*cis* complex of cobalt(III) with tmdda, and sixteen complexes of cobalt(III) with edda including various additional unidentate (ammonia, water, pyridine, or nitrite ion) or bidentate ligands (ethylenediamine, trimethylenediamine, 2,2′-bipyridine, 1,10-phenanthroline, ethanolamine, carbonate, oxalate or malonate). Comparison of the spectra of s-*cis* and uns-*cis* complexes, along with application of selective decoupling and deuteration techniques, allows assignment of most resonances to individual carbons. It was found that ^{13}C NMR can be useful in its application to the investigation of inorganic stereochemistry.

Radanović et al. [184] reported the uns-*cis*-[Cr(tmdda)(L)]$^-$ complexes (L = ox, mal) whose resolution was achieved using the $(-)_D$-[Co(en)$_2$(ox)]$^+$ to form diastereoisomers. The structures of the complexes were deduced from the electronic absorption spectra (by comparison with data of the corresponding s-*cis* complexes [177b]) and CD spectra. The CD curves of complexes are much different from those for cobalt(III) (see Table 19) and three CD components have been observed in the low energy (T_{2g},O_h) band region. Based on the dominant CD peak, the Δ absolute configuration was predicted for the $(-)_{546}$ isomers given in Table 19.

Finally, mixed amino acid complexes with the general formula [Co(tmdda)(*S*-am)] (*S*-am = *S*-alanine (*S*-ala), *S*-valine (*S*-val), *S*-proline (*S*-pro), *S*-hydrogen aspartate (*S*-aspH), or *S*-hydrogen glutamate (*S*-gluH)) have recently been reported by Hidaka and co-workers [185]. Three geometric isomers, uns$_1$-*cis* (*fac*), uns$_2$-*cis*(*mer*) and *s-cis*, are possible for the [Co(tmdda)(*S*-am)] type complex as shown in Fig. 4. The uns-*cis* isomers of these complexes were prepared from the $\mathrm{H[Co(tmdda)Cl_2]\cdot 0.5H_2O}$ by treatment with *S*-am in basic solution (pH 8.0) and chromatographically separated.

$$\mathrm{H[Co(tmdda)Cl_2]\cdot 0.5H_2O} + \text{excess } S\text{-am} + \mathrm{NaOH} \xrightarrow[\text{act. charcoal}]{\text{pH 8.0 (65°C)}}$$

$$\begin{tikzcd} & & \Delta\text{-}, \Lambda\text{-uns-}cis\text{-}mer \\ {[\mathrm{Co(tmdda)}(S\text{-am})]} \arrow[r, dash, "\text{chromatographic}", "\text{separation}"'] & {} \arrow[ur] \arrow[dr] & (\text{isomers}) \\ & & \Delta\text{-}, \Lambda\text{-uns-}cis\text{-}fac \end{tikzcd}$$

The complexes were separated into the fourteen isomers, Δ-, Λ-uns-*cis-mer* for the *S*-alaninato, *S*-valinato and *S*-prolinato complexes, and Δ-, Λ-uns-*cis-mer* and Δ-, Λ-uns-*cis-fac* for the *S*-hydrogen aspartato and *S*-hydrogen glutamato complexes. The uns-*cis-mer* isomer was formed dominantly, especially for the *S*-alaninato, *S*-valinato and *S*-prolinato complexes where little of the uns-*cis-fac* isomer was formed. The Λ-uns-*cis-mer* and Δ-uns-*cis-fac* isomers of the *S*-aspartato and *S*-glutamato complexes were formed stereoselectively, the formation ratios of isomers being estimated spectrophotometrically. Marked stereoselectivity was found for the Λ configuration of uns-*cis-mer*-$[\mathrm{Co(tmdda)}(S\text{-asp})]^-$ (Λ-*mer*: Δ-*mer* $= 81:6$) and for the Δ configuration of the uns-*cis-fac* isomer (Λ-*fac* : Δ-*fac* $= 0:13$). A similar trend was also observed for the isomers of the *S*-glutamato complex but with lower selectivity. The configurational CD contribution of the isomers was separated from the vicinal CD contribution due to the optically active ligand and the CD spectra were discussed in relation to their configurations. Each of the uns-*cis-mer* and uns-*cis-fac* isomers showed characteristic CD behavior in the second absorption band region (see Table 20). The absolute configurations of the isomers were assigned tentatively from the sign of a major CD band in the first absorption region.

*(iv) Other ligands structurally similar to ethylenediamine-*N,N′*-diacetate*

This section includes the complexes where edda was replaced by the analogous ligands having various structural changes in the carboxylate arms (the complexes of ethylenediamine-*N,N′*-di-*S*-α-propionate (*SS*-eddp) have been discussed under section E.(ii) [172]).

(a) (2S,2′S)-1,1′-(Ethane-1,2-diyl)bis(pyrrolidine-2-carboxylate) (pren)

The reaction of *S*-proline with 1,2-dibromoethane, under basic conditions, yields the quadridentate ligand, (2*S*,2′*S*)-1,1′-(ethane-1,2-diyl)bis(pyrroli-

TABLE 21

Absorption (AB) and circular dichroism (CD) data for [Co(*SS*-pren)X_2] ($X_2 = 2H_2O$, CO_3^{2-}, H_2OCl^-) and [Co(*SS*-eddiv)X_2] ($X_2 = 2H_2O$) complexes

Complex	AB		CD		Ref.
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	$\Delta\epsilon$	
Δ-(−)-s-*cis*-*SS*-[Co(*SS*-pren)(H_2O)$_2$]$^+$	17.98	111	15.26	−0.03	186b
			18.45	−1.86	
	25.44	74	22.98	−0.15	
			25.44	+0.07	
Δ-(−)-s-*cis*-*SS*-[Co(*SS*-pren)CO_3]$^-$	17.54	109	17.24	−3.04	186b
	19.23 sh	90			
	25.97	150	23.98	−0.31	
			26.04	+0.10	
Δ-(−)-s-*cis*-*SS*-[Co(*SS*-pren)(H_2O)Cl]	16.34	97	16.00	−1.55	186b
	22.88	72	23.14	+0.01	
Δ-(−)-s-*cis*-*RR*-[Co(*SS*-eddiv)(H_2O)$_2$]$^+$	19.30	130	18.08	−1.41	187
			21.36	+0.33	
	30.30	189	25.97	−0.27	
			32.78	+0.14	
			43.10	+2.14	
Δ-(−)-uns-*cis*-[Co(*SS*-eddiv)(H_2O)$_2$]$^+$	21.59	71	18.41	−1.36	187
			22.72	+0.09	
	29.41	126	28.16	−0.27	
			39.21	+0.40	
			46.51	−1.12	

dine-2-carboxylic acid) dihydrochloride [186a,b] (the deprotonated form, pren, of the ligand is shown in Table 12). A report by Woon and O'Connor [186b] cites ^{13}C NMR, CD, ORD and electronic spectral evidence for the exclusive formation of Δ-s-*cis*-*SS*-[Co(pren)X_2] complexes ($X = 2H_2O$, CO_3^{2-}, H_2OCl^-). The complex Δ-s-*cis*-[Co(pren)(H_2O)Cl] rapidly aquates with retention of configuration. All compounds having actual or near C_2 symmetry exhibit a strong negative CD band under the $^1A_{1g} \rightarrow {}^1T_{1g}$ cubic absorption band which is due to the $^1A_1 \rightarrow {}^1E$ tetragonal component, consistent with the Δ absolute configuration (see Table 21) imposed by the *S* configuration of the asymmetric carbon atom in the *S*-proline moiety. Thus, the complexes described are formed stereospecifically and coordinated nitrogen atoms necessarily have the *S* configuration.

(b) *Ethylenediamine*-N,N'-*di*-S-*α*-*isovalerate* (SS-*eddiv*)

In a recent article [187] Strašák et al. reported the synthesis and characterization of two of the five theoretically possible isomers of diaqua cobalt(III) complexes containing a new asymmetric quadridentate ethylenediamine-*N*,*N′*-di-*S*-α-isovalerate (*SS*-eddiv) ligand. The configurations of the asymmetric carbon atoms of the ligand are known because the ligand was prepared from *S*-valine and 1,2-dibromoethane. Assignments of complexes were made on the basis of electronic absorption, IR and CD spectra. A strong negative CD $^1A_{1g} \rightarrow {}^1T_{1g}$ cubic absorption band, belonging to the tetragonal $^1A_1 \rightarrow {}^1E$ component, has been observed for both (s-*cis* and uns-*cis*) $[\mathrm{Co}(SS\text{-eddiv})(\mathrm{H_2O})_2]^+$ complexes indicating the Δ absolute configuration (Table 21). The chirality of the ligand controlled stereospecifically the absolute configuration of the complex forming only the Δ-s-*cis*-*RR* and Δ-uns-*cis* isomers as was observed for similar complexes [186a,b].

(c) Other quadridentate ligands related to edda

The three edda related quadridentate ligands, dtma, i-dtma and aeida (dtma = 1-diethylenetriamineacetate, i-dtma = *N*,*N*-bis(2-aminoethyl)glycinate, aeida = *N*-(2-aminoethyl)iminodiacetate together with nitrilotriacetic acid (nta) complete the permutations possible for the simple aminecarboxylic acid quadridentate ligands.

The tripod-like quadridentate i-dtma and aeida ligands can take two different configurations in the six-coordinate metal complex: (a) s-type (symmetrical and achiral) and (b) uns-type (unsymmetrical and chiral) (see Fig. 24). The method [17] used for the correlation of the absolute configurations of complexes with multidentate ligands cannot be applied to uns-type isomers of the complexes with tripod-like ligands (which are chiral regardless

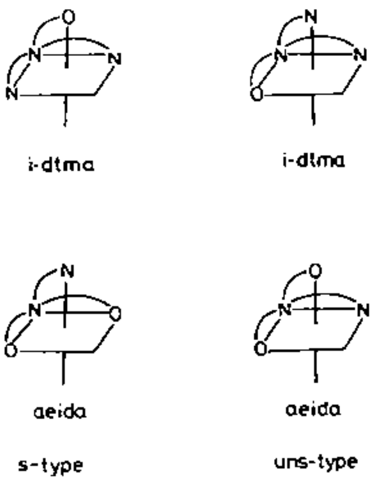

Fig. 24. Two different coordination modes of i-dtma and aeida ligands.

TABLE 22

Absorption (AB) and circular dichroism (CD) data of [Co(i-dtma)(AB)]-type complexes (AB = gly, *S*-ala, en, and *R*-pn) [a]

Complex	AB		CD	
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	$\Delta\epsilon$
(G-1)-[Co(i-dtma)(gly)]$^{+}$	18.50 sh	31.6		
(s-α)	21.51	70.8		
	28.45	93.3		
	45.25	20417.3		
$(-)_{589}$-(G-2)-[Co(i-dtma)(gly)]$^{+}$	20.77	120.2	19.31	−0.787
(uns-α)			21.74	+1.00
	28.45	144.5	28.41	−0.395
	45.66	19498.4	38.02	+2.30
			42.55	−4.60
			48.08	+1.88
(G-3)-[Co(i-dtma)(gly)]$^{+}$	19.27	134.8		
(uns-β)	26.00 sh	79.4		
	27.89	134.8		
	45.05	20417.3		
(G-4)-[Co(i-dtma)(gly)]$^{+}$	19.80	173.7		
(s-β)	25.50 sh	63.0		
	27.70	120.2		
	44.54	21877.6		
(A-1)-[Co(i-dtma)(*S*-ala)]$^{+}$	18.50 sh	31.6	18.12	+0.158
(s-α)	21.46	77.6	21.57	−0.489
	28.53	100.0	29.28	+0.062
	44.84	21877.6	36.90	−0.448
			42.55	−0.581
			45.66	+0.715
(A-2-a)-[Co(i-dtma)(*S*-ala)]$^{+}$	20.83	125.8	19.38	−1.20
(uns-α)			21.88	+0.867
	28.49	147.9	28.57	−0.401
	45.66	20417.3	38.02	+2.90
			42.55	−9.02
			47.62	+2.64
(A-2-b)-[Co(i-dtma)(*S*-ala)]$^{+}$	20.88	133.8	19.38	+1.44
(uns-α)			21.74	−2.32
	28.49	147.9	28.65	+0.917
	45.35	21379.6	38.17	−4.60
			43.29	+7.12
			47.85	−3.80

TABLE 22 (continued)

Complex	AB		CD	
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	$\Delta\epsilon$
(A-3-a)-[Co(i-dtma)(*S*-ala)]$^{+}$ [b]			18.89	+0.415
(uns-β)			21.10	−0.577
			25.64	−0.017
			28.09	+0.189
			37.59	−1.47
			43.01	+4.53
			47.06	−2.28
(A-3-b)-[Co(i-dtma)(*S*-ala)]$^{+}$	19.19	131.8	18.83	−0.906
(uns-β)			21.16	+0.701
	26.00 sh		25.84	+0.016
	27.93	131.8	28.53	−0.315
	44.94	19952.6	37.31	+0.913
			41.84	−4.18
(A-4)-[Co(i-dtma)(*S*-ala)]$^{+}$	19.84	151.3	18.45	−0.205
(s-β)			20.55	+0.422
	25.50 sh	63.0	25.20	−0.083
	27.86	112.2	27.59	−0.163
	44.35	20417.3	38.48	−1.24
			43.29	+1.88
			47.60	−2.20
$(-)_{589}$-(E-1)-[Co(i-dtma)(en)]$^{2+}$	20.53	120.2	19.53	−1.16
(uns-type)			22.17	+0.72
	28.94	131.8	26.00 sh	
			29.15	−0.310
	45.15	19498.4	37.74	+2.22
			43.96	−6.43
(E-2)-[Co(i-dtma)(en)]$^{+}$	20.83	100.0		
(s-type)	28.99	112.2		
	44.84	20892.9		
(P-1-a)-[Co(i-dtma)(*R*-pn)]$^{2+}$	20.58	117.4	19.65	+1.14
(uns-type α or β)			22.22	−0.587
	28.94	128.8	26.46	−0.096
			29.15	+0.216
	45.15	18620.8	37.12	−1.79
			44.24	+9.74
(P-1-b)-[Co(i-dtma)(*R*-pn)]$^{2+}$	20.58	120.2	19.49	−1.20
(uns-type)			22.10	+0.905
	28.88	125.8	29.03	−0.456
	45.25	17782.7	38.76	+3.11
			44.05	−1.43

TABLE 22 (continued)

Complex	AB		CD	
	$\tilde{\nu} \times 10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu} \times 10^{-3}$ (cm^{-1})	$\Delta\epsilon$
(P-2)-[Co(i-dmta)(*R*-pn)]$^{2+}$	20.88	97.7	19.98	-0.173
(*s*-type α or β)			22.27	-0.300
	28.94	112.2	26.88	-0.073
			29.24	-0.053
	44.69	20892.9	43.48	$+4.17$

[a] Data are from ref. 189a. [b] The $\Delta\epsilon$ values were determined on assumption that the absorption spectrum of A-3-a is identical with that of A-3-b.

of the residual ligands), because these isomers lack the ring-pairing chirality. Two different kinds of isomerism occur in the s-type [M(tripod)(bidentate)] complexes (bidentate = amino carboxylate or diamine): the geometrical isomerism (in the glycinato complexes) and the optical isomerism (in the *meso*-2,3-butanediamine complexes) where both bidentate ligands, gly and *meso*-2,3-bn are achiral. When bidentate ligands are chiral (such as *S*-ala and *R*-pn) the two kinds of isomerism (geometrical and optical) arise at the same time.

The work of Schneider and Collman [188] with dtma and i-dtma ligands is of interest since these authors, using ion-exchange chromatography found two of several possible isomers for [Co(dtma)(am)]$^+$ (am = amino carboxylate).

Recently, Shimura and co-workers [189a] have prepared four glycinato, six *S*-alaninato, and three *R*-propanediamine cobalt(III) complexes of a tripod-like i-dtma ligand. On the basis of their absorption and CD spectra, PMR spectra, the elution behavior on ion-exchange column chromatography, and the optical resolution of chiral isomers the complexes were assigned to have the structures given in Table 22. The absolute configurations of the chiral complexes have been assigned tentatively. The isomers A-2-a (uns-α) and A-3-b (uns-β) (see Table 22) were assigned to have the same absolute configurations as $(-)_{589}$-(G-2)-[Co(i-dtma)(gly)]$^+$ with regard to i-dtma. From the CD spectra the P-1-b (uns-type) isomer should have the same absolute configuration of i-dtma as that of $(-)_{589}$-[Co(i-dtma)(en)]$^{2+}$ and also those of A-2-a, A-3-b, and $(-)_{589}$-(G-2)-[Co(i-dtma)(gly)]$^+$, because the CD contribution from the uns-type configurational effect of i-dtma is expected to be larger than that from the vicinal effect of *R*-pn and to show the same pattern as that of *S*-alaninato complex in the first and second $d \rightarrow d$ transition band region.

TABLE 23

Absorption (AB) and circular dichroism (CD) data of [Co(aeida)(AB)]-type complexes (AB = gly, *S*-ala, en, *N*,*N*-dmen, *meso*-2,3-bn, *R*-pn and *RR*-chxn)[a]

Complex	AB		CD	
	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\tilde{\nu}\times10^{-3}$ (cm^{-1})	$\Delta\epsilon$
(G-3)-[Co(aeida)(gly)]	18.50 sh	31.6		
(uns-α)	20.55	109.6		
	27.66	131.8		
	45.15	19498.4		
(G-5)-[Co(aeida)(gly)]	18.87	199.5		
mer-(uns-β)	26.88	138.0		
	44.84	21877.6		
(A-3)-[Co(aeida)(*S*-ala)]	19.47	138.0	17.24	−0.116
(s-α)	22.00 sh	63.0	19.14	+0.057
			21.53	−0.685
	27.70	194.9	27.55	+0.375
	45.46	19054.6	42.02	−1.59
			47.85	−1.24
(A-5)-[Co(aeida)(*S*-ala)]	18.87	186.2	18.25	−0.632
fac-(uns-β)			20.35	+0.389
	26.92	134.8	25.00 sh	−0.08
			27.40	−0.094
	45.05	21379.6	38.76	−2.23
			43.86	+3.06
			47.85	−2.35
(E-1)-[Co(aeida)(en)]$^+$	19.05	144.5		
	22.00 sh	63.0		
	28.25	181.9		
	44.84	18197.0		
(E-2)-[Co(aeida)(en)]$^+$	20.06	131.8		
(uns-type)	27.93	144.5		
	44.15	19952.6		
(M-1)-[Co(aeida)(*N*,*N*-dmen)]$^+$	18.47	158.4		
(s-type)	21.50 sh	63.0		
	27.55	213.7		
	37.00 sh			
	43.01	20417.3		
	48.00 sh			
(M-2)-[Co(aeida)(*N*,*N*-dmen)]$^+$	19.18	158.4		
(uns-type)	27.66	190.5		
	37.00 sh			
	43.10	19952.6		
	48.00 sh			

TABLE 23 (continued)

Complex	AB		CD	
	$\bar{\nu}\times10^{-3}$ (cm^{-1})	ϵ	$\bar{\nu}\times10^{-3}$ (cm^{-1})	$\Delta\epsilon$
[Co(aeida)(*R*-pn)]$^+$ *trans*(O)-(s-type)	19.01	151.3	16.95	−0.045
	22.00 sh	63.0	19.35	−0.064
			22.12	+0.190
	28.13	181.9	28.53	−0.150
	44.94	20417.3	45.46	+5.48
[Co(aeide)(*RR*-chxn)]$^+$ *trans*(O)-(s-type)	18.94	151.3	16.53	−0.020
	22.00 sh	63.0	18.52	+0.111
			21.98	+0.208
	28.05	213.7	28.99	−0.071
			41.50 sh	+5.6
	44.44	21379.6	44.84	+7.75
$(+)_{589}$-(B-1)-[Co(aeida)(*meso*-2,3-(bn)]$^+$ *trans*(O)-(s-type)	18.94	151.3	18.66	+0.232
	22.00 sh	63.0	22.32	−0.208
	28.13	181.9	26.11	+0.009
			28.09	−0.035
	44.64	17782.7	35.71	−0.17
			40.65	+2.53
(B-2)-[Co(aeida)(*meso*-2,3-bn)]$^+$ *cis*(O)-(uns-type)	19.96	134.8		
	28.03	147.9		
	44.44	19952.6		

[a] Data are from ref. 189b.

The same authors [189b] have reported the preparation of the glycinato, *S*-alaninato, ethylenediamine, *N*,*N*-dimethylethylenediamine, *R*-propanediamine, *RR*-1,2-cyclohexanediamine and *meso*-2,3-butanediaminecobalt(III) complexes of a tripod-like ligand, *N*-(2-aminoethyl)iminodiacetate. The geometrical configurations of these complexes (see Table 23) have been assigned on the basis of their absorption, CD and PMR spectra. The *trans*(O) isomer of *meso*-2,3-butanediamine complex has been optically resolved and the relationship between the absolute configurations of the chiral 1,2-diamine complexes and their circular dichroism was discussed.

F. GENERAL CONCLUSIONS

(i) Geometrical preferences

The ligand configuration and metal ion size (Co < Cr < Rh) have profound effects on the coordination numbers of chelates and the distribution of geometrical isomers. The larger cations tend not to form hexadentate edta complexes because of ring strains. The edta-type ligands with longer chains are more favorable for hexadentate coordination and the ligands with mixed (five- and six-membered) carboxylate arms preferentially form isomers having six-membered (β-alaninate) rings in the G plane.

Because the strain is greater for the "in plane" chelate rings, the most favored isomer of quinquedentate ed3a-type complexes was found to be *cis*-eq (Fig. 3(b)) in the presence of the less stable *trans*-eq isomer (only when $X = NO_2^-$). However, a quinquedentate 1,3-pd3a ligand, depending on the conformation of the 1,3-propanediamine ring, allowed the formation of three isomers (equatorial-skew, polar-chair and polar-skew) derived from basic isomerism (Fig. 3(b)) and the polar-chair isomer was found to be the more stable form.

For quadridentate (edda-type) complexes it was noted that the tmdda M(III) complexes prefer the uns-*cis* configuration (Fig. 4), while the edda M(III) complexes (M = Co and Cr) prefer the s-*cis* configuration, indicating that the size of the diamine chelate ring has a profound effect on the distribution of geometrical isomers.

The effects of chain length have been rationalized in terms of two effects: (1) ring strain, and (2) steric hindrance. The ring strain effect was manifested in hexadentate complexes (in the M(III) edta and *trans*(O_6) complexes with eddda, *SS*-edds and (*S*)-eddams), quinquedentate complexes (in the *cis*-polar complexes with ed3a), and quadridentate complexes (in the *trans* complexes with edda). For the longer chain ligands related to edta (such as 1,3-pd3a and tmdda), as the chelate rings increase in size, the complexity of the ring conformations increases, and the magnitude of the interactions between adjacent ligands increases accordingly as described by Corey and Bailar [7], Buckingham et al. [8] and Gollogly and Hawkins [9]. This interaction may account for the distribution of isomers in the Co(III) complexes with 1,3-pd3a and s-*cis* and uns-*cis* isomers in the M(III) complexes with edda and tmdda ligands.

The effect of ligand asymmetry on the stereochemistry of complexes is seen to be greater than the effect of chain length. The presence of asymmetric centers on the ligand (at a donor atom or on carbon atoms) determines the geometrical configuration of the complex, the conformations of the chelate rings and also frequently controls the absolute configuration of the complex as a whole.

(ii) Optical activity

The methods proposed by Mason and co-workers [14b] and others [16,17,27c] have been employed for assigning absolute configurations to complexes discussed and, in many cases, the results obtained have been supported by the assignments made directly by crystallographic analysis or indirectly by using stereospecific ligands of known absolute configurations. The M(III) ion chromophores for these complexes have approximate tetragonal or rhombic symmetry, and their spectra are interpreted using pseudo-D_{4h} or lower (C_2) molecular symmetry.

(a) Hexadentates

The transition to the $A(C_2)$ state, derived from the $E_g^a(D_{4h})$ state is thought to be responsible for the low-energy CD peak for hexadentate $[M(N)_2(O)_4]$ type complexes of low-spin d^6 metal ions (M = Co) and the lowest energy CD components of these complexes ($A(C_2)$ or $E(D_{4h})$) are positive for the $\Lambda(\Lambda\Delta\Lambda)$ configuration. The sign of the dominant CD peak for Cr(III) (d^3) has been used as the basis for assigning absolute configurations, since the spectral characteristics are often similar for d^3 and d^6. The absolute configurations have been verified crystallographically for $(-)_{546}$-[Co(edta)]$^-$ [2b], $(-)_{546}$-[Co(1,3-pdta)]$^-$ [87] and $(-)_{589}$-[Cr(eddda)]$^-$ [109]. The CD pattern (−,+) for [Rh(*SS*-edds)]$^-$ (of known Λ configuration) did not correspond to that predicted by empirical correlations for Co(III) complexes and the assignment of the absolute configuration of this and other Rh(III) complexes was made on the basis of the stereospecificity of *SS*-edds and also from a crystallographic study [88]. The less-strained model complexes related to [Co(edta)]$^-$ have lower intensities for the visible absorption bands, as would be predicted because of the decrease in ring strain. However, the CD spectra of these complexes show an increase in net rotational strength, a result not expected from some theories of optical activity [23,24]. As was postulated, there is only a very small contribution to rotational strength due to the asymmetric nitrogen atoms in the [Co(*SS*-edds)]$^-$ system [108]. Thus, the contribution of the chelate rings to optical activity for [Co(edta)]$^-$ type complexes strongly depends on both their relative size, as postulated by Legg and Neal [107], and their disposition about an octahedron. This question of how large the relative contributions are, has not yet been clarified. The asymmetric carbon in $(-)_{546}$-[Co(*S*-pdta)]$^-$ [81] has little effect on the CD spectrum, while a greater contribution was found from *SS*-cdta and other ligands having very large substituents. The two model complexes, [Co(*SS*-sdta)]$^-$ and [Co(xdta)]$^-$, having the benzene rings in the backbone exhibited marked differences from any of the edta model complexes. The most significant feature of the CD spectrum of [Co(xdta)]$^-$ (containing a seven-membered ring in its backbone) is the unusually large $\Delta\epsilon$ values. Phenyl groups have a large and anisotropic polarizability and some theoretical models [86,190–193] can predict that such groups may produce unusual CD spectra. The substitution of phenyl groups into the edta analogs studied seems to support these theories.

(b) Quinquedentates

For the *cis*-eq-[Co(ed3a-type)(X)] complexes the relative order of the three transitions depends on the ligand-field splitting parameter for X. When X is a halide, the transition corresponding to the N–Co–O axis (Γ_{NO}) is lowest in energy, but when X is NO_2^- (or CN^-) the transition that transforms as the N–Co–X axis (Γ_{NX}) is lowest in energy. These complexes are of interest because the general methods for determining the net helicity due to a given arrangement of chelate rings predict no net helicity for the arrangement of rings present (i.e. they contain one Λ and one Δ pair) [10,16,17]. Also, when Richardson's method [27c] for determining the sign of the net *d–d* rotatory strength is applied to these complexes and only the contribution from chelate rings is considered, no net rotatory strength is predicted. However, it appears that there is a large contribution from the coordinated asymmetric nitrogen in the unsubstituted ed3a complexes where one of the substituents (H) on N is much different from the other two first neighbor substituent atoms. As was demonstrated [156] the benzyl substituent on the N atom caused a significant change in CD intensities in comparison to a methyl substituent and the "vicinal" contributions of $-CH_2C_6H_5$ and –H substituents are of reversed sign in comparison to $-CH_3$ in the case of $[Co(ed3a)(NO_2)]^-$ and its substituted complexes. The absolute configurations of quinquedentate edta complexes have been deduced from correlation with the Λ-$(-)_{546}$-$[Co(edta)]^-$ complex by a series of experiments based on reactions normally observed to occur with retention of configuration. CD spectra of ed3a and its N-substituted complexes are very similar to those for the quinquedentate edta complexes, enabling the absolute configurations to be assigned. These structures have been verified indirectly by using stereospecific ligands (*R*-pd3a and *R*-pdta) in the preparation of the nitro complexes [156].

(c) Quadridentates

Two important conclusions have been drawn from CD studies of s-*cis*-edda Co(III) complexes. (1) The rotational strengths of the first ($^1T_{1g}$) CD band appear to be remarkably independent of the bidentate ligand occupying the non-edda sites [174,179]. This was attributed to the dominant influence of the rigid edda chelate. (2) It was found that the contribution of the asymmetric nitrogens (vicinal effect) to the rotational strength may be comparable in magnitude to that of the configurational effect [156,178,179,194a]. The asymmetric nitrogens in these complexes [156] make opposite contributions to the rotational strength, depending upon whether the substituent on nitrogen was hydrogen or a benzyl group. Mason's hexadecal regional rule can be applied to predict the experimentally observed sign of the low-energy CD transition for the s-*cis*-$[Co(dbedda)(en)]^+$

complex. Also, the theoretical treatments of Richardson [194b] and Schipper [194c,195] show promise of adding to our understanding of the correlation of CD spectra and stereochemistry and the additivity of chiral contributions. The signs and magnitude of the CD curve of s-*cis*-$[Co(edda)(l\text{-stien})]^+$ agree with other studied s-*cis*-edda complexes, indicating that the edda portion dominates and that the benzene substitution on the carbons has little effect. However, for $[Co(l\text{-sdda})(en)]^+$, the sign of the low-energy peak in the CD spectrum is opposite to what is expected. Either the asymmetric nitrogens make a large contribution, opposite to that from the chiral arrangement of chelate rings to the rotational strength, or, contrary to the case for $[Co(edda)(l\text{-stien})]^+$, the benzene substituents on the carbons are making a significant contribution to the rotational strength. The other possibility requires the opposite (Λ) configuration with the large phenyl substituents in unfavorable axial positions.

Although the intensities of the absorption bands are significantly greater for the less symmetrical uns-*cis* complexes than for the corresponding s-*cis* complexes, the CD intensities are more than twice as great for the s-*cis* isomers (the diamine ring in contribution with the en backbone edda defines the opposite chirality in the uns-*cis* complexes). Also, the smaller splitting (A_2 and E) for uns-*cis* isomers would result in greater mutual cancellation. The two asymmetric N atoms must have the same absolute configuration for s-*cis* isomers, but they are not necessarily the same for uns-*cis* isomers. In the CD spectra of the uns-*cis* complexes, the A_2 component is reduced in intensity from the diammine to the trimethylenediamine complexes and it completely disappears for the ethylenediamine complex. These changes in the CD spectra of uns-*cis*-edda are in contrast with those of s-*cis*-edda complexes, in which the CD spectra appear to be remarkably independent of the nature of the bidentate "L" ligand.

The difference in the central ring size also produces changes in the shape of CD spectra. In the more rigid uns-*cis*-edda complexes, the intensity of the A_2 component is reduced from that of the less rigid uns-*cis*-tmdda complexes. The changes in the rigidity of the central ring of edda and tmdda and rigidity of bidentate ligands affect the intensity of the A_2 component in the same way.

The absolute configuration of s-*cis* and uns-*cis* complexes of ethylenediamine-N,N'-di-S-α-propionate ion (SS-eddp) could be determined from PMR studies [172] because of the optically active ligand, and this assignment provided a direct and reliable basis for assignments of absolute configurations of other edda-type complexes. The same assignments result for the complexes if one uses the sign of the net rotational strength in the $T_{1g}(O_h)$ band region as proposed by Richardson [27c] (or the sign of the major CD peak) and as related to $[Co(en)_3]^{3+}$. Besides, the assignments of absolute configuration based on empirical rules for uns-*cis*-[Co(edda)(diamine)]$^+$ complexes have been verified by an X-ray structure determination [171].

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