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# COMPLEXES OF COBALT(III) WITH FLEXIBLE TETRADENTATE LIGANDS

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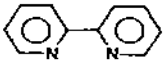
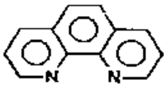
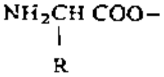
## ABBREVIATIONS

| | | |
|---|---|---|
| en | ethylenediamine | $NH_2CH_2CH_2NH_2$ |
| pn | 1,2-diaminopropane (propylenediamine) | $NH_2(CH_3)CH_2NH_2$ |
| tn | 1,3-diaminopropane (trimethylenediamine) | $NH_2CH_2CH_2CH_2NH_2$ |
| ox | oxalate dianion | $-OOCCOO-$ |
| mal | malonate dianion | $-OOCCH_2COO-$ |
| men | *N*-methylethylene diamine | $CH_3NHCH_2CH_2NH_2$ |
| dmen | *N,N'*-dimethylethylenediamine | $CH_3NHCH_2CH_2NHCH_3$ |
| een | *N*-ethylethylenediamine | $CH_3CH_2NHCH_2CH_2NH_2$ |
| deen | *N,N'*-diethylethylenediamine | $CH_3CH_2NHCH_2CH_2NHCH_2CH_3$ |
| bipy | α,α'-bipyridine |  |
| 1,10-phen | 1,10-phenanthroline |  |
| aa | generalized amino acid anion |  $NH_2\underset{\displaystyle R}{\underset{\vert}{C}}H\,COO-$ |
| gly | glycine | $R = H$ |
| Ogly | oxygen-bonded glycine | |
| ala | alanine | $R = CH_3$ |
| Oala | oxygen-bonded alanine | |
| val | valine | $R = CH(CH_3)_2$ |
| Oval | oxygen-bonded valine | |
| Oac | acetate anion | $CH_3COO-$ |

## A INTRODUCTION

Among the known complexes of six-coordinate metal ions, perhaps the greatest variety of structure and stereochemistry is displayed by complexes of cobalt(III) with flexible tetradentate ligands. In this context, flexible tetradentate ligands includes 3,6-diaza-1,8-octanediamine (triethylenetetraamine, trien, $NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$), 3,7-diaza-1,9-nonanediamine (2,3,2-tet, $NH_2CH_2CH_2NHCH_2CH_2CH_2NHCH_2CH_2NH_2$), 4,7-diaza-1,10-decanediamine (3,2,3-tet, $NH_2CH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2CH_2NH_2$), *N,N'*-ethanedinitrilodiacetic acid (ethylenediaminediacetic acid, EDDA, $HOOCCH_2NHCH_2CH_2NHCH_2COOH$), 3,6-dithia-1,8-octanediamine (eee, $NH_2CH_2CH_2SCH_2CH_2SCH_2CH_2NH_2$), 3,7-dithia-1,9-nonanediamine (ete, $NH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2NH_2$), 4,7-dithia-1,10-decanediamine (tet, $NH_2CH_2CH_2CH_2SCH_2CH_2SCH_2CH_2CH_2NH_2$), and various alkyl-substitutes derivatives. Branched ligands, such as nitrilotriacetic acid (NTA, $N(CH_2COOH)_3$), cyclic ligands, and those ligands which are constrained to a common plane about the central metal ion are specifically excluded *.

The significance of the complexes of cobalt(III) lies in the inherent substitution inertness which facilitates the isolation and characterization of the various isomeric products We believe that the isolation of products containing cobalt(III) provides evidence for the similar formation of complexes with other metal ions which cannot be isolated easily. Thus proton magnetic resonance spectra, for example, of carefully characterized cobalt(III) compounds serve as useful models for structurally related, though frequently labile, complexes with other metal ions As models for metallo enzymes and/or metal activated enzymes, the utility of cobalt(III) models lies not in the reactions of these species compared with the reactions of the enzyme under consideration, but rather in the ability of the cobalt(III) ion to preserve the coordination sphere for detailed study of steric interactions which might contribute to metal ion activation

## B. GENERAL CONSIDERATIONS

### *(i) Geometrical configuration of the coordinated ligand*

A linear flexible tetradentate ligand can occupy four of the six available coordination sites of the cobalt(III) ion to form one or all three of the possible geometrical isomers shown in Fig 1 Mixed ligand complexes with unsymmetrical bidentate ligands (e g amino acids, 1,2-diaminopropane) and flexible tetradentate ligands admit the possibility of isomerism of the unsymmetrical bidentate ligand with respect to the flexible tetradentate ligand in the uns-*cis* configuration. An example of such isomerism is shown in Fig 2 for a typical amino acid Complexes exhibiting each configuration have been characterized, all of these complexes are optically active, and many have been resolved

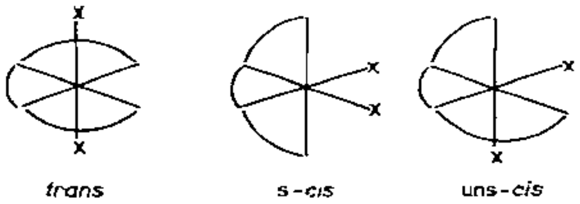


Fig 1 Geometrical isomerism of six-coordinate complexes including a flexible tetradentate ligand **

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* Among the ligands excluded are the phthalocyanines and porphyrins, for example These ligands like ethylenediamine-bis-salicylaldimine derivatives, occupy four coordination sites in a common plane, the stereochemistry of these complexes is, we believe, best discussed in the context of the chemistry of macrocyclic ligands

** The symmetrical-*cis*/unsymmetrical-*cis* (*s-cis*/uns-*cis*) nomenclature has been suggested by Worrell and Busch[1] as an alternative to the *α-cis*/*β-cis* nomenclature employed by Sargeson and Searle[2] or the *trans*/*cis* nomenclature of Legg and Cooke[3]

### (ii) Conformations of the chelate ring

The chelate rings formed by flexible tetradentate ligands may be likened to the saturated heterocyclic systems familiar to organic chemists The stereochemistry of individual chelate rings has been discussed in detail by Corey and Bailar[4] The principals of conformational analysis have been successfully applied to multidentate ligand systems by Buckingham et al [5] and by Gollogly and Hawkins[6] Though the conformational analysis of complexes with multidentate ligands is currently an area of intense research activity, the most elegant applications have appeared in support of X-ray structure determinations. We anticipate that the predictive powers of conformational analysis will be demonstrated within the next few years

### (iii) Stereochemically significant centers of the ligand

Complexes with flexible tetradentate ligands possess intrinsically optically active centers at the coordinated secondary donor atoms, as shown in Fig 3 Note that in each case the donor atom is approximately tetrahedral and, upon coordination, possesses neither center nor plane of symmetry. For flexible linear tetraamine ligands, to be discussed below, the contribution of the dissymetric donor atoms to the optical activity of several geometric isomers has been evaluated. The contribution of donor dissymmetry to the optical activity of other systems is often indistinguishable from chelate ring conformation contributions

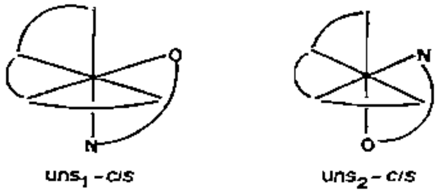

Fig 2 Geometrical isomerism introduced in a mixed unsymmetrical bidentate–flexible tetradentate ligand complex of uns-*cis* configuration *

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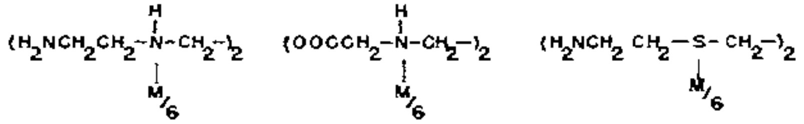
* We have adapted the nomenclature of Buckingham and co-workers, as applied to mixed ligand complexes of cobalt(III) with trien and amino acids The subscript 1 is applied to the uns-*cis* isomer in which the amine function of the amino acid is *trans* to a primary amine of the tetraamine ligand The subscript 2 is applied to the uns-*cis* isomer in which the amine function of the amino acid is *trans* to a secondary amine of the tetraamine ligand This useage is informal, it has not been applied to unsymmetrical diamine ligands such as 1,2-diaminopropane, and it has not yet been applied to flexible dithiadiamine or diaminedicarboxylate complexes



$(H_2NCH_2CH_2-\underset{\underset{M/6}{|}}{\overset{\overset{H}{|}}{N}}-CH_2-)_2$ $(OOCCH_2-\underset{\underset{M/6}{|}}{\overset{\overset{H}{|}}{N}}-CH_2-)_2$ $(H_2NCH_2CH_2-\underset{\underset{M/6}{\downarrow}}{S}-CH_2-)_2$

Fig 3 Optically active centers at the coordinated secondary donor atoms

Complexes with flexible tetradentate ligands in which alkyl substituents are introduced to generate additional dissymmetric centers on the ligands have been described, and will be discussed as derivatives of the parent ligands where appropriate.

### *(iv) Optical activity and the assignment of electronic states and absolute configurations*

Since the early sixties there has been a rapid growth in the use of optical activity in the form of optical rotatory dispersion (ORD) and later circular dichroism (CD) to analyze the electronic structure of cobalt(III) complexes and tentatively to assign absolute configurations It is not the purpose of this discussion to detail the development of this structural probe, but to point out generally its uses and limitations as applied to the cobalt(III) complexes discussed in this review Several surveys have appeared dealing with the application of optical activity to the study of coordination compounds[7] More detailed discussions pertinent to specific types of ligands will appear later in the review

From the outset it should be made clear that it is not yet possible to assign absolute configurations to the complexes discussed in this review a priori using ORD or CD data The only method available for determining absolute configurations directly is X-ray crystallography through the Bijvoet method of anomalous dispersion There are, then, essentially three methods available for assigning absolute configuration of related complexes (*1*) through analysis of the mechanism of a reaction which converts a complex of known absolute configuration to one of unknown absolute configuration, (*2*) through comparison of ORD and CD data between complexes of known and unknown absolute configuration, and (*3*) through stereochemical analysis of complexes formed from stereospecific ligands whose absolute configurations have been determined by X-ray crystallography.

In 1965, Mason and co-workers[8] proposed a method for relating absolute configurations of $Co(en)_2L_2{}^{n+}$ ($L_2$ = two monodentate ligands or a bidentate ligand) to $Co(en)_3{}^{3+}$ whose absolute configuration has been determined by X-ray analysis*. This involved tracing the *d–d* electronic transitions, as revealed in the CD spectra of these complexes with $\underset{\sim}{C}_2$ symmetry, to those of $Co(en)_3{}^{3+}$ ($\underset{\sim}{D}_3$) which Mason had previously assigned from the

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* The absolute configurations of the chelate complexes are related to the helix described by any pair of chelate rings of $Co(en)_3{}^{3+}$ as discussed in the IUPAC proposal[9] The chirality is left-handed for $(+)_{5461}-Co(en)_3{}^{3+}$ and this isomer is designated[38] Λ The configurations of all complexes in this work are designated using the $C_3$ or pseudo-$C_3$ axis to relate the helix to that of $Co(en)_3{}^{3+}$ This is equivalent to the IUPAC nomenclature except that in the case of multidentates IUPAC suggests that all skew lines pairs be given What has been done in this report is to give the "net contribution" obtained by summing the contribution from each pair[10] No problems arise in doing this for linear tetradentates, but there are cases in which a "net contribution" cannot be determined[9] It is important to note that the sense of the helix is opposite if one uses the $C_2$ or pseudo-$C_2$ axis as the reference axis These relationships are illustrated in Fig 5

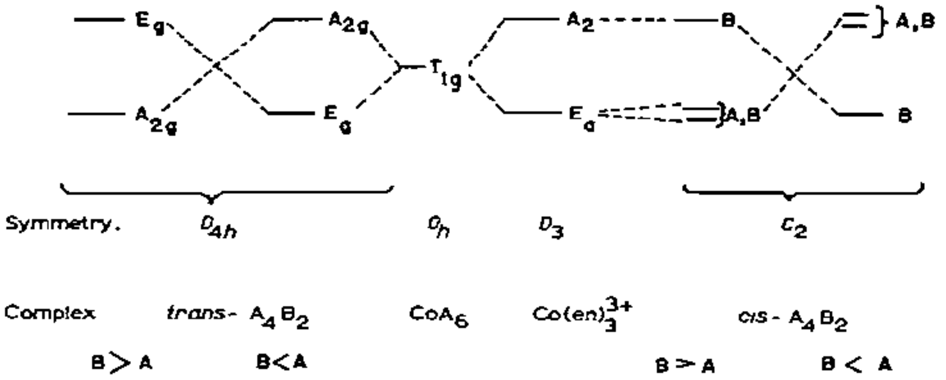

Fig 4 Correlation of energy levels in the $^1T_{1g}$ $(O_h)$ region for strong-field cobalt(III) in various symmetries (Separations are qualitative )

polarized CD spectrum of $Co(en)_3{}^{3+}$ This relationship is illustrated in Fig. 4 Mason recognized that the $A$ state ($\underset{\sim}{C}_2$ symmetry) had $E_a$ ($\underset{\sim}{D}_3$) parentage and argued that the $A$ state should be the dominant component in the CD spectrum of $Co(en)_2L_2{}^{n+}$ Thus, an antimere of $Co(en)_2L_2{}^{n+}$ is configurationally related to an antimere of $Co(en)_3{}^{3+}$ as illustrated in Fig 5 if the sign of the $A$ component in the former is the same as that of the $E_a$ component in the latter The order of the states in the $\underset{\sim}{C}_2$ complexes is a function of the relative ligand field strength of the ligands involved as shown in Fig 4

In using circular dichroism spectra to assign, tentatively, the absolute configurations to resolved complexes of linear tetradentate ligands, this approach or an approach similar to that outlined by Mason has been frequently employed Fortunately, in a number of instances, assignments have been strongly supported by studies of closely related diastereoisomers involving stereospecific ligands of known absolute configurations. At present there is no sound theoretical model which explains the sign and rotational strength of a given $d$–$d$ electronic transition ★.

The statement that two complexes are "configurationally related" has certain hidden implications Few would argue that the two complexes illustrated in Fig 5 are not "configurationally related" However, the more complex chelates such as those discussed in this review offer some interesting problems Legg and Douglas[10] developed a "ring pairing"

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★ Strictly speaking, it should not be possible to compare CD spectra in the manner just described to relate absolute configurations Consider the *s-cis* complexes of cobalt(III) with flexible tetradentate ligands The true symmetry of these complexes is no higher than $\underset{\sim}{C}_2$, there are, therefore, no degeneracies in any of the electronic states of the cobalt ion Within the manifold of the $d$–$d$ octahedral excited states, there should appear three components for each $T(\underset{\sim}{O}_h)$ state All three components are rarely observed, and the spectra are usually assigned assuming that $A$ and $B$ components arising from $E_a$ are only separated to a small degree, Fig 4 Furthermore, certain assumptions have to be made concerning the degree of mixing between states of like symmetry, e g the two $B$ states ($\underset{\sim}{C}_2$) arising from $E_a$ and $A$ ($\underset{\sim}{D}_3$) It would be naive to assume that the degree of splitting and mixing would not influence both the relative position and intensity of the A component

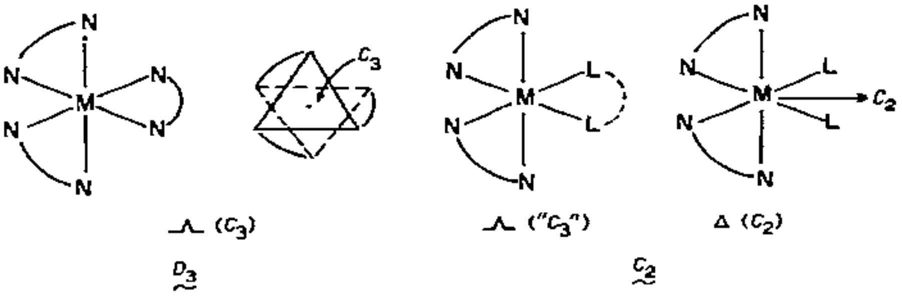


Fig 5 "Configuration relationship" behavior between $Co(en)_3{}^{3+}$ and $Co(en)_2L_2{}^{n+}$

scheme to relate the configurations of multidentate octahedral complexes The method has been applied to many complexes and thus far has been found to be consistent with the absolute configuration assignments made directly by crystallographic analysis or indirectly by using stereospecific ligands of known absolute configuration The "ring pairing" scheme is similar to the "octant sign" method for relating configurations proposed earlier by Hawkins and Larsen[11] and forms the basis for the recent tentative IUPAC rules for absolute configurations[9].

Finally, the Mason scheme for relating absolute configurations would suggest that the correct theoretical model for optical activity in these complexes should be derived from a consideration of metal–ligand orbital overlap where the ligand orbitals are the antibonding orbitals on the nonligating atoms[8] However, two recent studies suggest that this may not be the case[12] A crystallographic study by Wing and Eiss[12a] of $(+)_{5461}$–$Co(TRI)_2I_3$ (TRI = tribenzo [*b*, *f*, *j*] [1 5 9] triazocycloduodecine), a complex which cannot be "configurationally related" to $Co(en)_3{}^{3+}$ (it has no "ring pairs") but yet has a CD spectrum very similar to that of $Co(en)_3{}^{3+}$, strongly supports the trigonal twist model proposed by Piper and Karipides[13] and suggests that the "ring pairing" scheme may be limited to complexes with constraining ligands (i e those for which ligand–metal–ligand bond angles are less than 90°) Support for the Piper model also comes from the single crystal CD study of Δ–$[Co(tn)_3]^{3+}$ (tn = 1,3-diaminopropane) where it appears that the $E_a$ and $A_2$ transitions have interchanged leading to a reversal in the sign of $E_a$[12b] In this case a crystal structure study revealed that the N–Co–N bond angle was greater than 90°, and thus the observation on the CD spectrum are consistent with Piper's prediction.

The foregoing discussion serves only to point out the general state of flux which currently exists in the study of optical activity of complexes and its relationship to the assignment of electronic states and absolute configurations. Thus, the word "tentative" is essential when absolute configurations are assigned on the basis of relative optical activity alone

## C COMPLEXES WITH FLEXIBLE TETRAAMINE LIGANDS

Certainly the most extensively studied complexes of cobalt(III) with flexible tetradentate ligands have been the complexes with linear tetraamines Table 1 summarizes the flexible tetraamine ligands discussed in this review.

TABLE 1

Flexible linear tetraamine ligands

| *Ligand* | *Abbreviation* |
|---|---|
| 3,6-diaza-1,8-octanediamine | trien |
| 3,7-diaza-1,9-nonanediamine | 2,3,2-tet |
| 4,7-diaza-1,10-decanediamine | 3,2,3-tet |
| 3,6-diaza-2(S), 7(S)-dimethyl-1,8-octanediamine | L, L-2,7-$(CH_3)_2$-trien |
| 3,6-diaza-4-methyl-1,8-octanediamine | 5-metrien |
| 3,6-diaza-1(S), 8(S)-dimethyl-1,8-octanediamine | L, L-1,8-$(CH_3)_2$-trien |
| 3,6-diaza-4(S), 5(S)-dimethyl-1,8-octanediamine | 5(S), 6(S)-dimetrien |
| *N,N'*-bis (2-amino-3(S)-phenylpropyl)-*trans*-1(R), 2(R)-cyclohexanediamine | LDDL |
| *N,N'*-bis (β-aminoethyl)-*trans*-1(S), 2(S)-cyclohexanediamine | |
| *N,N'*-bis (2-picolyl)-1(R)-methyl-1,2-diaminoethane | picpn |
| *N,N'*-bis (2-picolyl)-2(R), 3(R)-butanediamine | bnpic |
| *N,N'*-bis (2-ethyl(2-pyridyl))-1,2-ethanediamine | bpdo |
| 2,5,8,11-tetraazadodecane | 1,10-$Me_2$trien |
| 6(R)-methyl-2,5,8,11-tetraazadodecane | D-1,5,10-$Me_3$trien |
| 4(S), 9(S)-dimethyl-2,5,8,11-tetraazadodecane | LL-1,3,8,10-$Me_4$trien |
| 3(S), 10(S)-dimethyl-2,5,8,11-tetraazadodecane | LL-1,2,9,10-$Me_4$trien |
| 2,5,9,12-tetraazatridecane | 1,11-$Me_2$-2,3,2-tet |

### *(i) 3,6-diaza-1,8-octanediamine, trien (or 2,2,2-tet)*

The tetradentate ligand system most completely studied to date has been 3,6-diaza-1,8-octanediamine (triethylenetetraamine) A series of complexes prepared by Basolo in 1948 included a purple salt, $[Co(trien)Cl_2]^+$, prepared from the aerial oxidation of cobalt (II) salts in the presence of the ligand

$$Co(II) + trien \xrightarrow[(2)HCl]{(1)O_2} [Co(trien)Cl_2]^+$$

This complex, the dinitro, oxalato, ethylenediamine, and carbonato derivatives were assigned *cis* geometries because of the similarity of the color and ultraviolet spectra to those of the corresponding bis(ethylenediamine)cobalt(III) complexes Though Basolo recognized the possible existence of *s-cis* and uns-*cis* isomers for these compounds, he did not consider the differences significant or the isomers separable at the time of his first report

Das Sarma and Bailar [15] resolved the purple $[Co(trien)Cl_2]^+$ complex with silver antimonyl tartrate, thereby confirming the postulated *cis* configuration But these authors, like Basolo, could not distinguish between the *s-cis* and uns-*cis* structures. Das Sarma and Bailar further reported that some *trans*-$[Co(trien)Cl_2]^+$ existed in equilibrium with the *cis* isomer in methanol but they could not isolate the *trans* complex

Selbin and Bailar [16] later claimed the preparation and isolation of two isomers of $[Co(trien)Br_2]^+$ including a "green" compound which was assigned the *trans* configuration Buckingham and Jones [17] have since refuted this claim and have shown that the "green" compound was actually a mixture of the *s-cis* and uns-*cis* isomers

Pearson et al.[18] reported the preparation of a complex of formula *cis*-$[Co(trien)(NH_3)Cl](ClO_4)_2$. Gillard and Wilkinson[19] prepared a number of other complexes including $[Co(trien)pn]I_3$ and $[Co(trien)ox]I$ and claimed that *trans*-$[Co(trien)Cl_2]Cl$ could be prepared by heating moist *cis*-$[Co(trien)Cl_2]Cl$ at 180°C. The latter result is in question since Buckingham, et al.[20] found the reaction to result chiefly in reduction to cobalt(II).

In a recent series of articles[2,21,22] Sargeson and Searle described the preparation and isolation of all three possible geometrical isomers for $[Co(trien)Cl_2]^+$ as well as that of several other s-*cis* and uns-*cis* mixed-ligand–cobalt(III) complexes containing triethylenetetramine. The s-*cis*-$[Co(trien)(NO_2)_2]Cl$ complex is the predominant product formed from the air-oxidation of $CoCl_2$ and trien·HCl in the presence of excess nitrite anion. This complex is converted to s-*cis*-$[Co(trien)Cl_2]Cl$ by treatment with concentrated HCl.

$$\begin{tikzcd}
\mathrm{Co(II) + trien{\cdot}HCl + excess\ NO_2^-} \arrow[r, "O_2"] & s\text{-}cis\text{-}[\mathrm{Co(trien)(NO_2)_2}]\mathrm{Cl} \arrow[d, "\mathrm{HCl}"] \\
 & s\text{-}cis\text{-}[\mathrm{Co(trien)Cl_2}]\mathrm{Cl}
\end{tikzcd}$$

Symmetrical-*cis*-$[Co(trien)CO_3]ClO_4$ is prepared from the s-*cis*-dichloro complex by treatment with $HCO_3^-$ in acidic solution. However, treatment of s-*cis*-$[Co(trien)Cl_2]Cl$ with $CO_3^{2-}$ in basic solution produces uns-*cis*-$[Co(trien)CO_3]Cl$.

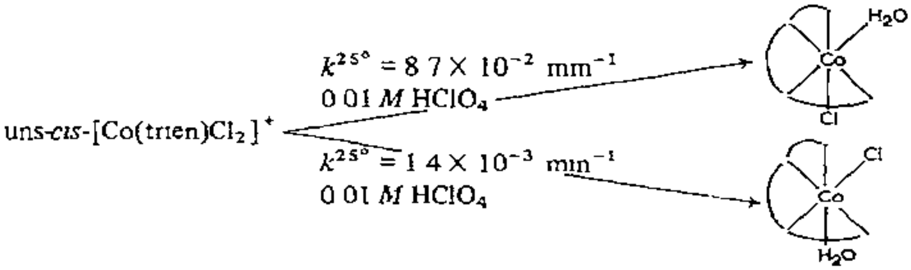
$$\begin{tikzcd}
 & & s\text{-}cis\text{-}[\mathrm{Co(trien)CO_3}]^+ \\
s\text{-}cis\text{-}[\mathrm{Co(trien)Cl_2}]^+ \arrow[urr, "\mathrm{NaHCO_3}"] \arrow[drr, "\mathrm{Li_2CO_3}"'] & & \\
 & & \text{uns-}cis\text{-}[\mathrm{Co(trien)CO_3}]^+
\end{tikzcd}$$

This complex provides acess to other members of the unsymmetrical *cis* series through simple substitution reactions. There is no known way in which the uns-*cis* series may be transformed to the s-*cis* series. *trans*-$[Co(trien)Cl_2]Cl$ may be prepared only from uns-*cis*-$[Co(trien)Cl_2]Cl$ by treatment with methanolic HCl.

$$\text{uns-}cis\text{-}[\mathrm{Co(trien)Cl_2}]^+ \xrightarrow[\Delta]{\mathrm{HCl/CH_3OH}} trans\text{-}[\mathrm{Co(trien)Cl_2}]^+$$

No isomerization of the s-*cis*-$[Co(trien)Cl_2]Cl$ occurs under similar conditions. The topologies of the *cis* isomers was established by careful measurement of the rates of aquation of the *cis*-$[Co(trien)Cl_2]^+$ complexes.[23]

$$\text{s-}cis\text{-}[Co(trien)Cl_2]^+ \xrightarrow[0.01\,M\,HClO_4]{k^{25°} = 9.4 \times 10^{-3}\,min^{-1}} \text{s-}cis\text{-}[Co(trien)ClH_2O]^{2+}$$



The two aquation rates for the uns-*cis* isomer correspond to the different environments of the chloride ligands, one *trans* to a secondary donor, and the other *trans* to a primary donor. Proton magnetic resonance spectra of the s-*cis* and uns-*cis* isomers in aqueous acid conform to these assignments [22] In the region of the NH proton signals, the spectrum of the s-*cis* isomer is simpler than that of the uns-*cis* isomer, as expected from the non-equivalence of the donor atoms in the latter complexes These assignments were later found to be in agreement with the infrared spectra [17] although recent work casts doubt on the usefulness of IR data for such assignments [24,25] The kinetics of the aquation reactions of the $[Co(trien)Cl_2]^+$ isomers have been studied extensively In addition to the work previously mentioned, Sargeson [30] has studied the nature of the intermediate in the aquation reaction of the s-*cis*- and uns-*cis*-isomers, and Sargeson and Searle [31] have summarized most of the aquation data

Details of the resolutions of the s-*cis* and uns-*cis*-$[Co(trien)X_2]^{n+}$, ($X = Cl^-$, $NO_2^-$ or $H_2O$), s-*cis* and uns-*cis*-$[Co(trien)Cl(H_2O)]^+$, and s-*cis* and uns-*cis*-$[Co(trien)CO_3]^+$ ions have been reported [22] Assignments of absolute configurations from optical activity data relate these complexes to the corresponding $[Co(en)_2X_2]^{n+}$ ions [2], and are fully consistent with chemical and mechanistic evidence These assignments provide the basis for much of the subsequent work with flexible tetraamine complexes with cobalt(III) The circular dichroism spectra obtained for these complexes are summarized in Table 2.

The synthesis and resolution of s-*cis*- and uns-*cis*-$[Co(trien)en]^{3+}$ has recently been described [26], providing an example of ORD–CD curves for the geometrical isomers of the $CoN_6$ chromophore. That these spectra, Table 3, are more similar to the spectra of other trien complexes (e g. s-*cis*- and uns-*cis*-$[Co(trien)ox]^+$) than to the spectra of other $CoN_6$ chromophores (e g $[Co(en)_3]^{3+}$) suggests that the topology of the tetraamine ligand and the concomitant strain in the chelate rings significantly influences the optical activity of these species

Due to the presence of the two asymmetric coordinated secondary nitrogen atoms (Fig 3), the *trans* complex exists in optically active and meso forms. The preparation, stereochemistry, and aquation of the optically active *trans*-$[Co(trien)Cl_2]^+$ ion has been reported [20] The compound was prepared by treatment of optically active uns-*cis*-$[Co(trien)Cl_2]Cl$ with methanolic HCl The uns-*cis*-$[Co(trien)Cl_2]Cl$ complex can be assigned an absolute configuration by comparison of the Cotton effects which it gives to those given by the corresponding *cis*-$[Co(en)_2Cl_2]Cl$ complex

TABLE 2

Circular dichroism data for s-*cis*-$Co(tren)L_2^{n+}$

| *Compound* | $\lambda_{max}$ (nm) | $(\epsilon_l - \epsilon_d)_{max}$ | *Compound* | $\lambda_{max}$ (nm) | $(\epsilon_l - \epsilon_d)_{max}$ |
|---|---|---|---|---|---|
| $(+)_{589}$-$Co(tren)Cl_2^+$ | 595 | −1.6 | $(+)_{589}$-$Co(tren)CO_3^+$ | 520 | +4.5 |
| | 525 | +2.9 | | 390 | +0.8 |
| | 420 | +0.4 | | 360 | −0.1 |
| | 380 | −0.9 | | 330 | +0.2 |
| | 320 | −1.6 | $(+)_{546}$-$Co(tren)(H_2O)_2^{3+}$ | 560 | −1.1 |
| $(+)_{589}$-$Co(tren)ClH_2O^{2+}$ | 590 | −1.1 | | 490 | +1.9 |
| | 510 | +2.2 | | 380 | +0.7 |
| | 400 | +0.4 | | 350 | −0.05 |
| | 370 | −0.3 | | 325 | +0.05 |
| | | | $(+)_{546}$-$Co(tren)(NO_2)_2^+$ | 460 | +1.2 |
| | | | | 395 | −0.2 |
| | | | | 340 | −3.2 |

$$\begin{tikzcd}
\Lambda\text{-uns-}cis\text{-SS-}[Co(tren)Cl_2]^+ \arrow[rr, shift left, "CH_3OH/HCl"] \arrow[dr] & & (+)\text{-}trans\text{-SS-}[Co(tren)Cl_2]^+ \arrow[ll, shift left, "0.01\,M\ HClO_4"] \arrow[dl] \\
& \Lambda\text{-uns-}cis\text{-SS-}[Co(tren)Cl(H_2O)]^{2+} &
\end{tikzcd}$$

Likewise active *trans*-$[Co(tren)Cl_2]Cl$ aquates stereospecifically to the corresponding active uns-*cis*-$[Co(tren)Cl(H_2O)]^+$ ion whose configuration can be assigned from CD data. The known configuration of these two uns-*cis* complexes allows assignment of configura-

TABLE 3

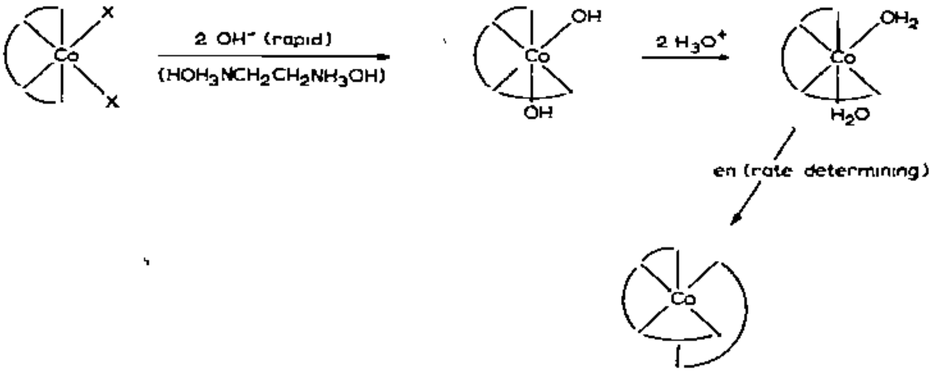
Circular dichroism data for *cis*-$Co(tren/2,3,2\text{-tet})(amine)^{3+}$

| *Compound* | $\lambda_{max}$ *(nm)* | $(\epsilon_l - \epsilon_d)_{max}$ | *Ref* |
|---|---|---|---|
| (+)-s-*cis*-$[Co(tren)en]^{3+}$ | 492 | 2.17 | 26 |
| | 434 | −0.46 | |
| | 354 | 0.50 | |
| (+)-uns-*cis*-$[Co(tren)en]^{3+}$ | 478 | 1.50 | 26 |
| | 335 | −0.07 | |
| | 300 | 0.02 | |
| (+)-uns-*cis*-$[Co(tren)tn]^{3+}$ | 479 | 1.45 | 60 |
| | 340 | −0.17 | |
| (+)-$[Co(2,3,2\text{-tet})en]^{3+}$ | 500 | 1.40 | 60 |
| | 448 | −0.76 | |
| | 340 | 0.19 | |

tion to the active *trans*-[Co(trien)$Cl_2$]Cl. This assignment was later confirmed by comparison of the CD spectrum of (+)-*trans*-SS-[Co(trien)$Cl_2$]Cl * with those of (+)-*trans*-[Co(3(S), 8(S)-(+)-dimetrien)$Cl_2$]Cl and $(+)_{546}$-*trans*-[Co(S-pn)$_2$$Cl_2$]Cl [27]. The detection of the two internal diastereoisomers (i e. racemic, RR, SS, and meso, RS) for the uns-*cis*-[Co(trien)$(H_2O)_2$]$^{3+}$ ion was also reported [20]

Kuroda and Goto [32] have reported the preparation of the *trans*-bis-(acetato)- and bis(propionato)triencobalt(III) complexes from [Co(trien)$CO_3$]$^+$ and acetic acid at high temperatures Later a series of *cis*- and *trans*-bis-(halogenoacetato)triencobalt(III) complexes were also reported [33]

Kyuno and Bailar [34–37] studied the base hydrolysis of some optically active dihalotriethylenetetraaminecobalt(III) ions It was found that the base hydrolysis of the Λ-s-*cis* isomer proceeded with isomerization whereas that of the Λ-uns-*cis* isomer proceeded with retention of configuration The basis for this conclusion was that any stereochemical change during a reaction of Λ-s-*cis*-[Co(trien)$Cl_2$]$^+$ to Λ-uns-*cis* or Λ-s-*cis* requires movement of two chelate rings and is assumed to be less likely than a change involving the movement of one chelate ring such as Λ-s-*cis* or Δ-uns-*cis* From this consideration and relationships deduced from ORD curves, isomerization was found to be accompanied by a change in the sign of the dominant Cotton effect in the 400–700 nm region during the course of the reaction Thus it was observed that Λ-s-*cis*-[Co(trien)$Cl_2$]Cl reacts with aqueous or anhydrous ethylenediamine to produce [37] Δ-uns-*cis*-[Co(trien)en]$Cl_3$, and with aqueous propylenediamine to produce [34] Δ-uns-*cis*-[Co(trien)pn]$Cl_3$ through the proposed formation of Δ-uns-*cis*-[Co(trien)$(OH)_2$]$^+$ as an isomerized intermediate.



The base hydrolysis of optically active uns-*cis*-[Co(trien)$X_2$]$^+$, however, was found to proceed with retention of configuration [36] An associative mechanism has been proposed for the isomerization/inversion step in these reactions [23,31,34].

The [Co(trien)$X_2$]$^{n+}$ moiety has been used to promote the hydrolysis of amino acid esters and peptides The uns-*cis*-[Co(trien)OH$(H_2O)$]$^{2+}$ ion was found to react with amino

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* The R–S nomenclature for absolute configurations of tetrahedral carbon and nitrogen atoms is that of Cahn et al [28] as described by Roberts and Caserio [29]

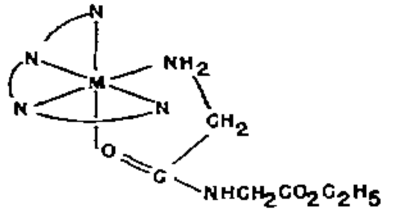


Fig. 6 Intermediate in peptide hydrolysis by Co(III) complex

acids, amino acid esters, amino acid amides, and peptides to form [39,40] a chelated complex uns-*cis*-[Co(trien)aa]$^{2+}$. The rate is a function of pH and temperature. The hydrolysis of the esters and glycinamide give a rate law first-order in uns-*cis*-[Co(trien)OH(H$_2$O]$^{2+}$ and in the free base form of the amino acid derivative [40]. An intermediate complex, uns$_2$-*cis*-[Co(trien)(glyglyoet)$^{3+}$] has been isolated from the reaction with glyclyglycine ethyl ester [41,42], Fig. 6. The stereochemistry of the product which contains the chelated amino acid has been characterized for uns$_1$-*cis*- and uns$_2$-*cis*-[Co(trien)gly]$^{2+}$ ions by means of electronic, infrared, and PMR spectra, the CD and ORD data for the resolved isomers, and the stereospecific syntheses [43]. Lin and Douglas [44] have since prepared the conformational isomers of the uns$_2$-*cis*-[Co(trien)aa]$^{2+}$ complexes for several amino acids. The CD spectra of these and related complexes are summarized in Table 4.

*(ii) Substituted derivatives of 3,5-diaza-1,8-octanediamine*

Tetraamine ligands have been prepared which are related to trien, but which have one or more protons selectively replaced by alkyl groups. One such ligand is 2,9-diamino-4,7-diazadecane $NH_2CH(CH_3)CH_2NHCH_2CH_2NHCH_2CH(CH_3)NH_2$, S,S-1,8'-dimetrien. This ligand has two asymmetric carbon atoms but was prepared from S-alanine so that the configuration of both carbon atoms is known. Asperger and Liu [45,46] have isolated the three possible dichloro cobalt(III) isomers of this ligand. Structural assignments were made on the basis of electronic and PMR spectra. A single methyl doublet is seen in the PMR spectra of the s-*cis* and *trans* isomers due to the equivalence of the two methyl groups of the tetradentate ligand in these isomers. The PMR spectrum of the uns-*cis* isomer shows no less than seven resonance signals from the non-equivalent methyl groups. Asperger and Liu [46] claim that unpublished ORD curves show that the optically active ligand coordinates stereospecifically in the *cis* complexes forming only the Λ-s-*cis* and Δ-uns-*cis* isomers.

Mixed ligand amino acid complexes with the general formula [Co(S,S-1,8-dimetrien)aa]$^{2+}$ have been reported. The Λ-s-*cis* complexes are prepared by the direct action of the amino acid on the dichloro complex [47] at pH 7.2. The Δ-uns-*cis* complexes are prepared by first aquating the Λ-s-*cis*-[Co(S,S-1,8-dimetrien)Cl$_2$]$^{2+}$ complex to Λ-s-*cis*-[Co(S,S-1,8-dimetrien)Cl(H$_2$O)]$^{2+}$, followed by treatment with the amino acid at pH 7.2. The uns-*cis* isomer is distinguished from the s-*cis* isomer by means of the methyl group PMR signals [48], absolute configurations have been assigned from ORD data.

TABLE 4

Circular dichroism data for *cis*-Co(trien)(aa)$^{2+}$ and related complexes

| *Compound* | $\lambda_{max}$ *(nm)* | $(\epsilon_l - \epsilon_d)_{max}$ | *Ref* |
|---|---|---|---|
| (+)-[Co(en)$_2$gly]$^{2+}$ | 505 | + 2.10 | 44 |
| | 370 | + 0.088 | |
| | 328 | + 0.128 | |
| (+)-[Co(tn)$_2$gly]$^{2+}$ | 510 | + 1.00 | 44 |
| | 436 | − 0.06 | |
| | 340 | − 0.05 | |
| Λ-(+)-uns$_1$-*cis*-SS-[Co(trien)gly]I$_2$·H$_2$O | 512 | + 2.30 | 44 |
| | 382 | + 0.20 | |
| | 342 | − 0.13 | |
| Λ-(+)-uns$_2$-*cis*-SS-[Co(trien)gly]I$_2$·H$_2$O | 488 | + 2.13 | 44 |
| | 339 | − 0.15 | |
| Λ-(+)-uns$_2$-*cis*-SR-[Co(trien)gly]I$_2$·H$_2$O | 488 | + 1.92 | 44 |
| | 339 | − 0.13 | |
| Λ-(+)-uns$_1$-*cis*-SS-[Co(trien)(S-ala)]I$_2$·H$_2$O | 501 | + 2.02 | 44 |
| | 379 | + 0.08 | |
| | 341 | − 0.15 | |
| Λ-(−)-uns$_1$-*cis*-RR-[Co(trien)(S-ala)]I$_2$·H$_2$O | 517 | − 2.07 | 44 |
| | 383 | − 0.18 | |
| | 341 | − 0.13 | |
| uns$_1$-*cis*-(SS,RR)-[Co(trien)(S-ala)]I$_2$·H$_2$O | 524 | − 0.25 | 44 |
| | 482 | + 0.18 | |
| | 433 | − 0.05 | |
| | 333 | − 0.08 | |
| Λ-(+)-uns$_2$-*cis*-SS-[Co(trien)S-ala)]I$_2$·H$_2$O | 491 | + 2.38 | 44 |
| | 370 | + 0.05 | |
| | 337 | − 0.05 | |
| Δ-(−)-uns$_2$-*cis*-RR-[Co(trien)(S-ala)]I$_2$·H$_2$O | 476 | − 2.37 | 44 |
| | 348 | + 0.30 | |
| uns$_2$-*cis*-(SS,RR)-[Co(trien)(S-ala)]I$_2$·H$_2$O | 539 | − 0.05 | 44 |
| | 493 | + 0.35 | |
| | 450 | − 0.60 | |
| | 345 | + 0.05 | |
| Λ-(+)-uns$_2$-*cis*-SS-[Co(trien)(R-ala)]I$_2$·H$_2$O | 457 | + 2.37 | 44 |
| | 348 | − 0.30 | |
| Δ-(−)-uns$_2$-*cis*-RR-[Co(trien)(R-ala)]I$_2$·H$_2$O | 491 | − 2.37 | 44 |
| | 370 | − 0.05 | |
| uns$_2$-*cis*-(SS,RR)-[Co(trien)(R-ala)]I$_2$·H$_2$O | 539 | + 0.05 | 44 |
| | 493 | − 0.35 | |
| | 450 | + 0.60 | |
| | 345 | − 0.05 | |
| Λ-(+)-uns$_2$-*cis*-SR-[Co(trien)(S-ala)]I$_2$·H$_2$O | 488 | 1.83 | 44 |
| | 339 | − 0.08 | |
| Δ-(−)-uns$_2$-*cis*-RS-[Co(trien)(S-ala)]I$_2$·H$_2$O | 488 | − 2.04 | 44 |
| | 339 | + 0.10 | |
| uns$_2$-*cis*-(RS,SR)-[Co(trien)(S-ala)]I$_2$·H$_2$O | 488 | − 0.10 | 44 |
| Λ-(+)-uns$_2$-*cis*-SR[Co(trien)(R-ala)]I$_2$·H$_2$O | 488 | + 2.04 | 44 |
| | 339 | − 0.10 | |

TABLE 4 (continued)

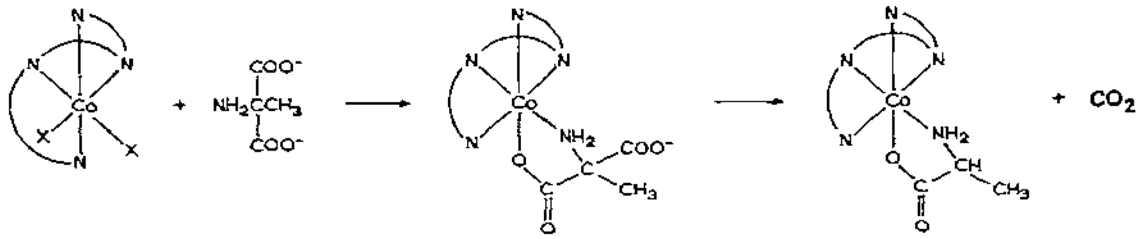
| *Compound* | $\lambda_{max}$ *(nm)* | $(\epsilon_l - \epsilon_d)_{max}$ | *Ref* |
|---|---|---|---|
| Δ-(−)-uns$_2$-*cis*-RS-[Co(trien)(R-ala)]I$_2$·H$_2$O | 488 | − 1.83 | 44 |
| | 339 | + 0.08 | |
| uns$_2$-*cis*-(RS,SR)-[Co(trien)(R-ala)]I$_2$·H$_2$O | 488 | + 0.10 | 44 |
| Λ-(+)-uns$_1$-*cis*-SS-[Co(trien)(S-meth)]I$_2$·H$_2$O | 500 | + 1.95 | 44 |
| | 385 | + 0.08 | |
| | 341 | − 0.24 | |
| Δ-(−)-uns$_1$-*cis*-RR-[Co(trien)(S-meth)]I$_2$·H$_2$O | 510 | − 2.05 | 44 |
| | 385 | − 0.18 | |
| | 348 | − 0.08 | |
| uns$_1$-*cis*-(RR,SS)-[Co(trien)(S-meth)]I$_2$·H$_2$O | 524 | − 0.25 | 44 |
| | 483 | + 0.15 | |
| | 385 | − 0.10 | |
| | 345 | − 0.10 | |
| Λ-(+)-uns$_2$-*cis*-SS-[Co(trien)(S-meth)]I$_2$·H$_2$O | 484 | + 2.38 | 44 |
| | 339 | − 0.15 | |
| Δ-(−)-uns$_2$-*cis*-RR-[Co(trien)(S-meth)]I$_2$·H$_2$O | 473 | − 2.20 | 44 |
| | 347 | + 0.26 | |
| uns$_2$-*cis*-(RR,SS)-[Co(trien)(S-meth)]I$_2$·H$_2$O | 543 | - 0.08 | 44 |
| | 495 | + 0.28 | |
| | 444 | − 0.68 | |
| | 351 | + 0.07 | |
| Λ-(+)-uns$_2$-*cis*-SR-[Co(trien)(S-meth)]I$_2$·H$_2$O | 480 | + 1.90 | 44 |
| | 345 | − 0.15 | |
| Δ-(−)-uns$_2$-*cis*-RS-[Co(trien)(S-meth)]I$_2$·H$_2$O | 480 | − 2.03 | 44 |
| | 345 | + 0.15 | |
| uns$_2$-*cis*-(RS,SR)-[Co(trien)(S-meth)]I$_2$·H$_2$O | 488 | − 0.10 | 44 |
| Λ-(+)-uns$_1$-*cis*-SS-[Co(trien)(S-prol)]I$_2$·H$_2$O | 539 | − 0.23 | 44 |
| | 488 | + 1.80 | |
| | 348 | − 0.28 | |
| Δ-(−)-uns$_1$-*cis*-RR-[Co(trien)(S-prol)]I$_2$·H$_2$O | 522 | − 1.90 | 44 |
| | 438 | − 0.08 | |
| | 376 | − 0.23 | |
| uns$_1$-*cis*-(RR,SS)-[Co(trien)(S-prol)]I$_2$·H$_2$O | 529 | − 0.86 | |
| | 482 | + 0.64 | |
| | 369 | − 0.25 | |
| Λ-(+)-uns$_2$-*cis*-SS-[Co)trien)(S-prol)]I$_2$·H$_2$O | 554 | − 0.27 | 44 |
| | 493 | + 2.45 | |
| | 346 | − 0.36 | |
| Δ-(−)-uns$_2$-*cis*-RR-[Co(trien)(S-prol)]I$_2$·H$_2$O | 493 | − 1.43 | 44 |
| | 467 | − 1.53 | |
| | 351 | + 0.18 | |
| uns$_2$-*cis*-(RR,SS)-[Co(trien)(S-prol)]I$_2$·H$_2$O | 538 | + 0.36 | 44 |
| | 495 | + 0.50 | |
| | 444 | − 0.43 | |
| | | − 0.08 | |
| (+)-uns$_2$-*cis*-[Co(2,3,2-tet)gly]$^{2+}$ | 522 | + 1.32 | 60 |
| | 460 | − 0.40 | |
| | 361 | − 0.10 | |
| | 328 | + 0.04 | |
| (+)-uns$_2$-*cis*-[Co(2,3,2-tet)(S-ala)]$^{2+}$ | 515 | + 1.35 | 50 |
| | 455 | − 0.43 | |
| | 360 | − 0.14 | |

TABLE 4 (continued)

| *Compound* | $\lambda_{max}$ *(nm)* | $(\epsilon_l - \epsilon_d)_{max}$ | *Ref* |
|---|---|---|---|
| (+)-uns$_2$-*cis*-[Co(2,3,2-tet)(S-val)]$^{2+}$ | 517 | + 0.86 | 60 |
| | 458 | − 0.27 | |
| | 356 | − 0.07 | |
| | 325 | + 0.04 | |
| (−)-uns$_2$-*cis*-[Co(2 3,2-tet)(S-val)]$^{2+}$ | 523 | − 1.53 | 60 |
| | 470 | + 0.12 | |
| | 373 | − 0.16 | |
| | 340 | − 0.18 | |
| uns$_2$-*cis*-[Co(2,3,2-tet)(S-val)]$^{2+}$ | 530 | − 0.31 | 60 |
| | 490 | + 0.03 | |
| | 450 | − 0.13 | |
| | 350 | − 0.11 | |
| (+)-uns$_2$-*cis*-[Co(2,3,2,-tet)sar]$^{2+}$ | 535 | + 0.77 | 60 |
| | 477 | − 0.33 | |
| | 414 | + 0.03 | |
| | 361 | − 0.06 | |
| | 340 | + 0.04 | |
| (+)-$s_{46}$-s-*cis*-[Co(3,2,3-tet)gly]$^{2+}$ | 550 | − 0.45 | 60 |
| | 490 | + 1.32 | |
| | 350 | − 0.16 | |

$$\begin{tikzcd}
 & \Lambda\text{-s-}cis\text{-}[Co(S,S\text{-}1,8\text{-dimetrien})aa]^{2+} \\
\Lambda\text{-s-}cis\text{-}[Co(S,S\text{-}1,8\text{-dimetrien})Cl_2]^{+} \arrow[ur, "aa,\ pH\ 7.2"] \arrow[dr, "H_2O"'] & \\
 & \Lambda\text{-s-}cis\text{-}[Co(S,S\text{-}1,8\text{-dimetrien})Cl(H_2O)]^{2+} \arrow[d, "aa,\ pH\ 7.2"] \\
 & \Delta\text{-uns-}cis\text{-}[Co(S,S\text{-}1,8\text{-dimetrien})aa]^{2+}
\end{tikzcd}$$

A partial asymmetric synthesis of alanine has been attained [49] by preparing the complex ion α-amino-α-methylmalonato S,S-1,8-dimethyltriethylenetetraaminecobalt(III) which was then decarboxylated to yield Δ-uns-*cis*-[Co(S,S-1,8-dimetrien)(S-ala)]$^{2+}$



Dichloro complexes with cobalt(III) and the ligands (+)-3(S),8(S)-dimethyltriethylenetetraamine and racemic 5-methyltriethylenetetraamine have been prepared[49]. The [Co(5-metrien)$Cl_2$] Cl formed a purple compound of *cis* configuration which was assigned the uns-*cis* configuration from the infrared spectrum The [Co(3(S),8(S)-dimetrien)$Cl_2$] Cl forms a green *trans* complex The configurations of the asymmetric carbon atoms of the latter ligand are known because the ligand was prepared from S-alanine. From this knowledge and other stereochemical considerations, along with the circular dichroism spectrum of (+)-*trans*-[Co(3(S),8(S)-dimetrien)$Cl_2$] Cl, it is possible to show that the (+)-*trans*-[Co(3(S),8(S)-dimetrien)$Cl_2$] Cl complex is formed stereospecifically and that this complex has the same configuration as (+)-*trans*-SS-[Co(trien)$Cl_2$] Cl. Goto and co-workers[50,50a] have recently reported the results of a detailed spectroscopic analysis of chelate ring conformations and the absolute configurations of the *trans* dichloro and *trans* dinitro cobalt (III) complexes with 2,5,8,11-tetraazadodecane, 6(R)-methyl-2,5,8,11-tetraazadodecane, 4(S),9(S)-dimethyl-2,5,8,11-tetraazadodecane, 3(S),10(S)-dimethyl-2,5,8,11-tetraazadodecane, and the extended chain derivative 2,5,9,12-tetraazatridecane

Other cobalt(III) complexes containing triethylenetetraamine derivatives C-substituted at the central ethylene bridge have been reported by Goto et al[51] These included the dinitro and dichloro cobalt(III) complexes with the ligands 5(R)-methyltriethylenetetraamine, 5(S),6(S)-dimethyltriethylenetetraamine, and *trans-N,N'*-bis(β-aminoethyl)-cyclohexane-1(S),2(S)-diamine. It was found that for all of these complexes the uns-*cis* isomer was formed. Moreover, the chirality of the ligand, controlled stereospecifically the absolute configuration of the complex so that for the ligand of S-configuration the complex was of Δ-uns-*cis* configuration, and for that of R-configuration the complex formed was Λ-uns-*cis* All the dichloro complexes rearranged in methanol to form the corresponding optically active *trans* isomers

Bosnich[52] has reported that *N,N'*-bis(2-picolyl)-1-methyl-1,2-diaminoethane produces the s-*cis*-[Co(picpn)$X_2$]$^+$ isomer stereospecifically, in contrast with the topological preference of 5-methyltriethylenetetraamine A recent report by Bosnich and Kneen[53] cites proton magnetic resonance, CD and electronic spectral evidence for the exclusive formation of Δ-S,S-uns-*cis*-[Co-(bnpic)$X_2$]$^+$ ions ($X = Cl^-, NO_2^-$), wherein bnpic is the tetraamine (+)-*N,N'*-bis(2-picolyl)-2(R),3(R)-butanediamine Though molecular models do not readily demonstrate the observed geometric specificity, the reported CD curves support the authors' assigned topologies Philip et al[54] has recently described the synthesis of a binuclear complex of cobalt(III) with *N,N'*-bis(2-ethyl-(2-pyridyl))-1,2-ethanediamine.

Finally, Asperger[55] has reported that the *trans* configuration is most stable for complexes with *N,N'*-bis-(R-2-amino-3-phenylpropyl)-*trans*-S-1,2-cyclohexanediamine This result is surprising, since molecular models suggest that the Δ-s-*cis* isomer should be preferred.

### *(iii) Complexes with other flexible tetraamine ligands*

#### *(a) 3,7-diaza-1,9-nonanediamine, 2,3,2-tet*

Complexes with ligands related to triethylenetetraamine, but with lengthened alkyl chains, have been prepared. The complex [Co(2,3,2-tet)$Cl_2$]$^+$ was described independently by

Hamilton and Alexander [56] and by Bosnich et al [57] The *trans* isomer predominates, but under controlled conditions a *cis* isomer may be prepared Hamilton and Alexander [58] showed that *trans*-meso-$[Co(2,3,2\text{-tet})Cl_2]^+$ is produced in the standard aerial oxidation synthesis [56,57], while treatment of uns-*cis*-$[Co(2,3,2\text{-tet})\text{-}CO_3]^+$ with HCl produces the racemic *trans* complex The aquation of uns-*cis*- and *trans*-$[Co(2,3,2\text{-tet})Cl_2]^+$ has been studied Aquation of the meso (RS) *trans* complex produces *trans*-$[Co(2,3,2\text{-tet})Cl(H_2O)]^{2+}$, while the aquation of racemic (RR,SS) *trans* complex produces [24,59] uns-*cis*-$[Co(2,3,2\text{-tet})Cl(H_2O)]^{2+}$ The *cis* dichloro isomer has been assigned [24,59] the unsymmetrical configuration but no other *cis*-diacido (2,3,2-tet)cobalt(III) complexes have been characterized

$$\begin{tikzcd}
 & \textit{trans}\text{-RS-}[Co(2,3,2\text{-tet})Cl(H_2O)]^{2+} \\
Co^{2+} + 2,3,2\text{-tet} \arrow[r, "(1)\ O_2", "(2)\ HCl"'] & \textit{trans}\text{-RS-}[Co(2,3,2\text{-tet})Cl_2]^{+} \arrow[u, "H_3O^+"'] \arrow[d, "Na_2CO_3"] \\
 & \text{uns-}\textit{cis}\text{-RR,SS-}[Co(2,3,2\text{-tet})CO_3]^{+} \arrow[d, "HCl"] \\
 & \textit{trans}\text{-RR,SS-}[Co(2,3,2\text{-ete})Cl_2]^{+} \arrow[d, "H_3O^+"] \\
 & \text{uns-}\textit{cis}\text{-RR,SS-}[Co(2,3,2\text{-tet})Cl(H_2O)]^{2+}
\end{tikzcd}$$

Numerous mixed ligand complexes of cobalt(III) with 2,3,2-tet have been prepared [60]. Of these, the diacido complexes $[Co(2,3,2\text{-tet})Br_2]^+$, $[Co(2,3,2\text{-tet})(Oac)_2]^+$, $[Co(2\ 3,2\text{-tet})(Ogly)_2]^{3+}$, $[Co(2,3,2\text{-tet})(Oala)_2]^{3+}$ have been shown from their electronic spectra and chemical properties to exist in the *trans* forms Optically active samples of the *trans* dichloro and dibromo complexes have been prepared from the resolved oxalato(2,3, 2-tet)cobalt(III) cation by treatment with the appropriate acid under anhydrous conditions [61] Comparison of the PMR spectra and of the signs of the Cotton effects observed for the oxalato and derivative *trans* diacido species with those of the known trien complexes indicates that only the uns-*cis*-oxalato(2,3,2-tet)cobalt(III) ion is isolated The CD spectra of these complexes are given in Tables 5 and 6

Among the mixed bidentate-2,3,2-tet complexes, one geometrical isomer, believed to be uns-*cis*, of $[Co(2,3,2\text{-tet})(en)]^{3+}$ and $[Co(2,3,2\text{-tet})(ox)]^+$ has been resolved Brubaker et al report that mixed ligand amino acid chelates appear to form the $uns_2$-*cis* isomers exclusively, though four isomers of uns-*cis*-$[Co(2,3,2\text{-tet})(S\text{-pn})]^{3+}$ have been separated chromatographically using microcrystalline cellulose [24] That the amino acid chelates contain only the uns-*cis* isomer is convincingly demonstrated by the ready conversion of the amino acid chelates to the active *trans*-$[Co(2,3,2\text{-tet})\text{-}Cl_2]^+$ by the action of anhydrous hydrogen chloride [62].

TABLE 5

Circular dichroism data for Co(tet)$L_2^{n+}$

| *Compound* | $\lambda_{max}$ *(nm)* | $(\epsilon_l - \epsilon_d)_{max}$ | *Ref* |
|---|---|---|---|
| (−)-*trans*-SS-[Co(2,3,2-tet)$Cl_2$]$^+$ | 650 | + 0.45 | 60 |
| | 583 | − 0.24 | |
| | 455 | + 0.27 | |
| | 390 | − 0.28 | |
| (−)-*trans*-RR-[Co(3,2,3-tet)$Cl_2$]$^+$ | 652 | + 0.28 | 60 |
| | 570 | − 0.01 | |
| | 491 | + 0.09 | |
| | 426 | + 0.08 | |
| (+)-*trans*-SS-[Co(2,3,2-tet)$Br_2$]$^+$ | 694 | + 0.43 | 60 |
| | 621 | − 0.17 | |
| | 465 | + 0.21 | |
| (+)-*trans*-RR-[Co(3,2,3-tet)$Br_2$]$^+$ | 630 | − 0.10 | 60 |
| | 450 | + 0.22 | |
| (−)-uns-*cis*-[Co(2,3,2-tet)Cl($H_2O$)]$^{2+}$ | 580 | − 0.56 | 60 |
| | 500 | + 0.48 | |
| | 369 | − 0.13 | |

TABLE 6

Circular dichroism data for some oxalatotetraamine complexes of cobalt(III)

| *Compound* | $\lambda_{max}$ *(nm)* | $(\epsilon_l - \epsilon_d)_{max}$ | *Ref* |
|---|---|---|---|
| (+)-[Co(en)$_2$ox]$^+$ | 521 | 2.6 | |
| | 385 | 0.12 | |
| | 360 | − 0.03 | |
| | 335 | 0.21 | |
| (+)-[Co(tn)$_2$ox]$^+$ | 508 | 1.21 | 60 |
| | 355 | − 0.14 | |
| (+)-s-*cis*-[Co(trien)ox]$^+$ | 515 | 2.95 | 60 |
| | 381 | 0.57 | |
| | 338 | 0.32 | |
| (+)-uns-*cis*-[Co(trien)ox]$^+$ | 515 | 2.09 | 60 |
| | 388 | 0.15 | |
| | 355 | − 0.05 | |
| (+)$_{546}$-s-*cis*-[Co(3,2,3-tet)ox]$^+$ | 555 | − 0.76 | 60 |
| | 493 | 1.88 | |
| | 353 | − 0.22 | |
| (+)-uns-*cis*-[Co(2,3,2-tet)ox]$^+$ | 535 | 1.47 | 60 |
| | 475 | − 0.48 | |
| | 370 | − 0.06 | |
| | 340 | 0.15 | |

### (b) *4,7-diaza-1,10-decanediamine,3,2,3-tet*

Hamilton and Alexander prepared *trans*-dichloro(3,2,3-tet)cobalt(III) chloride, presumably as the racemic RR, SS mixture which aquates to produce the *trans*-chloroaquo complex[24,63] Treatment of *cis*-$[Co(3,2\ 3\text{-tet})CO_3]^+$ with HCl produces only *trans*-dichloro(3,2,3-tet)cobalt(III) chloride, in contrast with the 2,3,2-tet system. The *trans*-diacido complexes, $[Co(3,2,3\text{-tet})Cl_2]^+$, $[Co(3,2,3\text{-tet})Br_2]^+$, $[Co(3,2,3\text{-tet})(Oac)_2]^+$, $[Co(3,2,3\text{-tet})(Ogly)_2]^{3+}$, $[Co(3,2,3\text{-tet})(Oala)_2]^{3+}$, and $[Co(3,2,3\text{-tet})(Oval)_2]^{3+}$ have been prepared (and optical isomers have been separated in some cases) and characterized through the electronic spectra and chemical properties[64] There is no evidence for the formation of *cis*-diacido(3,2,3-tet)cobalt(III) complexes

In addition to the carbonato complex described by Hamilton and Alexander, mixed-ligand complexes with oxalato, ethylenediamine and various chelated amino acids have been prepared[60] For example, $[Co(3,2,3\text{-tet})ox]^+$ has been prepared and resolved All of the spectroscopic properties of this complex conform most closely with those of the related *s-cis*-$[Co(trien)ox]^+$ ion

An interesting series of reactions has been observed which attests not only to the reproducibility of the *cis–trans* interconversion of 3,2,3-tet complexes, but also to the steric influence of the chelated dissymetric secondary donor atoms The complex (+)-*s-cis*-$[Co(3,2,3\text{-tet})(ox)]^+$ is converted to (+)-*trans*-SS-$[Co(3,2,3\text{-tet})Cl_2]^+$ by the action of dry HCl, the reverse reaction occurs in molar oxalic acid with greater than 90% retention of optical activity for the complete cycle[65]

$$\Lambda\text{-}s\text{-}cis\text{-RR-}[Co(3,2\ 3\text{-tet})(ox)]^+ \underset{H_2C_2O_4}{\overset{HCl}{\rightleftarrows}} trans\text{-RR-}[Co(3,2,3\text{-tet})Cl_2]^+$$

$$[M]_{521} = 5{,}000^\circ \qquad\qquad [M]_D = +\,390^\circ$$

The configuration of each complex was determined by comparison with the corresponding trien complex.

The only evidence to date for the formation of uns-*cis* isomers in mixed ligand complexes with 3,2,3-tet comes from the chromatograms of $[Co(3,2,3\text{-tet})(S\text{-pn})]^{3+}$ on microcrystalline cellulose Four components have been observed, indicating that the uns-*cis* isomer may be formed under some conditions[24]

### (iv) *Conclusions based on studies of flexible tetraamine ligand complexes of cobalt(III)*

The study of the complexes of the homologous series of flexible tetraamine ligands and some substituted derivatives, described above, leads to some generalizations about the steric influence of chelate ring size and chelate ring dissymmetry. The effects of changes in donor atoms will be discussed in subsequent sections

Chain length has a profound effect on the distribution of geometrical isomers in the synthesis of various cobalt(III) complexes Thus, all three geometrical isomers are found in complexes with triethylenetetraamine, the formation of the *s-cis* and uns-*cis* isomers depending more on the remaining ligand(s) than on the properties of triethylenetetraamine, and the formation of the *trans* isomer strongly inhibited by strain in the chelate rings

Complexes with 3,2,3-tet in the *trans* and *s-cis* configurations have been characterized, and there is some evidence for the formation of uns-*cis* isomers. No *cis*-diacido(3,2,3-tet) cobalt(III) complexes are known, in contrast with the trien and 2,3,2-tet systems. The ligand 2,3,2-tet forms complexes only in the *trans* and uns-*cis* configurations, in contrast with the trien system.

The effects of chain length have been rationalized in terms of two effects: (*1*) ring strain; and (*2*) steric hindrance. The first effect is apparently manifested only in the *trans* complexes with trien, wherein the tetrahedral secondary amine groups are significantly distorted by the formation of three coplanar five-membered chelate rings. For the longer-chain tetraamine ligands, this effect seems of minor importance, as evidenced by the preponderance of *trans* isomers. As the chelate rings increase in size, however, the complexity of the ring conformations increases, and the magnitude of the interactions between adjacent chelate rings increases accordingly as described by Corey and Bailar [4], Buckingham et al. [5], and Gollogly and Hawkins [6] It is this interaction between adjacent chelate rings which may account for the distribution of *s-cis* and uns-*cis* isomers for the complexes of 2,3,2-tet and 3,2,3-tet.

The effect of ligand asymmetry on the stereochemistry of mixed-ligand complexes with cobalt(III) is seen to be vastly greater than the effect of chain length The presence of asymmetric centers on the ligand, either at a donor atom or on remote carbon atoms, not only determines the geometrical configuration of the product complex and the conformations of the chelate rings, but also frequently controls the absolute configuration of the complex as a whole Moreover, complexes with dissymmetric tetraamine ligands are relatively resistant to configurational and conformational change, a feature which has profound effects on the chemical properties of these complexes

## D COMPLEXES WITH FLEXIBLE DITHIADIAMINE LIGANDS

Recently the preparation and stereochemistry for a number of complexes of the type [Co(NSSN)X$_2$]$^{n+}$ were reported by Worrell et al [1,66,67] and later by Bosnich et al [68,69]. The tetradentate ligand NSSN refers to a donor atom sequence, nitrogen—sulfur—sulfur—nitrogen. A number of ligands of this type have been prepared and are listed in Table 7.

TABLE 7

Flexible linear dithiadiamine ligands

| *Ligand* | *Abbreviation* |
|---|---|
| 3,6-dithia-1,8-octanediamine | eee |
| 3,7-dithia-1,9-nonanediamine | ete |
| 4,7-dithia-1,10-decanediamine | tet |
| 4-methyl-3,6-dithia-1,8-octanediamine | epe |
| 4,7-dithia-2,9-diaminodecane | pep |

The preparative chemistry is very similar to that for the triethylenetetraamine complexes The ligand monohydrohalide and a cobalt(II) salt are oxidized by air in the presence of sodium nitrite. The physical properties and initial yield of [Co(NSSN)$(NO_2)_2$]$^+$ made it the fundamental compound from which the dichloro derivatives are most easily prepared Octahedral complexes of the general type [Co(NSSN)$X_2$]$^{n+}$ where monodentate X is $Cl^-$, $Br^-$, $NO_2^-$, $SCN^-$, $N_3^-$, or bidentate $X_2$ is $CO_3^{2-}$, $C_2O_4^{2-}$, en, 1,10-phen, bipy, or $NH_2CH_2COO^-$, are prepared by metathetical interaction of [Co(NSSN)$Cl_2$]$^+$ with the appropriate salt $Na_2X$ or NaX

Like triethylenetetraamine, the NSSN moiety was expected[70] to form three octahedral geometric isomers. s-*cis*, uns-*cis* and *trans*, (Fig 1) with cobalt(III) The structures of several isolated complexes have been deduced from high resolution nuclear magnetic resonance spectra, visible electronic absorption and infrared vibrational spectra[1] In addition, Worrell and Busch[66] have employed circular dichroism and optical rotatory dispersion measurements in conjunction with chemical interconversions, to deduce structure.

### (i) Proton magnetic resonance and stereochemistry

The most conclusive evidence presented for the symmetrical *cis* geometry was the 100 Hz PMR spectrum of s-*cis*-[Co(eee)$(NO_2)_2$]$^+$ which exhibited an AA′BB′ pattern representative of a backbone chelate ring having two equivalently positioned sets of axial and equatorial protons. A very similar AA′BB′ pattern was observed by Williams[71] for the backbone ethylene linkage in [Co(EDTA-$d_8$)]$^-$ in which all the protons of EDTA, except those for the ethylene linkage, were replaced by deuterium atoms Legg and Cooke [3] also observed this distinctive intense quartet with several weaker side resonances in a s-*cis*-[Co(EDDA)en]$^+$ complexes where it was unequivocally assigned to the ethylene linkage protons The center for the backbone ethylene linkage PMR patterns for [Co(EDTA)]$^-$, [Co(EDDA)en]$^+$, and [Co(eee)$(NO_2)_2$]$^+$ are at 3.10, 3 61, and 3.77 p p m. from TMS respectively This latter value reflects the pronounced de-shielding influence of the adjacent sulfur donor atoms for the eee complex

### (ii) Electronic spectra and stereochemistry

Absorption spectra have been used to distinguish between the three isomers The expected splittings for the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition were calculated semiempirically by Bosnich[68] in terms of the spectrochemical effects of the donor atoms which are arranged differently in the three isomers. In each case, the $^1T_{1g}$ manifold should give rise to two transitions with the energy difference between components sufficient to enable one to assign geometry, Fig 4. Experimentally, the s-*cis*-dichloro isomers show an absorption envelope which is shifted significantly to low energy (red shift) and exhibit a less intense shoulder on the high-energy side of the envelope. Unsymmetrical *cis* isomers show a single symmetric envelope having a center at higher energy than observed for the s-*cis* *Trans* geometries are distinguished on the basis of molar extinction coefficients about 50–100, in contrast to 200–375 for *cis* topologies. In addition, electronic absorption spectra for complexes derived from NSSN ligands show a characteristically intense change transfer band at about 350—400 nm, which in most cases completely obscures the second *d—d* band normally observed with compounds of cobalt(III)

Bosnich et al. [68] have employed these empirical spectral characteristics in assigning the geometries for several $(Co(ete)Cl_2]^+$ isomers It is interesting to note that such data alone suggest that the ligand ete adopts ***trans*** and uns-***cis*** topologies, whereas tet produces exclusively s-*cis* and uns-*cis* geometric arrangements. That eee and epe give only s-*cis* topologies has been discussed at length by Worrell et al [1,66,67,72]

## *(iii) Infrared spectra and stereochemistry*

The use of infrared spectroscopy in assigning geometric arrangements has been fairly successful for diacido complexes of cobalt(III) containing the ligand trien Buckingham and Jones [17] have pointed out the special infrared characteristics uniquely associated with the s-*cis*, uns-*cis*, and *trans* isomers of $[Co(trien)X_2]^{n+}$

Infared spectra of complexes of the type $[Co(NSSN)X_2]^{n+}$ present a distinct contrast to the analogous complexes of trien For example, the number of N—H stretch bands in the range 2900—3500 cm$^{-1}$, the N—H deformation bands at 1500—1600 cm$^{-1}$ as well as selective skeletal C—H vibrational bands have been shown to be a strong function of the anion and alkyl substitutient on the chelate rings [1,72] Thus, the infrared spectra of s-*cis*-$[Co(eee)Cl_2]^+$ and s-*cis*-$[Co(epe)Cl_2]^+$ are sufficiently different, as are the spectra for s-*cis*-$[Co(eee)(NO_2)_2]^+$ and s-*cis*-$[Co(epe)(NO_2)_2]^+$, to obscure a correct topological assignment based only on infrared data Fundamentally more important is the fact that different diacido complexes of the same topology and same NSSN ligand give very different vibrational spectra in the wavelength regions routinely used to empirically distinguish structure for the analogous trien complexes

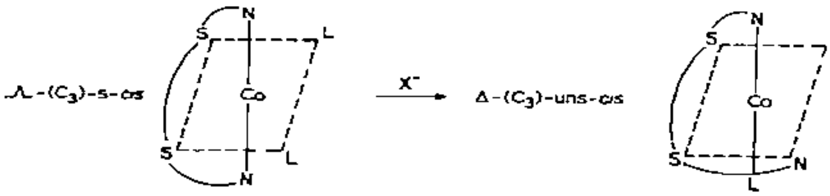
## *(iv) Optical activity and absolute configuration*

A number of $[Co(NSSN)X_2]^{n+}$ ions have been separated into optically pure isomers and their absolute configurations assessed relative to Λ-$(C_3)$-$(+)_{589}$-$[Co(en)_3]^{3+}$ using circular dichroism and optical rotatory dispersion data [73] The $[Co(eee)Cl_2]^+$ ion was expeditiously resolved using the antimony d-tartrate anion, which afforded the isolation of above average yields of both (+) and (—) isomers having equal and opposite maximum rotations ($[\alpha]_{545} = \pm 2313$) The $[Co(eee)(NO_2)_2]^+$ ion was separated [74] into its enantiomorphs, ($[\alpha]_{546} = \pm 602$), by optically pure isomers of $Na[Co(en)ox_2]$ A very clean, high-yield resolution resulted

Optically active $[Co(eee)Cl_2]^+$ ions undergo a number of transformation reactions with retention of configuration,

$$\begin{tikzcd}
\Lambda\text{-}(+)\text{-s-}cis\text{-}[Co(eee)Cl_2]^+ \arrow[r, "H^+"] \arrow[dd, shift right, "NaNO_2"'] & \Lambda\text{-}(+)\text{-s-}cis\text{-}[Co(eee)Cl(H_2O)]^{2+} \arrow[d, "Li_2CO_3 \text{ or } NaHCO_3"] \\
 & \Lambda\text{-}(-)\text{-s-}cis\text{-}[Co(eee)CO_3]^+ \arrow[d, "Li_2CO_3 \quad H^+"] \\
\Lambda\text{-}(-)\text{-s-}cis\text{-}[Co(eee)(NO_2)_2]^+ \arrow[uu, shift right, "12\,M\ HCl"'] & \Lambda\text{-}(+)\text{-s-}cis\text{-}[Co(eee)(H_2O)_2]^{3-} \arrow[l]
\end{tikzcd}$$

The surprising rigidity of the s-*cis* moiety when the ligand is eee, is apparent especially in the reversible conversion reactions between the optically active dichloro and dinitro compounds. When $(+)_{546}$-s-*cis*-$[Co(eee)Cl_2]^+$ is treated with $NaNO_2$ in water, substitution of $NO_2^-$ occurs at a rate which is extremely rapid relative to normal aquation. Rate studies suggest that nitrite substitution is preceeded by electron transfer [74]. Under such conditions, one would expect labilization possibly followed by isomerization to the uns-*cis* topology. Had isomerization occurred at any step in the transformation sequence, an immediate change in the shape and intensity of the circular dichroism curves would have resulted, since as illustrated below, isomerization requires a change in the absolute configuration of the product molecule ion.



Both ORD and CD measurements using $[Co(eee)X_2]^{n+}$ ions demonstrate that isomerization does not occur under the conditions which produce isomeric changes for the corresponding trien compounds.

A number of $[Co(NSSN)X_2]^{n+}$ ions had their absolute configurations assigned by Worrell and are summarized in Table 8. Data for the structurally related tetraamines are given in Table 2. Examination of the data in Tables 2 and 8 suggests that $[Co(NSSN)X_2]^{n+}$ ions are unique in several respects. The intensities of the CD bands are consistently greater than reported for any complexes. Since the $(\epsilon_l-\epsilon_d)$ intensity generating parameters are, as yet, not understood, complexes of this type may well provide a basis for both experimental and theoretical work in this rapidly expanding area. Further, a unique contrast in axial and in-plane electric fields exists for s-*cis*-$[Co(trien)(NO_2)_2]^+$ and s-*cis*-$[Co(NSSN)(NO_2)_2]^+$ ions. Substitution of nitrite ion into the coordination sphere of s-*cis*-$[Co(trien)(NO_2)_2]^+$, causes the in-plane electrostatic field to become considerably greater than the axial field. As a result, the electronic levels derived from the $T_1$ manifold are inverted, the lowest energy transition being $A_1 \rightarrow A(E_a) + B(E_a)$, Fig. 4. The electric field caused by the in-plane thioether groups of s-*cis*-$[Co(NSSN)(NO_2)_2]^+$ is so weak that even with the presence of in-plane nitrite ions, the axial field remains greater than the in-plane field. The energy levels are thus not inverted for this complex. The negative low-energy CD component is assigned the $A_1 \rightarrow B(A_2)$ transition and the positive higher energy component is assigned the composite transition $A \rightarrow A(E_a) + B(E_a)$. The above considerations are unique and pertinent to the assignment of absolute configurations for the dinitro derivatives using CD data.

Bosnich and Phillip [69] noted this characteristic inversion of CD peaks in their study of the similar $Co(pep)(NO_2)_2^+$ ion. They reasoned that the assignment of CD bands for

**TABLE 8**

Circular dichroism data for s-*cis*-Co(eee)L$_2$$^{n+}$ and s-*cis*-Co(epe)L$_2$$^{n+}$ (refs 66 and 72 respectively)

| *Compound* | $\lambda_{max}$ *(nm)* | $(\epsilon_l - \epsilon_d)_{max}$ | *Compound* | $\lambda_{max}$ *(nm)* | $(\epsilon_l - \epsilon_d)_{max}$ |
|---|---|---|---|---|---|
| $(+)_{546}$-Co(eee)Cl$_2$$^+$ | 623 | − 4.85 | $(+)_{546}$-[Co(epe)Cl$_2$]$^+$ | 620 | − 4.70 |
| | 539 | + 7.30 | | 538 | + 7.15 |
| | 392 | − 5.20 | | 393 | − 5.05 |
| $(+)_{546}$-Co(eee)ClH$_2$O$^{2+}$ | 602 | − 4.20 | $(+)_{546}$-[Co(epe)ClH$_2$O]$^{2+}$ | 602 | − 4.15 |
| | 526 | + 5.15 | | 525 | + 5.65 |
| | 378 | − 4.05 | | 378 | − 4.35 |
| $(+)_{546}$-Co(eee)(H$_2$O)$^{3+}$ | 575 | − 4.95 | $(+)_{546}$-[Co(epe)(H$_2$O)$_2$]$^{3+}$ | 598 | − 5.20 |
| | 504 | + 3.15 | | 508 | + 3.67 |
| | 471 | + 0.70 | | 415 | + 0.25 |
| | 360 | − 2.75 | | 363 | − 3.00 |
| $(+)_{546}$-Co(eee)(OH)$_2$$^+$ | 594 | − 2.80 | $(+)_{546}$-[Co(epe)(OH$_2$)]$^+$ | 596 | − 2.68 |
| | 514 | + 2.20 | | 516 | + 2.58 |
| | 376 | − 2.75 | | 376 | − 2.65 |
| $(-)_{546}$-Co(eee)CO$_3$$^+$ | 532 | + 3.65 | $(+)_{546}$-[Co(epe)CO$_3$]$^+$ | 535 | + 4.10 |
| | 471 | − 0.75 | | 470 | − 0.40 |
| | 421 | + 0.40 | | 425 | + 0.20 |
| | 380 | − 2.90 | | 380 | − 3.10 |
| $(-)_{546}$-Co(eee)(NO$_2$)$_2$$^+$ | 504 | − 1.99 | $(-)_{546}$-[Co(epe)(NO$_2$)$_2$]$^+$ | 495 | − 0.75 |
| | 448 | + 2.30 | | 442 | + 1.77 |

this ion is complicated by the fact that the sulfur donors displace the CD components to lower energy, whereas the nitro ligands displace the components to higher energies Because the positive CD component occurs at 23,000 cm$^{-1}$, a higher energy than the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition in Co(en)$_3$$^{3+}$, they conclude the negative CD absorption at 20,400 cm$^{-1}$ for the Co(pep)(NO$_2$)$_2$$^+$ ion corresponds to the transition $^1A \rightarrow {}^1A + {}^1B$ and that the other absorption must arise from the $^1A \rightarrow {}^1B$ transition, diagnostic of absolute configuration The eee, epe and pep ligand systems demonstrate that intensity and parental arguments should be approached with caution in the assignment of absolute configurations.

The basic chemistry and stereochemistries of the eee and epe complexes of cobalt(III) are similar in that optical isomers can be separated, they undergo substitution reactions with retention of geometry and absolute configuration, and each exists in a single stable topology, the symmetrical *cis* arrangement.

### *(v) Stereospecificity of [Co(epe)Cl$_2$]$^+$*

The ligand epe presents an additional stereochemical feature in that it contains an optically active center and coordinates stereospecifically. The s-*cis* geometry establishes the possibility of four optically unique s-*cis*-[Co(epe)Cl$_2$]$^+$ isomers. Extensive efforts to separate four isomers were unsuccessful, instead, only two optically pure forms were isolated, namely $(+)_{589}$-s-*cis*-[Co(+epe)Cl$_2$]$^+$ and $(-)_{589}$-s-*cis*-[Co(−epe)Cl$_2$]$^+$ Worrell et al.[67,72] have demonstrated by decomposing both enantiomers of $[Co(epe)Cl_2]^+$ with cyanide ion, that $(+)_{589}$-s-*cis*-$[Co(epe)Cl_2]^+$ contains only $(+)_{589}$-epe. Bosnich and Phillip[75] assigned the absolute configuration of $(+)_{589}$-epe as R relative to R-alanine or R-propylenediamine[76,77] (see footnote, p. 172), and from circular dichroism spectra coupled with detailed ring conformation arguments the absolute configurations of $(+)_{589}$-s-*cis*-$[Co(+epe)Cl_2]^+$ and $(-)_{589}$-s-*cis*-$[Co(-epe)Cl_2]^+$ were determined.[72]

### *(vi) Aquation reactions for $[Co(NSSN)Cl_2]^+$ ions*

The rates of aquation for s-*cis*-$[Co(eee)Cl_2]^+$ have been measured by Worrell and Fortune[78] under various concentrations of complex, hydrogen ion, and mercury(II) ion as well as ionic strength and temperature. Aquation occurs in two stages as illustrated by reactions (1) and (2) below. At 25°C the first $Cl^-$ in $[Co(eee)Cl_2]^+$ is replaced by $H_2O$ at a measurable rate, however, reaction (2) at 25°C is extremely slow and is incomplete even after six months in 0.10 *M* $HClO_4$.

$$\text{s-}cis\text{-}[Co(eee)Cl_2]^+ + H_2O \xrightarrow[H^+]{k_1} \text{s-}cis\text{-}[Co(eee)ClH_2O]^{2+} + Cl^- \tag{1}$$

$$\text{s-}cis\text{-}[Co(eee)ClH_2O]^{2+} + H_2O \xrightarrow[H^+]{k_2} \text{s-}cis\text{-}[Co(eee)(H_2O)_2]^{3+} + Cl^- \tag{2}$$

Both reactions are acid independent in the range $1.0\,M > H^+ > 0.01\,M$ and can occur with complete retention of geometry. Under the conditions $[H^+] = 0.10\,M$, [complex] = $6.0 \times 10^{-4}\,M$ and temperature = 50°C, the observed pseudo first-order rate constants $k_1 = 1.77 \pm 0.08 \times 10^{-4}$ sec$^{-1}$ ($0.120 \times 10^{-4}$ at 25°C) whereas $k_2 = 1.09 \pm 0.02 \times$ $\times\ 10^{-6}$ sec$^{-1}$. Temperature-dependence studies for reaction (1) gave $\Delta H^\ddagger = 20.4$ kcal/mole and $\Delta S^\ddagger = -12.6$ e.u. The aquochloro complex is thermally unstable and slowly decomposes at elevated temperatures. Initiated at 50°C decomposition is undetectable but becomes pronounced after 140 h of reaction. At acid concentrations $0.009\,M > H^+ > 0.001\,M$ and 50°C, thermal decomposition of the aquochloro compound is much more rapid, increasing with a decrease in $[H^+]$. This suggests the possibility of a base-catalyzed aquation path or an isomerization reaction. Ion exchange and spectrophotometric analysis demonstrated that the products are Co(II) and uncoordinated ligand, not the anticipated isomerization products uns-*cis*-$[Co(eee)ClH_2O]^{2+}$ or uns-*cis*-$[Co(eee)(H_2O)_2]^{3+}$.

Reactions (1) and (2) are also catalyzed by mercury(II) ion. Aquation of $[Co(eee)Cl_2]^+$ in the presence of Hg(II) is so rapid that a detailed study involving the Hg(II) and temperature dependence has not been possible using normal spectrophotometric techniques. At 18°C and $1.0 \times 10^{-3}\,M$ complex, $0.10\,M$ $[H^+]$ and $0.10\,M$ Hg(II), the first aquation step is complete within two minutes with a second-order catalyzed rate constant of $0.95 \pm 0.09\,M^{-1}$ sec$^{-1}$. Unlike the initial stage, aquation of the s-*cis*-$[Co(eee)ClH_2O]^{2+}$ ion was examined in detail over a wide range of Hg(II) concentration and temperature. The second-order catalyzed rate constant for reaction (2) at 50°C, $0.10\,M$ $H^+$, and $6.0 \times 10^{-4}\,M$ complex, is $8.41 \times 10^{-2}\,M^{-1}$ sec$^{-1}$ ($3.84 \times 10^{-3}\,M^{-1}$ sec$^{-1}$ at 25°C) with the thermodynamic functions $\Delta H^\ddagger = 23.2$ kcal/mole and $\Delta S^\ddagger = -0.23$ e.u.

### (vii) Contrasts between the [Co(NSSN)$X_2$]$^{n+}$ and [Co(NNNN)$X_2$]$^{n+}$ systems

In comparing the stereochemistries of cobalt(III) having ligands with a donor atom sequence of NNNN with ligands of the type NSSN, several unique and important contrasts become apparent. The *s-cis*-[Co(eee)X$_2$]$^{n+}$ and *s-cis*-[Co(epe)X$_2$]$^{n+}$ ions do not isomerize to the uns-*cis* or *trans* geometries in basic solution or in the presence of basic Li$_2$CO$_3$ solution as do the corresponding complexes derived from triethylenetetraamine. In addition, numerous interconversion reactions proceed without isomeric change in the eee and epe compounds. The relative stabilities of the geometric isomers are determined by somewhat different effects. Goto et al. recently studied a number of methyl substituted triethylenetetraamine ligands and demonstrated that substitution of a methyl group on one of the carbon atoms of the central chelate ring causes the exclusive production of the unsymmetrical *cis* isomers[51]. The chelate ring size, as controlled by varying the number of CH$_2$ groups between adjacent nitrogens, greatly effects the relative stabilities of the geometric isomers. As ring size increases, *trans* isomers appear to increase in stability for flexible tetraamine ligands.

Bosnich and Phillip's work with pep, tet and ete suggest that ring size is not the critical factor governing the most stable geometries for NSSN complexes. Size and stereochemistry of the individual thioether donor groups, presents the unique situation in which *cis* geometries must predominate, with ete the only ligand reportedly complexing with cobalt(III) in the *trans* topology.

Available mechanistic and rate data demonstrate a distinct contrast between the reactivity of trien and eee complexes. The first aquation step for *s-cis*-[Co(eee)Cl$_2$]$^+$ is very slow, having a half-life of 966 min relative to the replacement of the first Cl$^-$ in *s-cis*-[Co(trien)Cl$_2$]$^+$ which has a half-life of 76 min at 25°C and 0.10 *M* H$^+$. Under these conditions, both complexes aquate with complete retention of configuration. Examination of the activation parameters for the eee and trien complexes suggests that the differences in reaction rates reside predominantly in the entropy term ($\Delta S^{\ddagger}_{\text{eee}} = -12.6$ e.u., $\Delta S^{\ddagger}_{\text{tren}} = -5.8$ e.u.). The enthalpy of activation for both *s-cis*-dichloro complexes were found to be quite similar ($\Delta H^{\ddagger}_{\text{eee}} = 20.4$ kcal/mole, $\Delta H^{\ddagger}_{\text{tren}} = 21.5$ kcal/mole).

The exceptionally low entropy value for *s-cis*-[Co(eee)Cl$_2$]$^+$ reflects the rigidity imposed by the eee ligand once it is coordinated. Molecular models show that *s-cis*-[Co(eee)Cl$_2$]$^+$ and *s-cis*-[Co(trien)Cl$_2$]$^+$ are encapsulated in similar solvation spheres so that arguments relative to a transition state in which [Co(trien)Cl$_2$]$^+$ is more readily solvated in the vicinity of the coordinated Cl$^-$ ions cannot be justifiably invoked to explain the approximately thirteen-fold greater primary aquation rate for *s-cis*-[Co(trien)Cl$_2$]$^+$. Other factors which deserve consideration are the Co—Cl bond strengths *trans* to either N—H and R—S—R donor groups as well as electronic-charge distribution features which are unique to the thioether donor.

That *s-cis*-[Co(eee)Cl$_2$]$^+$ does not possess secondary nitrogen donor atoms on the back side of the chelate ring system, make it an interesting candidate for contrasting the role of the NH group in isomerization processes which involve the SN$_1$CB mechanism. Such studies are now in progress in these laboratories.

TABLE 9

Flexible linear diaminedicarboxylate and related ligands

| *Ligand* | *Abbreviation* |
|---|---|
| Ethylenediamine-*N,N′*-diacetate | EDDA |
| *N,N′*-Dimethylethylenediamine-*N,N′*-diacetate | DMEDDA |
| *N,N′*-Diethylethylenediamine-*N,N′*-diacetate | DEEDDA |
| Ethylenediamine-*N,N′*-di-*L*-α-propionate | LL-EDDP |
| 1-Diethylenetriamineacetate | DTMA |
| 4-Diethylenetriamineacetate | i-DTMA |
| β-Aminoethyliminodiacetate | AEIDA |

## E COMPLEXES WITH FLEXIBLE DIAMINEDICARBOXYLATE LIGANDS

The study of cobalt(III) chelates of ethylenediamine-*N,N′*-diacetate (EDDA, *N,N′*-ethanedinitrilodiacetate) and related tetradentate ligands during the last five years has yielded a wealth of stereochemical information. Table 9 summarizes the ligands based on or related to EDDA which have been investigated. Although the last three ligands listed are not linear and, therefore, do not strictly fall into the confines of this review, they are included because of their close relationship to the linear ligands.

The presence of the glycine unit in these ligands offers a unique probe into chelate stereochemistry not found in the tetraamine and dithiadiamine complexes. This rigid chelate ring yields an AB PMR spectrum which is usually easily identifiable compared to the complex second-order spectra commonly encountered for the chelated tetraamines. Furthermore, the methylene protons of the chelated glycine ring are selectively labilized to isotopic deuterium exchange in $D_2O$ solutions [79–81,83] thus enhancing the PMR probe. Since most of the reported studies are related to EDDA, to which much of the work with the other ligands is directly or indirectly related, the following discussion will use the chemistry of EDDA as its central theme.

Until recently [82,83] studies of Co(III)–EDDA complexes had been mostly limited to EDDA in the *s-cis* configuration, Fig. 1. Most of the complexes investigated had ethylenediamine, some N- or C-substituted analogue, or an amino acid occupying the remaining two coordination sites. It was postulated [3] that non-bonding interactions between the sterically restricted amine protons and EDDA prevented the formation of substantial amounts of the *uns-cis*-isomers. However, when these steric interactions were eliminated by employing bidentate ligands (carbonate, oxalate, malonate) or monodentate ligands ($H_2O$, $Cl^-$) substantial quantities of the *uns-cis* isomers were obtained [82,83]. As of yet, no cobalt(III) complexes having EDDA or any of the other linear diaminedicarboxylate ligands in the planar (requires monodentate ligands) configuration (*trans* isomer in Fig. 1) have been reported. It is of interest to note, though, that by using $Cl_2$ in an oxidative addition, Liu [84] appears to have obtained *trans*-$[Pt(EDDA)Cl_2]^-$ (a low-spin $d^6$ complex, like the cobalt(III) complexes) from planar Pt(EDDA).

The investigation of EDDA and related chelates has focused on two main areas (*i*) PMR and stereochemistry and (*ii*) optical activity (circular dichroism) and absolute configuration. Although the studies under (*ii*) have been strongly supported by PMR investigations, it is logical to review this work using the above division.

### *(i) Proton magnetic resonance and stereochemistry*

Mori et al [85] were the first to report the systhesis of a cobalt(III) complex of EDDA They prepared the carbonato, diaquo, and dinitro complexes. They offered no concrete evidence to identify the isomer(s) prepared but postulated the s-*cis* configuration from a comparative analysis of absorption spectra Van Saun and Douglas [86] have recently prepared and identified s-*cis*-$[Co(EDDA)(CO_3)]^-$ as well as the oxalate and malonate analogues on the basis of their PMR spectra A preliminary report on the synthesis and PMR identification of both the s-*cis* and uns-*cis* isomers of the diaquo and carbonato complex has recently appeared [82]

Legg and Cooke prepared [Co(EDDA)(am)], (am = en, $2NH_3$), and the N-alkyl substituted analogues (DMEDDA and DEEDDA, see Table 9) with ethylenediamine They obtained the s-*cis* and uns-*cis* isomers for the EDDA complexes, although the latter isomers were obtained in trace quantities only 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, Fig. 7, on the basis of bond anisotropics

In a carefully conceived study, Sudmeier and Occupati [81] demonstrated that the less sterically hindered proton in s-*cis*-$[Co(EDDA)en]^+$, $H_A$ in Fig 7, exchanged with deuterium in $D_2O$ approximately ten times more rapidly than $H_B$ (ca 40 h as compared to 400 h). 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* They were also able to assign $H_A$ and $H_B$ by applying the Karplus relationship to the observed $H-N-C-H_{A(or\ B)}$ proton–proton coupling (the amine protons are slow to exchange in acidic $D_2O$) These two studies confirmed the assignments previously made by Legg and Cooke on the basis of bond anisotropies

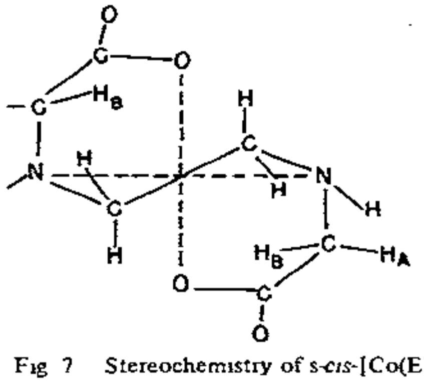


Fig 7 Stereochemistry of s-*cis*-$[Co(EDDA)(en)]^+$

Of importance to these stereochemical observations on the EDDA chelate system is the work of Terrill and Reilley [80] They examined the selective deuteration of the out-of-plane glycinates of CoCyDTA$^-$(CyDTA = *trans*-1,2-cyclohexanediamine-*N,N,N'N'*-tetraacetate) where $H_B$ is even more sterically blocked by the cyclohexane "backbone" than the analogous $H_B$ in EDDA, Fig 7 They discovered that the chemical shifts of $H_A$ and $H_B$ for the out-of-plane glycinates were interchanged relative to $H_A$ and $H_B$ in s-*cis*-[Co(EDDA)en]$^+$ Thus more than bond anisotropic shielding must be invoked to explain the chemical shifts Terrill and Reilley postulated an electron orbital interaction as an explanation Later Sudmeier and Occupati [81] suggested that steric compression (a situation where atoms are brought into close proximity by the formation of the molecule concerned and which is predicted to cause a down-field shift of the nuclear resonance signals) between $H_B$ and a cyclohexane proton caused this interchange. Recently, Dabrowiak and Cooke [87] have used steric compression to assign absolute configurations effectively to several new amino acid complexes as well as to confirm the absolute configuration assigned by other means to related cobalt(III) diastereoisomers It should be pointed out, though, that certain assumptions concerning chelate conformations have to be made.

Legg and Cooke [3] also assigned the PMR spectrum to uns-*cis*-[Co(EDDA)-en]$^+$ They supported their assignment 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, table 9) were comparable to those between uns-*cis*-[Co(EDDA)en]$^+$ and Co(EDTA)$^+$ where chelated EDTA can be thought of as an "N-alkylated" uns-*cis*-EDDA It was later demonstrated by Legg and coworkers [83], using selective deuterium exchange on a series of uns-*cis*-EDDA complexes, that the original assignment of $H_B$ by Legg and Cooke was incorrect The new assignment was significantly different from the original assignment, thus casting some doubt on the explanation of chemical shift differences based only on bond anisotropies

Deuterium exchange techniques [79–81,83], H–N–C–H spin–spin coupling [81,88], and anisotropy arguments [3,88] have been used subsequently to assign the PMR spectra and consequently the stereochemistries to a large number of cobalt(III) complexes related to the EDDA chelates first investigated s-*cis*-Co(EDDA)(L), (L = S-pn, S-ala, gly) [89], and (L = dmen, deen) [90], s-*cis* and uns-*cis*-[Co(LL-EDDP)L]$^+$, (L = en, S-pn) [91], isomers of [Co(AEIDA)en]$^+$ [92]; s-*cis*-[Co(EDDA)L]$^+$, (L = $CO_3$, ox, mal) [83,86], uns-*cis*-[Co(EDDA)L]$^-$, (L = ox, mal) [83], and s-*cis*- and uns-*cis*-[Co(EDDA)L], (L = $[H_2O]_2$, $Cl_2$, $CO_3$) [93] Legg and co-workers [83] have compiled PMR data for a series of s-*cis* and uns-*cis*-EDDA chelate systems and compared these to data obtained for related tetra-, penta-, and hexadentate ligands They have classified the chemical shifts observed for the various types of glycinate rings in a manner which should be helpful to stereochemists working with multidentate aminecarboxylate chelates

### *(ii) Optical activity and absolute configuration*

Legg et al. [89] first reported the resolution of a Co(III)EDDA complex when they resolved s-*cis*-[Co(EDDA)L], (L = en, S-pn, S-ala, gly) 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.

Later, Legg[94] demonstrated the high sensitivity of ion-exchange chromatography by completely separating the four isomers of uns-*cis*-$[Co(EDDA)(S\text{-}pn)]^+$. 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 S-pn in the uns-*cis* isomer, Fig 2 Legg and Douglas[90] also demonstrated the utility of ion-exchange cellulose to achieve rapid partial resolution of ionic complexes by partially resolving s-*cis*-Co(L)(am) where L = EDDA, DMEDDA, and am = en, men, een, dmen, and deen in various combinations, as well as $Co(EDTA)^-$ and related anionic complexes. Brubaker et al[95] had previously achieved total resolution of a trinuclear cobalt(III) complex using the same technique

The resolution of s-*cis*-$[Co(EDDA)(en)]^+$ and related complexes led to some interesting developments concerning absolute configurations As pointed out earlier, Mason and coworkers[8] devised a method by which complexes with $\underset{\sim}{C}_2$ symmetry could be tentatively assigned an absolute configuration using the CD spectra of the complexes Although complexes of the type $[Co(en)_2X_2]^{n+}$ could be configurationally related to $[Co(en)_3]^{3+}$ (Fig 5), in the case of s-*cis*-$[Co(EDDA)(en)]^+$, the relationship was not obvious It was tempting to relate this complex to $Co(EDTA)^-$ which is of known absolute configuration through the common "backbone" as shown in Fig 8, A and B. That this was not the correct relationship was demonstrated by the imaginative work of Cooke and coworkers[91] They designed an asymmetric ligand analogue of EDDA, ethylenediamine-*N*,*N*′-di-L-α-propionate (LL-EDDP) which, when coordinated with cobalt(III), resulted in known positions (see $H_A$ and $H_B$ in Fig 7) for the methyl group in the alaninate chelate ring for a given diastereoisomer This assignment was possible because the asymmetric carbons of the ligand were of known absolute configurations From an analysis of the PMR spectra, absolute configurations were assigned to the diastereoisomers Comparison of CD and ORD data of the LL-EDDP and EDDA analogues provided a check on the assignment of absolute configuration to the EDDA complexes. The results required that configurations B and C, Fig 8, of $Co(EDTA)^-$ and s-*cis*-$[Co(EDDA)(en)]^+$ be related contrary to what had been originally proposed This is consistent with the "ring pairing" scheme proposed by Legg and Douglas[10]

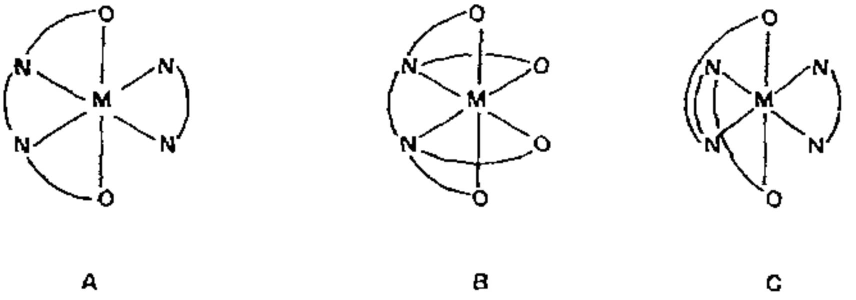


Fig 8. Configurational comparison between s-*cis*-$[Co(EDDA)(en)]^+$ and $[Co(EDTA)]^-$

Legg et al [89] found an additional check on the assignment of absolute configuration to the *s-cis*-Co(EDDA) complexes by comparing the PMR spectra obtained for the two diastereoismers of [Co(EDDA)(S-pn)]$^+$ where S-pn is of known absolute configuration. They found that in one of the isomers the "outside" proton, $H_A$ (Fig. 8), was split into a doublet. This could be explained in terms of the close non-bonding proton—proton interactions between $H_A$ and the S-pn amine protons in one of the isomers Dabrowiak and Cooke [87] have used steric compression to explain the chemical shifts and assign absolute configurations in this and related complexes as previously discussed

Recently Van Saun and Douglas [86] reported the resolution of *s-cis*-[Co(EDDA)(L)]$^-$, (L = $CO_3$, mal, and ox), using optically active [Co(en)$_2$ox]$^+$ as a resolving agent They tentatively assigned absolute configurations on the basis of CD spectra using the previously discussed methods and noted that the ring size of the bidentate chelate had little effect on the rotational strengths of the *d*–*d* transitions

*(iii) Conclusions based on studies of flexible diaminecarboxylate ligands*

The study of cobalt(III) chelates of EDDA and related ligands has led to significant advances in several areas These include the development of several previously available experimental techniques. The various chromatographic techniques developed, particularly in ion-exchange chromatography, have proven invaluable in the separation and identification of pure isomeric forms of these complexes The use of ion-exchange cellulose to achieve rapid partial resolution of optical antimeres should also be noted. Thin-layer chromatography, a rapid diagnostic tool for the most part ignored by inorganic chemists, has been applied successfully to the separation of some of these complexes [96]. We are currently finding this technique to be of great value in our studies of peptide hydrolysis by metal ion complexes

Detailed structural analyses have resulted from PMR studies of these chelates which contain as part of the ligand structure glycine and alanine units Isotopic deuterium exchange studies have been instrumental in this work Analysis of the PMR spectra of diastereoisomers containing ligands of known absolute configuration has helped to establish the absolute configurations of these complexes These investigations have also led to some interesting observations concerning the relationship between absolute configuration The tentative IUPAC rules for absolute configurations [9] arose from the consideration of the "ring-pairing" scheme

Although isomerism with respect to the asymmetric nitrogen in tetraamine chelate systems has been extensively investigated as previously discussed, such isomerism has not yet been observed for the analogous EDDA chelates [83] Although configurational isomerism studies are in progress [82,93] no such studies for EDDA systems have been yet reported Such studies as well as substitution reactions have been extensively investigated for the flexible tetraamine and dithiodiamine cobalt(III) chelates and have played an important part in understanding their stereochemistries

The work of Schneider and Collman [97] with the two EDDA related tetradentate ligands DTMA and i-DTMA (see Table 9) is of interest since these researchers using ion-exchange chromatography found only two of several possible isomers for [Co(DTMA)(aa)]$^+$

TABLE 10

Complexes of EDDA with metal ions other than cobalt(III)

| *Metal ion* | *Type of study* | *Ref.* |
|---|---|---|
| Pt(II), Pt(IV) | Synthesis and stereochemistry by IR | 84 |
| Pt(II) | Isomerism, N–H proton exchange and inversion at asymmetric coordinated nitrogens by PMR, pH, and temperature dependence | 98 |
| Pt(II) | Kinetics of $Cl^-$ exchange in EDDA–Cl complexes by UV spectroscopy, pH and temperature dependence | 99 |
| Pd(II) | Stereochemistry of EDDA–Cl complexes by PMR, pH and temperature dependence | 100 |
| Cr(III) | Synthesis of EDDA-(acac) complexes<br>Halogenation of acac | 101 |
| Ni(II) | Stability constant | 102 |

These two ligands together with nitrilotriacetic acid complete the permutations possible for the simple aminecarboxylic acid tetradentate ligands Some related studies have been reported for EDDA complexes of other metal ions, both inert (of the $d^6$, $d^3$, and $d^8$ strong-field type) and labile Although these complexes do not fall within the scope of this review, they are listed for reference in Table 10 Information gained and techniques developed from the study of these "model" systems has been invaluable in our current studies of the interaction of cobalt(III) with the more complex amino acids and related peptides

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