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Ethylenediaminediacetate Complexes of Cobalt(III). Part I. The Preparations and Configurations of some Ethylenediamine-N,N′-diacetate Cobalt(III) Complexes

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The following series of cobalt(III) complexes of the ethylenediaminediacetate (edda) ion have been prepared in both the α-cis and β-cis configurations: $[Co(CO_3)(edda)]^-$, $[Co(edda)(OH_2)_2]^+$, $[Co(NO_2)_2(edda)]^-$, $[CoCl_2(edda)]^-$, $[CoCl(edda)(OH_2)]$, $[Co(mal)(edda)]^-$.[a] *The complexes have been characterised by analysis, proton magnetic resonance, infrared, and visible spectroscopy. Absolute configurations were established from optical rotatory dispersion measurements and an x-ray diffraction study.*

Introduction

Previous to this work Mori *et al.*[1] reported the preparation of the carbonato, diaqua, and dinitro complexes of cobalt(III) with edda. The complexes appear to have been incorrectly characterised, and attempts here and elsewhere[2] to reproduce this work have been unsuccessful. Legg and Cooke[3] have studied the stereochemistry of some edda and substituted edda complexes of cobalt(III). These complexes were characterised from their pmr spectra. More recently other work on Co^{III}–edda complexes has appeared,[2–8] the most significant with respect to this work being reports on the circular dichrcism of these complexes[2,5] and a pmr investigation.[4]

The coordination of edda gives three possible geometric isomers of the formula $[CoX_2(edda)]^+$. These are designated the *α-cis*, *β-cis* and *trans* forms in accordance with the nomenclature adopted for the triethylenetetramine (trien) system.[9] The *α-cis* and *β-cis* isomers are both disymmetric and therefore give optical isomers. The optical isomers are described[10] as Λ or Δ since it is readily seen that they are related to the Λ and Δ forms of $[Co(en)_3]^{3+}$ [11,12] (Figure 1). If non-identical unidentate groups or an unsymmetrical bidentate ligand occupies the two available positions in a *β-cis* complex, a further two *β-cis* isomers are possible (Figure 2).

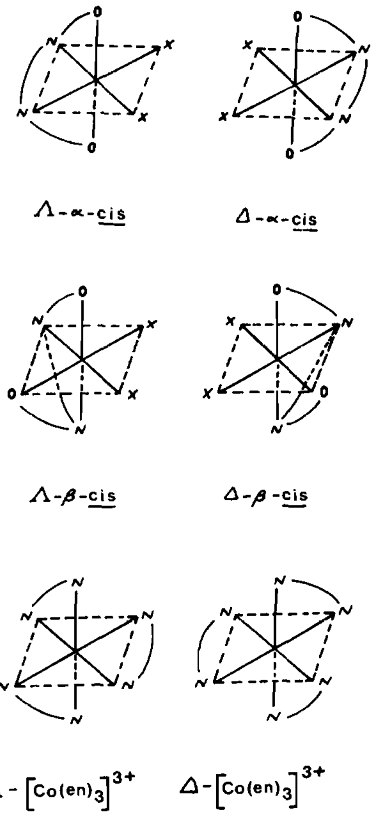

Figure 1. Relationship of Λ and Δ-*α-cis* and *β-cis*-$[CoX_2(edda)]^{\pm}$ to Λ and Δ forms of $[Co(en)_3]^{3+}$.

Further isomers are possible in the $[COX_2(edda)]^{\pm}$ system if cognizance is taken of the mode of coordination of the secondary nitrogen (*sec*-N) atoms. The presence of this source of asymmetry in cobalt(III) chemistry was shown in $[Co(sar)(NH_3)_4]^{2+}$ (sar = N-methylglycinate)[13] and has subsequently been demonstrated in other cobalt(III) complexes.[14–17] In

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[a] mal ≡ malonate ion.

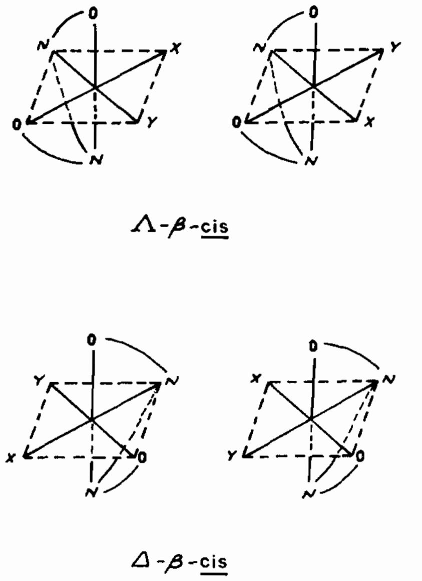

Figure 2. Isomers of *Λ-β-cis* and *Δ-β-cis* forms of [CoXY (edda)]$^{\pm}$.

the *Λ*- and *Δ-α-cis* isomers the two *sec*-N protons are stereospecifically orientated (Figure 3a). Thus no new isomers arise from consideration of the mode of coordination of the *sec*-N atoms. The configuration about the *sec*-N atom is described as *R* or *S* according to a set of rules proposed by Cahn, Ingold and Prelog.[18] The *α-cis* isomers are therefore described as *Λ-α-cis*-(*RR*) and *Δ-α-cis*-(*SS*). In the *β-cis* isomers one of the *sec*-N atoms is "planar"[19] and this permits the *sec*-N proton to adopt either of two possible orientations (Figure 3b, c). Thus for the *Λ* configuration of the ligand the *Λ-β-cis*-(*SS*) and *Λ-β-cis*-(*SR*) isomers are possible (the configuration about the normal trigonal *sec*-N atom is described before that of the "planar" *sec*-N[19]). In the *Λ-β-cis*-(*SS*) isomer the "planar" *sec*-N proton is directed towards the out-of plane oxygen whilst in the *Λ-β-cis*-(*SR*) isomer it is directed away from the same oxygen. Two comparable isomers, *Δ-β-cis*-(*RR*) and *Δ-β-cis*-(*RS*), exist for the *Δ* configuration of the ligand. The *trans* isomer possesses two "planar" *sec*-N atoms and can exist in three forms (Figure 3d). The *trans*-(*RR*) and *trans*-(*SS*) forms are antimeric but the *trans*-(*RS*) form would be optically inactive.

An identical set of isomers exist for the [CoX_2(trien)]$^{n+}$ and [CoX_2(edda)]$^{(n-2)+}$ systems. Sargeson *et al.*[9,19,20] have identified the *Λ-α-cis*-(*RR*), *Δ-α-cis*-(*SS*), *Λ-β-cis*-(*SS*), *Δ-β-cis*-(*RR*), *Λ-β-cis*-(*SR*), *trans*-(*SS*) and *trans*-(*RR*) isomers in the [CoX_2(trien)]$^{n+}$ system. Their investigations[13–17] have shown that racemisation at *sec*-N centres occurs via proton exchange and these centres should therefore be inert in acidic solutions.

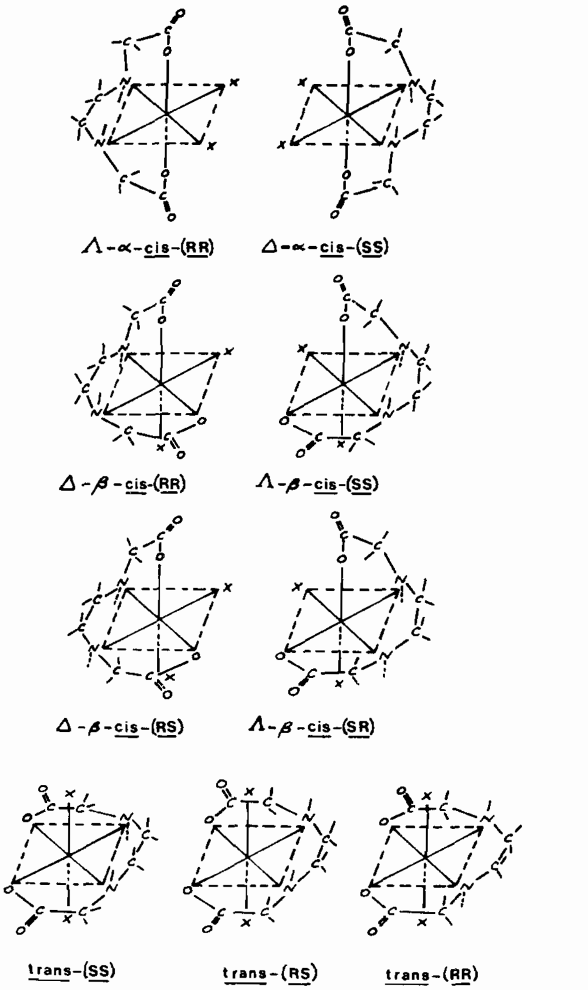

Figure 3. Isomers arising from mode of coordination of the secondary nitrogen atoms (a) Row 1, *Λ* and *Δ-α-cis*-isomers (b) and (c) Rows 2 and 3, *Λ* and *Δ-β-cis*-isomers (d) Row 4, *trans*-isomers.

Weakliem and Hoard[21] devised a nomenclature to describe the chelate rings in ethylenediaminetetraacetate complexes which is applicable to [CoX_2(edda)]$^{\pm}$ complexes. The ethylenediamine (Co–N–C–C–N–Co) ring is described as an E ring. The glycinate (Co–O–C–C–N–Co) rings can be in-plane or out-of-plane with respect to the E ring. The in-plane rings were described as G rings and the out-of-plane as R rings.

Experimental

A. Preparation of Complexes

(i) [Co(CO$_3$)(edda)]$^-$ complexes

A slurry of 30 g of $Na_3[Co(CO_3)_3]\cdot3H_2O$[22] and 14.6 g of H_2edda in 30 ml of water was heated at 50°

for 10 min with stirring. The deep violet solution was filtered and the filtrate cooled in ice. The slow addition of ethanol precipitated 21 g of a mixture of Na *α-cis* and *β-cis*-[Co(CO_3)(edda)]. This was filtered, washed with 50% aqueous ethanol, ethanol and acetone and air dried.

This solid was dissolved in 65 ml of water and filtered. The filtrate was added to a column of 300 ml of strong-acid cation-exchange resin (Dowex 50W–X8, 50–100 mesh, K^+ form) and eluted at 1 ml/min. Slow addition of 50 ml of ethanol to the chilled eluent precipitated 4.7 g of blue–violet K*α-cis*-[Co(CO_3)(edda)]·$4H_2O$. Addition of a further 260 ml of ethanol produced 13 g of violet K*β-cis*-[Co(CO_3)(edda)]·H_2O. Both isomers were recrystallized from water by chilling and adding ethanol. Anal. Calc. for K*α-cis*-[Co(CO_3)(edda)]·$4H_2O$: Co, 14.6; C, 20.8; H, 4.5; N, 6.9%. Found: Co, 14.5; C, 20.9; H, 4.8; N, 6.8%. Calc. for K*β-cis*-[Co(CO_3)(edda)]·H_2O: Co, 16.8; C, 24.0; H, 3.5; N, 8.0%. Found: Co, 16.8; C, 24.0; H, 3.4; N, 7.9%.

(ii) [Co(edda)(OH$_2$)$_2$]$^+$ complexes

20 g of the mixed Na*α-cis*- and *β-cis*-[Co(CO_3)(edda)] was treated with excess (25 ml) 5*M* $HClO_4$. 200 ml of ethanol and 800 ml of ether were added to the chilled red solution producing 17 g of crude diaqua product (I). This was filtered, washed with ethanol and ether and dried over magnesium perchlorate.

5 g of (I) was dissolved in 50 ml of water and heated at 60° for one hour during which the solution turned from red to violet. The solution was added to a column containing 150 ml of strong-acid cation-exchange resin (Dowex 50W–X8, 50–100 mesh, H^+ form) and eluted with 0.5*M* $HClO_4$ at 0.5 ml/min. Three bands developed, the first and strongest being the *α-cis* isomer. This was collected (150 ml), cooled in ice and 800 ml of ethanol and 4 l of ether were added. Filtration and washing with ethanol and acetone produced 3 g of product. The second and third bands contained *β-cis* and an impurity of higher charge respectively, but were not recovered. Anal. Calc. for *α-cis*-[Co(edda)(OH_2)$_2$]ClO_4: Co, 16.0; C, 19.6; H, 3.8; N, 7.6%. Found: Co, 15.9; C, 19.5; H, 3.8; N, 7.3%.

5 g of (I) was dissolved in 50 ml of 0.001*M* $HClO_4$ and added to a 150 ml column of the cation-exchange resin and eluted as above. The major band of *β-cis* (preceded by a weak band of *α-cis*) was treated as for the *α-cis* isomer to yield 3 g of product. Anal. Calc. for *β-cis*-[Co(edda)(OH_2)$_2$]ClO_4: Co, 16.0; C, 19.6; H, 3.8; N, 7.6%. Found: Co, 15.7; C, 19.5; H, 4.1; N, 7.3%.

α-cis-[Co(edda)(OH_2)$_2$]Cl was prepared as for the perchlorate salt except that 0.5*M* HCl was used as the eluting agent.

(iii) [Co(NO$_2$)$_2$(edda)]$^-$ complexes

H_2edda (14.1 g) and NaOH (3.2 g) were dissolved in water (50 ml) and added to 100 ml of an aqueous solution containing 19.9 g of Co(CH_3COO)$_2$·$4H_2O$. 11 g of $NaNO_2$ and 8 g of charcoal were added and oxidation accomplished by the gradual addition of 18 ml of 30% H_2O_2. The mixture was heated on a steam bath for 10 min, cooled and filtered. The filtrate was eluted through a 360 ml column of Dowex 50W–X8 cation-exchange resin in the K^+ form and the eluent (300 ml) allowed to stand overnight. 5 g of K*α-cis*-[Co(NO_2)$_2$(edda)]·H_2O precipitated and was filtered, washed with ethanol and acetone and air dried. The filtrate was evaporated in a current of air to 60 ml to yield a precipitate of 10 g of the potassium salt of the *β-cis* isomer. Both isomers were recrystallized from water by adding ethanol. Anal. Calc. for K*α-cis*-[Co(NO_2)$_2$(edda)]·H_2O: Co, 15.4; C, 18.9; H, 3.2; N, 14.7%. Found: Co, 15.3; C, 18.9; H, 3.3; N, 14.4%. Calc. for K*β-cis*-[Co(NO_2)$_2$(edda)]: Co, 16.2; C, 19.8; H, 2.8; N, 15.4. Found: Co, 16.0; C, 19.8; H, 3.1; N, 15.3%.

*(iv) [Co(Cl$_2$(*edda*)]$^-$ complexes*

The hydrogen salts of the *α-cis* and *β-cis* isomers of this complex were obtained by the addition of 30 ml of 10*M* HCl to 3 g of K*α-cis*-[Co(CO_3)(edda)]·$4H_2O$ and K*β-cis*-[Co(CO_3)(edda)]·H_2O respectively. The resulting solution was filtered and allowed to stand for one day. The product was filtered, washed with ice cold water, ethanol, and acetone and air dried. Anal. Calc. for H*cis*-[$CoCl_2$(edda)]·H_2O: C, 22.3; H, 4.1; N, 8.7; Cl, 22.0%. Found for *α-cis*: C, 22.0; H, 4.1; N, 8.8; Cl, 22.3% and for *β-cis*: C, 22.7; H, 3.7; N, 8.9; Cl, 22.4%.

The corresponding potassium salts were obtained in similar purity by the addition of equivalent amounts of cold potassium acetate solution and reclamation with ethanol. Alternatively these salts can be obtained from the appropriate K[Co(CO_3)(edda)] salt (5 g) by heating in 30 ml of ethanolic HCl, at 60° C for 30 min. The yield here is quantitative and the products can be recrystallized from ice cold water with ethanol. Anal. Calc. for K*cis*-[$CoCl_2$(edda)]·H_2O: Co, 16.3; C, 20.0; H, 3.4; N, 7.8; Cl, 19.6%. Found for *α-cis*: Co, 16.3; C, 19.7; H, 3.3; N, 7.6; Cl, 19.7% and for *β-cis*: Co, 16.1; C, 20.3; H, 3.5; N, 7.6; Cl, 19.5%.

(v) [CoCl(edda)(OH$_2$)] complexes

3 g of K*α-cis*-[$CoCl_2$(edda)]·H_2O was dissolved in water and allowed to stand for 18 hr at room temperature. The precipitated *α-cis*-[CoCl(edda)(OH_2)] (2.3 g) was filtered, washed with ethanol and acetone and air dried. Anal. Calc. for *α-cis*-[CoCl(edda)(OH_2)]·H_2O: Co, 19.4; C, 23.7; H, 4.6; N, 9.2; Cl, 11.6%. Found: Co, 19.3; C, 23.7; H, 4.6; N, 9.1; Cl, 11.6%.

Hβ-*cis*-[$CoCl_2$(edda)]·H_2O (1.6 g) and $AgNO_3$ (0.8 g) were stirred in 20 ml of cold water for 5 min. The solution was filtered and the filtrate passed in turn through a 20 ml ice-jacketed Dowex 1–X8 (Cl^- form) anion-exchange column and a 30 ml ice-jacketed Dowex 50W–X8 (H^+ form) cation-exchange column. The eluent (25 ml) was cooled in ice and the product (0.5 g) precipitated by the addition of ethanol (100 ml) and ether (400 ml). This was filtered and washed with ethanol and ether. Anal. Calc. for β-*cis*-[CoCl(edda)(OH_2)]·$2H_2O$: C, 22.3; N, 8.7; H, 5.0; Cl, 11.0%. Found: C, 22.3; N, 8.6; H, 4.8; Cl, 10.8%.

(vi) [$Co(CH_2(COO)_2)$(edda)]$^-$ complexes

Malonic acid (15.8 g) and 6 g of NaOH were dissolved in 30 ml of water. $Co(CH_3COO)_2 \cdot 4H_2O$ (12 g), 6 ml of 50% acetic acid and 10 g of PbO_2 were added to the solution and the resulting mixture was stirred in an ice bath for 30 min. 8.8 g of H_2edda was added and the green mixture heated for 20 min at 50° with stirring. The resultant red–violet mixture was cooled in ice for 30 min and filtered. Addition of 500 ml of ethanol to the filtrate produced two phases. The supernatant liquid was decanted and the remaining oily paste dissolved in water and chromatographed by the method of Legg *et al.*[4] The yields of the calcium salts were 4.2 g of the α-*cis* and 3.0 g of the β-*cis* isomer.

The potassium salt of the α-*cis* isomer was prepared by passing a solution of the calcium salt through a Dowex 50W–X8 (K^+ form) cation-exchange column and evaporating the eluent to dryness. Anal. Calc. for Kβ-*cis*-[$Co(CH_2(COO)_2)$(edda)]·$3H_2O$: C, 25.2; H, 4.2; N, 6.5%. Found: C, 25.4; H, 3.8; N, 6.6%.

The silver salt of the β-*cis* isomer was prepared by an analogous procedure using a cation-exchange resin in the Ag^+ form. Anal. Calc. for Agβ-*cis*-[$Co(CH_2(COO)_2)$(edda)]·H_2O: C, 23.4; H, 3.1; N, 6.1%. Found: C, 23.3; H, 2.8; N, 6.1%.

B. Resolution of Complexes

(i) Kα-cis-[$Co(CO_3)$(edda)]·$4H_2O$

(+)[$Co(C_2O_4)(en)_2$](+)α-*cis*[$Co(CO_3)$(edda)]·$3H_2O$ was prepared after Van Saun and Douglas.[2] The diastereoisomer (2 g) and $NaClO_4$ (5 g) were stirred in 10 ml of ice cold water and the resolving agent filtered off as the insoluble perchlorate. The addition of ethanol to the filtrate precipitated Na(+)α-*cis*-[$Co(CO_3)$(edda)]·$4H_2O$ which when filtered, washed with ethanol and acetone, yielded 0.6 g. Anal. Calc. for Na(+)α-*cis*-[$Co(CO_3)$(edda)]·$4H_2O$: C, 21.7; H, 4.7; N, 7.2%. Found: C, 21.7; H, 4.3; N, 7.4%.

(ii) Kβ-cis-[$Co(CO_3)$(edda)]·H_2O

(–)[$Co(C_2O_4)(en)_2$]Br·H_2O[23] (2 g) and $AgCH_3COO$ (0.9 g) in 20 ml of water were heated at 60° for 10 min and the silver bromide filtered. The filtrate was cooled in ice and 4 g of Kβ-*cis*-[$Co(CO_3)$(edda)]. H_2O dissolved with stirring. After standing for 30 min the diastereoisomer (–)[$Co(C_2O_4)(en)_2$](+)β-*cis*-[$Co(CO_3)$(edda)] was filtered, washed with ethanol and acetone and air dried. Yield 1.4 g. The diastereoisomer (1 g) and $NaClO_4$ (2 g) were stirred in 2 ml of ice cold water and the (–)[$Co(C_2O_4)(en)_2$]ClO_4 filtered. Careful addition of ethanol to the filtrate precipitated Na(+)β-*cis*-[$Co(CO_3)$(edda)]·$3H_2O$ (0.5 g) which was filtered, washed with ethanol and acetone and dried over magnesium perchlorate. Anal. Calc. for Na(+)β-*cis*-[$Co(CO_3)$(edda)]·$3H_2O$: C, 22.7; H, 4.4; N, 7.6%. Found: C, 22.3; H, 4.0; N, 7.6%.

(iii) α-cis-[Co(edda)$(OH_2)_2$]Cl

d-Tartaric acid (1.1 g) and silver d-tartrate[5] (2.6 g) were added to a solution of α-*cis*-[Co(edda)$(OH_2)_2$]Cl (4.3 g) in 20 ml of water. The mixture was stirred in the dark for 5 min and the silver chloride filtered. The filtrate was cooled in ice and the careful addition of 5 ml of ethanol precipitated (–)α-*cis*-[Co(edda)$(OH_2)_2$]Htart which was filtered (filtrate I), washed with ethanol and acetone and air dried. Yield 2.2 g. Anal. Calc. for (–)α-*cis*-[Co(edda)$(OH_2)_2$]Htart: C, 28.7; H, 4.6; N, 6.7%. Found: C, 28.9; H, 4.7; N, 6.5%.

Addition of more ethanol (50 ml) to the filtrate (I) precipitated (+)α-*cis*-[Co(edda)$(OH_2)_2$]Htart which was filtered, washed with ethanol and acetone and air dried. Yield 2.1 g. Conversion of (–)α-*cis*-[Co(edda)$(OH_2)_2$]Htart to the perchlorate salt was achieved by passing a solution of the hydrogentartrate salt through an anion exchange resin in the perchlorate form, adding 70% $HClO_4$ to the eluent to make it 0.1*M* in $HClO_4$, and evaporating to dryness. Anal. Calc. for (–)α-*cis*-[Co(edda)$(OH_2)_2$]ClO_4: C, 19.6; H, 3.8; N, 7.6%. Found: C, 19.7; H, 3.8; N, 7.6%.

(iv) β-cis-[Co(edda)$(OH_2)_2$]$^+$ salts

Various attempts to resolve β-*cis* diaqua salts were unsuccessful, resulting in the formation of oils. (–)β-*cis*-[Co(edda)$(OH_2)_2$]ClO_4 was prepared from (+)[$Co(C_2O_4)(en)_2$](–)β-*cis*-[$Co(CO_3)$(edda)] as follows.

0.9 g of (+)[$Co(C_2O_4)(en)_2$](–)β-*cis*[$Co(CO_3)$(edda)] was treated with 9 ml of 1*M* $HClO_4$ and the (+)[$Co(C_2O_4)(en)_2$]ClO_4 filtered. The filtrate was evaporated over magnesium perchlorate until (–)β-*cis*-[Co(edda)$(OH_2)_2$]ClO_4 commenced to precipitate. Ethanol and ether were then added and the solution was cooled in ice. The product was filtered, washed with ethanol and acetone and dried over magnesium perchlorate. Yield 0.4 g. Anal. Calc. for (–)β-*cis*-[Co(edda)$(OH_2)_2$]ClO_4: C, 19.6; H, 3.8; N, 7.6%. Found: C, 19.4; H, 4.0; N, 7.5%.

(v) Kα-cis-[Co(NO$_2$)$_2$(edda)]·H$_2$O

(+)[Co(C_2O_4)(en)$_2$]Br·H_2O (1.3 g) and AgCH$_3$COO (0.6 g) were heated at 60° in 30 ml of water for 10 min and the silver bromide filtered. The filtrate was reheated to 60° and 2.5 g of Kα-*cis*-[Co(NO$_2$)$_2$(edda)]·H_2O dissolved with vigorous stirring. The solution was cooled in an ice bath and fractions were filtered after 10 min (1 g) and 30 min (1 g). K(+)α-*cis*-[Co(NO$_2$)$_2$(edda)]·H_2O was obtained from the first fraction by adding 3 g of KI to a slurry of the diastereoisomer in 10 ml of water, filtering the (+)[Co(C_2O_4)(en)$_2$]ClO$_4$ and adding ethanol to the cooled filtrate. The product was filtered, washed with ethanol and acetone and air dried. Yield 0.4 g. Anal. Calc. for K(+)α-*cis*-[Co(NO$_2$)$_2$(edda)]·H_2O: C, 18.9; H, 3.2; N, 14.7%. Found: C, 19.1; H, 3.1; N, 15.2%.

K(–)α-*cis*-[Co(NO$_2$)$_2$(edda)] was obtained from the filtrate after the removal of the first two fractions. KI (3 g) was added to the solution and the (+)[Co(C_2O_4)(en)$_2$]ClO$_4$ filtered. The addition of ethanol to the filtrate precipitated K(–)α-*cis*-[Co(NO$_2$)$_2$(edda)]. Yield 0.6 g.

(vi) Kβ-cis-[Co(NO$_2$)$_2$(edda)]

(+)[Co(C_2O_4)(en)$_2$]Br·H_2O (1 g) and AgCH$_3$COO (0.45 g) in 5 ml of water were heated at 60° for 10 min and the silver bromide filtered. Kβ-*cis*-[Co(NO$_2$)$_2$(edda)] (1 g) was dissolved in the filtrate with gentle heating and the solution cooled in ice. The diastereoisomer (+)[Co(C_2O_4)(en)$_2$](–)β-*cis*-[Co(NO$_2$)$_2$(edda)] was filtered after 10 min. K(–)β-*cis*-[Co(NO$_2$)$_2$(edda)]·H_2O was obtained by adding excess KI (3 g) to a slurry of the diastereoisomer in 5 ml water, filtering the (+)[Co(C_2O_4)(en)$_2$]ClO$_4$ and adding ethanol to the cooled filtrate. The product was filtered, washed with ethanol and acetone and air dried. Yield 0.4 g. Anal. Calc. for K(–)β-*cis*-[Co(NO$_2$)$_2$(edda)]·H_2O: C, 18.9; H, 3.2; N, 14.7%. Found: C, 19.3; H, 3.1; N, 14.9%.

(vii) Kα-cis-[CoCl$_2$(edda)]·H$_2$O

(+)[Co(C_2O_4)(en)$_2$]Br·H_2O (1.9 g) and AgCH$_3$COO (0.9 g) were heated at 60° in 15 ml of water for 10 min and the silver bromide filtered. The filtrate was cooled to 20° and 1.5 g of Kα-*cis*-[CoCl$_2$(edda)]·H_2O dissolved rapidly with stirring. The solution was cooled in ice and (+)[Co(C_2O_4)(en)$_2$](–)α-*cis*-[CoCl$_2$(edda)] filtered (I) after 10 min. Yield 1 g. The diastereoisomer (1 g) and NaClO$_4$ (3 g) were stirred in 5 ml of ice cold water and the (+)[Co(C_2O_4)(en)$_2$]ClO$_4$ filtered. Na(–)α-*cis*-[CoCl$_2$(edda)]·2H_2O was precipitated by the addition of ethanol to the filtrate. This was filtered, washed with ethanol and acetone and dried over magnesium perchlorate. Yield 0.5 g. Anal. Calc. for Na(–)α-*cis*-[CoCl$_2$(edda)]·2H_2O: C, 19.9; H, 3.9; N, 7.7; Cl, 19.5%. Found: C, 19.6; H, 3.6; N, 7.7; Cl, 19.3%.

NaClO$_4$ (3 g) was added to the filtrate (I) and the (+)[Co(C_2O_4)(en)$_2$]ClO$_4$ filtered. Ethanol was added to the filtrate to precipitate Na(+)α-*cis*-[CoCl$_2$(edda)] which was filtered, washed with ethanol and acetone and dried over magnesium perchlorate. Yield 0.3 g.

(viii) Hβ-cis-[CoCl$_2$(edda)]·H$_2$O

(+)[Co(C_2O_4)(en)$_2$]Br·H_2O (2 g) and AgCH$_3$COO (0.9 g) in 30 ml of water were heated at 60° for 10 min and the AgBr filtered. The filtrate was cooled in ice and 2 g of Hβ-*cis*-[CoCl$_2$(edda)]·H_2O added with stirring. The solution was rapidly filtered and the filtrate cooled in ice. (+)[Co(C_2O_4)(en)$_2$](+)β-*cis*-[CoCl$_2$(edda)] (1.2 g) was filtered after 10 min. The diastereoisomer (1.2 g) and NaClO$_4$ (3 g) were stirred in 6 ml of ice-cold water and the (+)[Co(C_2O_4)(en)$_2$]ClO$_4$ filtered. The addition of ethanol to the filtrate precipitated Na(+)β-*cis*-[CoCl$_2$(edda)] which was filtered washed with ethanol and acetone and dried over magnesium perchlorate. Yield 0.5 g. Anal. Calc. for Na(+)β-*cis*-[CoCl$_2$(edda)]: C, 20.9; H, 3.5; N, 8.1%. Found: C, 20.8; H, 3.9; N, 8.3%.

(ix) [Co(CH$_2$(COO)$_2$)(edda)]$^-$ complexes

The potassium salt of the α-*cis* isomer was resolved following Van Saun and Douglas[2] and isolated as the sodium salt. Anal. Calc. for Na(+)α-*cis*-[Co(CH$_2$(COO)$_2$)(edda)]·3H_2O: C, 26.2; H, 4.4; N, 6.8%. Found: C, 25.8; H, 4.0; N, 6.6%.

The β-*cis* isomer was resolved by heating 0.6 g of (+)[Co(C_2O_4)(en)$_2$]Br·H_2O and 0.8 g of Agβ-*cis*-[Co(CH$_2$(COO)$_2$)(edda)]·H_2O in 6 ml of water at 50° for 5 min. The filtered AgBr was washed with 2 ml of water and the total filtrate cooled in ice. The diastereoisomer (+)[Co(C_2O_4)(en)$_2$](+)β-*cis*-[Co(CH$_2$(COO)$_2$)(edda)]·2H_2O (0.2 g) was filtered after 90 min, and washed with ethanol and ether. Anal. Calc. for (+)[Co(C_2O_4)(en)$_2$](+)β-*cis*-[Co(CH$_2$(COO)$_2$)(edda)]·2H_2O: C, 28.2; H, 5.1; N, 13.2%. Found: C, 27.7; H, 4.8; N, 13.4%.

C. Physical Measurements

Carbon, hydrogen and nitrogen analyses were carried out by Australian Microanalytical Services, chloride analysis by potentiometric titration, and cobalt analyses by electrodeposition.

Visible spectra were recorded on a Perkin Elmer 450 spectrophotometer.

Infrared spectra were recorded of Nujol and fluorolube mulls using a Unicam SP.200G spectrophotometer.

All pmr spectra were recorded on a Varian A–60 spectrometer at probe temperature in 99.75% (Australian Atomic Energy Commission) D_2O as solvent.

Chemical shifts were recorded relative to t-BuOH as internal standard, which is shifted 1.233 ppm downfield of sodium 2,2-dimethyl-2-silapentane-5-sulphonate. Acidification was by concentrated aqueous HNO_3 and Na_2CO_3 was added to achieve basic conditions.

Optical rotatory dispersion spectra were measured using an ORD attachment with the Perkin Elmer 450 spectrophotometer. The sign of the rotation is described as (+) or (–) for the sodium D line. Chloro complexes were studied in cold $0.01M$ $HClO_4$ immediately after solution. Diaqua complexes were studied in $0.01M$ $HClO_4$ and dinitro, carbonato, and malonato complexes in water. Solutions of the *β-cis* malonato complex were made by dissolving the diastereoisomer $(+)[Co(C_2O_4)(en)_2](+)$*β-cis*-$[Co(CH_2(COO)_2)(edda)]\cdot 2H_2O$ in $0.5M$ $NaClO_4$ and filtering off the precipitated $(+)[Co(C_2O_4)(en)_2]ClO_4$.

Results and Discussion

A. Visible and Infrared Spectra

The positions of two ligand field bands for each of the compounds are tabulated in Table I. The results confirm[4] in each case that the low energy band is at higher wavelengths for the *α-cis* than the *β-cis* isomer, and that the *β-cis* isomers (C_1 symmetry) have more intense spectra than their *α-cis* analogues (C_2 symmetry).

Infrared spectra, using the criteria of Busch *et al.*[24–26] were used to establish that both carboxylate groups of the edda ligand were coordinated. All the complexes were found to exhibit bands at 1630 cm^{-1}, characteristic of the coordinated COO stretching band in cobalt(III) complexes.[27] Although infrared spectra was found useful to distinguish geometric isomers in the analogous trien complexes of cobalt(III),[28] this was not pursued here because of the more certain information provided by the pmr investigations.

B. Pmr Spectra

Pmr has been used extensively in the characterisation of metal chelates containing aminocarboxylate ligands.[2–5,8,29–42] Kula *et al.*[34] reported the general effect[3] that the glycinate methylenic protons resonate at lower fields than the E ring protons. This results from the combined deshielding of the glycinate protons by the carboxylate and amine groups, while the ethylenic protons are influenced only by the inductive effect of the amine groups. In complexes in which the glycinate rings are fixed the methylenic protons may be in different chemical environments, producing a symmetrical AB quartet. Where R and G rings are present two overlapping AB patterns occur.[35,41,43]

Busch and Williams[36] observed the exchange of the glycinate methylenic protons of $[Co(edta)]^-$ [a] in slightly alkaline D_2O. The enhanced acidity of the glycinate methylenic protons is general for aminocarboxylate chelates. The R ring protons exchange more readily but in alkaline solution the G ring protons also undergo deuteration.[4,8,36]

The configuration of some $[CoX_2(edda)]^{\pm}$ complexes have been unequivocally assigned from their pmr spectra.[2–5] The *α-cis* isomers (two R rings) give only one AB quartet while the *β-cis* (one R and one G ring) show two AB patterns. The pmr results from this work are summarised in Table II.

(i) α-cis isomers

Consistent with the above[2–5] the *α-cis* isomers of the carbonato, diaqua, dichloro, and dinitro complexes showed a single AB quartet (just upfield from the HOD peak) and a symmetrical AA'BB' pattern further upfield. (The spectrum of *α-cis*-$[Co(edda)(OH_2)_2]^+$, Figure 4, is typical). The R ring methylenic protons are designated H_A and H_B following Legg and Cooke's assignment[3] which has been confirmed by Sudmeier and Occupati.[8] The coupling constant of 18 cps is typical of R ring methylenic protons.[2–5] The E ring protons give an AA'BB' pattern because of the different chemical shifts of the axial and equatorial protons.

The amine protons exchanged rapidly in neutral D_2O but in acid solution exhibit a broad peak centred about 7.5 ppm. The spectrum of *α-cis*-[Co(edda)

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[a] edta = ethylenediaminetetraacetate.

TABLE I. Band maxima of the visible spectra of some [CoXY(edda)] complexes.[a]

Complex	*α-cis*				*β-cis*			
	λ_1	ε_{λ_1}	λ_2	ε_{λ_2}	λ_1	ε_{λ_1}	λ_2	ε_{λ_2}
$[Co(CO_3)(edda)]^-$	565	114	382	128	533	234	390	182
$[Co(edda)(OH_2)_2]^+$	537	136	387	75	515	180	383	137
$[Co(NO_2)_2(edda)]^-$	510	153	–	–	468	238	–	–
$[CoCl_2(edda)]^-$	588	184	416	134	575	171	416	170
$[CoCl(edda)(OH_2)]$	564	150	402	100	542	157	400	165
$[Co(mal)(edda)]^-$	560	134	386	110	526	202	383	172

[a] Wavelength (λ) in nm. Extinction coefficient (ε) in l mol^{-1} cm^{-1}.

TABLE II. Chemical shifts (δ) of the glycinate ring methylene protons in various $[CoX_2(edda)]^{\pm}$ complexes.[a]

Complex	R rings[b]		G rings[c,d]	
	δ_{HA}	δ_{HB}	δ_{HA}	δ_{HB}
α-*cis*-$[Co(CO_3)(edda)]^-$	4.18 (0.88)[e]	3.30		
α-*cis*-$[CoCl_2(edda)]^-$	4.16 (1.04)	3.12		
α-*cis*-$[Co(NO_2)_2(edda)]^-$	4.31 (1.04)	3.27		
α-*cis*-$[Co(edda)(OH_2)_2]^+$	4.07 (0.88)	3.19		
β-*cis*-$[Co(NO_2)_2(edda)]^-$	4.14 (1.09)	3.05	3.65	
β-*cis*-(*SR,RS*)-$[Co(CO_3)(edda)]^-$	3.93 (0.90)	3.03	3.57 (0.13)	3.44
β-*cis*-(*SS,RR*)-$[Co(CO_3)(edda)]^-$	3.76 (0.73)	3.03		
β-*cis*-(*SR,RS*)-$[Co(edda)(OH_2)_2]^+$	4.20 (0.88)	3.32	3.55 (0.22)	3.33
β-*cis*-(*SS,RR*)-$[Co(edda)(OH_2)_2]^+$	4.09 (0.79)	3.30		

[a] Values in ppm from T.M.S. [b] J_{AB} for R ring protons of α-*cis* and β-*cis* isomers was 17–18 cps. [c] For G ring protons J = 16.8 cps for β-*cis*-(*SR,RS*)-$[Co(CO_3)(edda)]^-$, J = 15.6 cps for β-*cis*-(*SR,RS*)-$[Co(edda)(OH_2)_2]^+$. [d] Where an AB quartet was observed for the G ring protons the low field proton has been designated H_A in accordance with nomencalature already devised.[4,30] [e] $\delta_{H_A}-\delta_{H_B}$.

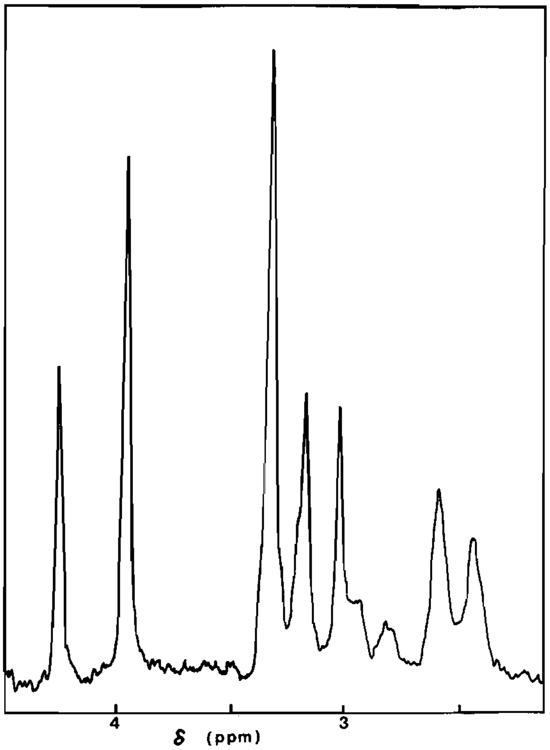

Figure 4. Pmr spectrum of α-*cis*-$[Co(edda)OH_2)_2]^+$ in D_2O.

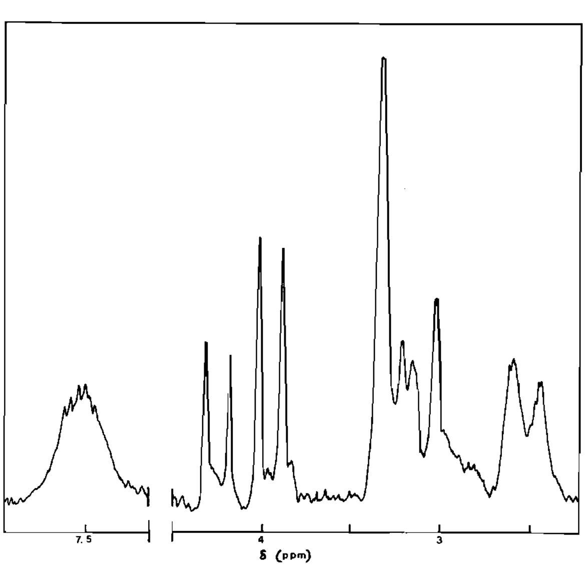

Figure 5. Pmr spectrum of α-*cis*-$[Co(edda)(OH_2)_2]^+$ in 0,1*M* DNO_3.

$(OH_2)_2]^+$ in 0.1*M* DNO_3 is shown in Figure 5. In addition to the N–H peak at 7.5 ppm the vicinal acetate proton resonances have been split due to coupling with the N–H protons. For the low field H_A protons J = 7.2 cps but the high field H_B resonances are only broadened. This is consistent with the smaller H–N–C–H_A dihedral angle compared with the H–N–C–H_B dihedral angle, providing the Karplus Equation[43] is applicable to H–N–C–H couplings.

(ii) β-cis isomers

The spectrum of β-*cis*-$[Co(NO_2)_2(edda)]^-$ consists of a single intense peak (3.65 ppm) superimposed on an AB pattern (4.31, 4.01, 3.18 and 2.88 ppm) with a complex ABCD pattern at higher field strength (Figure 6). This is similar to the spectra observed for the β-*cis* isomers of the oxalato, malonato and ethylene-diamine complexes.[4]

The AB pattern, assigned to the R ring protons, is similar to the AB quartets observed for the α-*cis* isomers. Selective deuteration of the low field H_A protons in the malonato, oxalato and ethylenediamine complexes provides additional support for the assignment.[4]

The intense peak at 3.65 ppm with an integrated value of two protons is assigned to the G ring protons. These protons are in different chemical environments from the R ring protons and should give rise to a separate AB quartet, as was found for the $[Co(edta)]^-$ complex.[34] The singlet is an extreme case of an AB system in which the environments of the two protons are virtually identical. Legg *et al.*[3] proposed that the G ring protons are symmetrically disposed with respect to the neighbouring carbonyl group and more symmetrically disposed with respect to the adjacent E ring N–C bond than the R ring protons. This accounts for

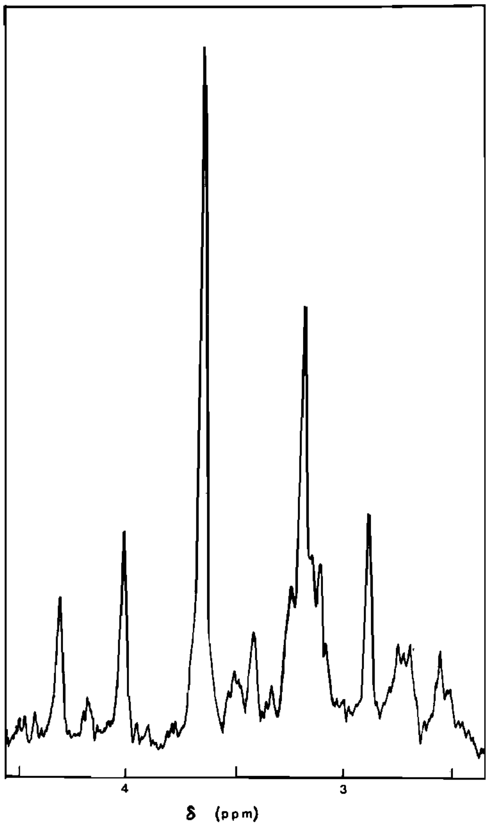

Figure 6. Pmr spectrum of β-*cis*-$[Co(NO_2)_2(edda)]^-$ in D_2O.

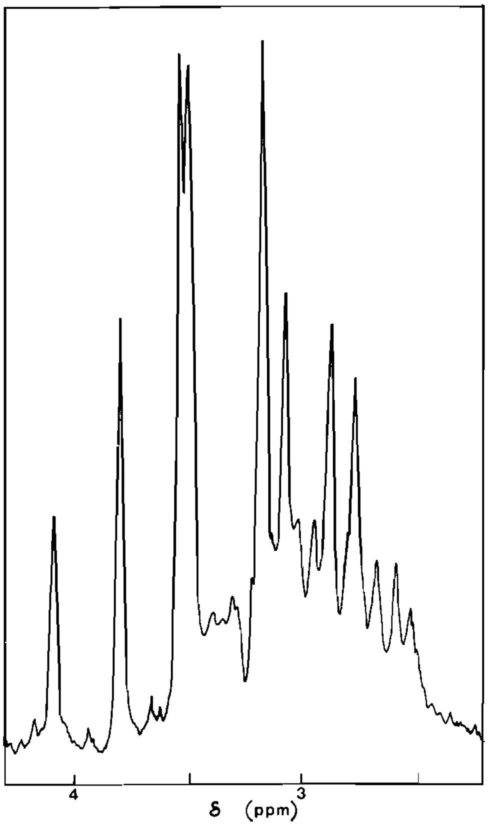

Figure 7. Pmr spectrum of β-*cis*-$[Co(CO_3)(edda)]^-$ in 0,01*M* DNO_3.

the similar chemical environments of the G ring protons.

The unsymmetrical ABCD pattern found at higher fields is expected for E ring protons as in the β-*cis* isomer the two proton sets are not equivalent.

In the spectrum of β-*cis*-$[Co(NO_2)_2(edda)]^-$ in acidified D_2O, as with the α-*cis* complexes, the low field R ring resonances are split (J = 7.8 cps) while the H_B resonances are only broadened. The singlet at 3.65 ppm is also split (J = 8.4 cps) into a doublet (3.72 ppm and 3.58 ppm), confirming this to be a G ring resonance.

The spectra of β-*cis*-$[Co(CO_3)(edda)]^-$ in 0.01*M* DNO_3 and neutral D_2O are shown in Figures 7 and 8. The DNO_3 converted a small amount (<2%) of the carbonato complex to β-*cis*-$[Co(edda)(OH_2)_2]^+$ but the solution remained acidic.

The acid spectrum, Figure 7, exhibits an AB quartet (4.10, 3.80, 3.16 and 2.86 ppm) due to the R ring protons. The low field H_A protons integrate to a value of one proton but the high field signals overlap with an ABCD pattern due to the ethylene backbone (E ring) and could not be accurately integrated. The upfield H_B protons are assigned to the resonances at 3.16 and 2.86 ppm. These resonances decrease in intensity in alkaline solution whereas those at 3.07 and 2.77 ppm remain constant after an initial decrease in intensity due to complicating isomerisation reactions. When the spectrum is measured in 0.1*M* DNO_3 the low field H_A protons are split (J = 7.2 cps) and a broad peak attributed to the N–H protons appears at 6.5 ppm.

The closely spaced peaks at 3.52 and 3.49 ppm are assigned to the two centre peaks of an AB quartet of the G ring protons. As the chemical shifts of the protons in an AB system become closer, the two centre peaks increase in intensity at the expense of the outside peaks.[44] In Figure 7 the two centre peaks integrate to a value of 1.8 protons but the weak side peaks are difficult to locate with certainty. A small shoulder is discernible at 3.21 ppm and if this is the high field outside peak of the quartet the other resonance should occur at 3.80 ppm which corresponds with an R ring resonance. The spectrum of the β-*cis* carbonato complex differs from that of the β-*cis* dinitro complex in that the chemical shifts of the G ring protons are sufficiently different to observe an AB pattern whereas in the dinitro spectrum a single intense peak was observed.

The spectrum of β-*cis*-$[Co(CO_3)(edda)]^-$ in neutral D_2O (Figure 8) contains resonances not present in a freshly prepared acid solution. The spectrum in acidified D_2O changes to that observed in neutral so-

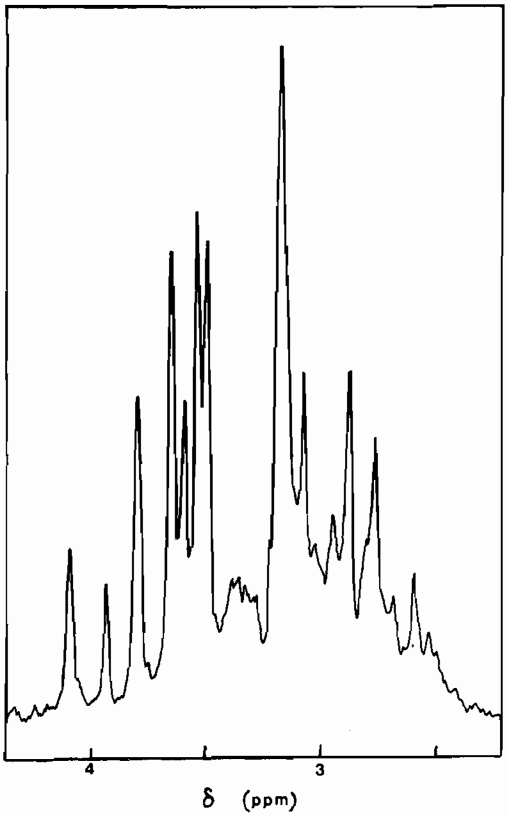

Figure 8. Pmr spectrum of β-*cis*-$[Co(CO_3)(edda)^-$ in D_2O.

lution at a rate which is inversely dependent on hydrogen ion concentration. The kinetics of this process have been studied and will be reported later. The peaks at 4.10, 3.80, 3.52 and 3.49 ppm (Figure 7) decrease, accompanied by the appearance of peaks at 3.93, 3.65 and 3.60 ppm (Figure 8). The peak at 3.16 ppm broadens and in Figure 8 a shoulder is evident at 3.14 ppm. In neutral D_2O the peaks at 4.10 and 3.80 ppm integrate to a value of 0.6 protons compared with one proton for the initial spectrum in acidified D_2O. Clearly a second species is formed and in neutral D_2O solutions, equilibrium is attained before spectral measurement.

The possible existence of two β-*cis* isomers arising from the mode of coordination of the planar *sec*-N atom was discussed earlier. It is postulated that the two species present in a solution of the β-*cis* carbonato complex are the β-*cis*-(*SR,RS*) and β-*cis*-(*SS,RR*) forms. The additional peaks in Figure 8 which are due to the second β-*cis* isomer are assigned as follows. The resonances at 3.93 and 3.65 ppm (J = 17 cps) constitute the low field half of an AB quartet due to the R ring protons. The upfield resonances are placed at 3.14 (shoulder) and 2.86 ppm but cannot be assigned with certainty. The resonances at 3.65 (coincident with an R ring resonance) and 3.60 ppm constitute the central peaks of an AB pattern in which the chemical shifts of the two protons are similar. The weaker outside peaks cannot be located. When a solution of β-*cis*-$[Co(CO_3)(edda)]^-$ is made alkaline, all the resonances which have been attributed to the R and G ring protons of both β-*cis* forms eventually exchange with the D_2O, confirming their assignments as acetate protons. Detailed information on the relative rates of deuteration of these protons could not be determined due to accompanying partial isomerisation to the α-*cis* isomer.

The possibility that the second species in solution arose from the dissociation of an acetate arm is extremely unlikely. In $[Co(edta)]^-$ the dissociation of an acetate arm is favoured in acidic solutions[31,45–47] whereas this process is retarded in acid solution.

It has been established that the initial rupture of a Co–O bond is the rate determining step in the aquation of carbonato complexes[48] and large concentrations of carbonatoaqua species (in which the carbonate is monodentate) are not formed. If the second species in solution was the carbonatoaqua complex, treatment of a solution of the two species with excess acid would convert both the carbonato and carbonatoaqua species to the diaqua complex and it should be possible to interpret the resulting spectrum in terms of a single β-*cis* diaqua species, but this is not so.

Thus pmr evidence indicates that the solid Kβ-*cis*-$[Co(CO_3)(edda)]\cdot H_2O$ isolated consists of one form but when dissolved in aqueous solution it reacts rapidly to establish an equilibrium with a second form. It was not possible to assign the β-*cis*-(*SS,RR*) or β-*cis*-(*SR,RS*) configuration to the solid form on the basis of the pmr spectra. However an x-ray structure determination on β-*cis*-$[Co(edda)(OH_2)_2]ClO_4$ indicates the solid carbonato is the β-*cis*-(*SR,RS*) racemate.[a]

The spectrum of β-*cis*-$[Co(edda)(OH_2)_2]^+$ in D_2O (Figure 9) is similar to the initial spectrum of the β-*cis* carbonato complex in acidified D_2O. The AB quartet (4.37, 4.07, 3.44 and 3.14 ppm) is assigned to the R ring protons. A second AB pattern (3.74, 3.48, 3.40 and 3.14 ppm), superimposed on the first, is assigned to the G ring protons. The coupling constant for these protons is 15.6 cps. The coupling constants for the G ring protons in $[Co(edta)]^{-29}$ and $[Co(NO_2)(ed3A)]^{-30,b}$ are both 16 cps whereas the coupling constants of most R ring protons are about 18 cps (Table II).

The spectrum of β-*cis*-$[Co(edda)(OH_2)_2]^+$ in acidic D_2O is shown in Figure 10. The N–H protons

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[a] We are grateful to cand. scient. B. L. Pedersen and Dr. K. J. Watson, Department of Physical Chemistry, H.C. Orsted Institute, University of Copenhagen, for making the structure determination. Detailed results of this analysis will be published separately. [b] ed3A ≡ ethylenediaminetriacetate.

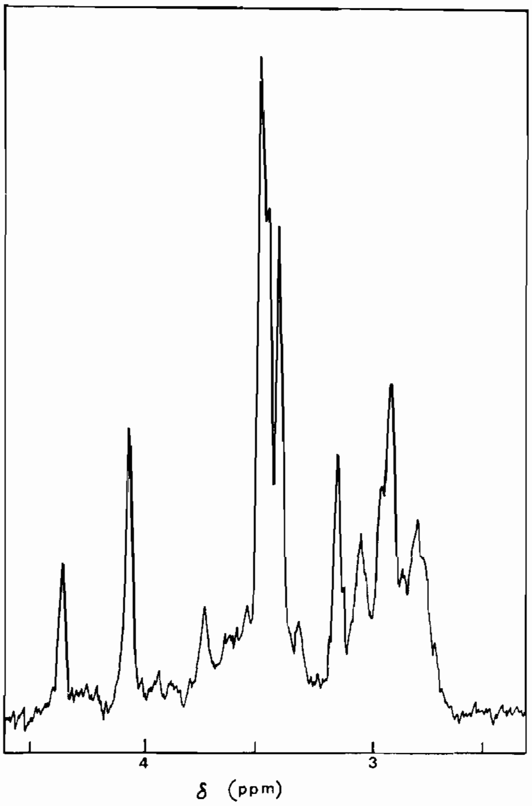

Figure 9. Pmr spectrum of *β-cis*-[Co(edda)$(OH_2)_2$]$^+$ in D_2O.

cause splitting of the low field R ring proton resonances (J = 7.2 cps) as described for *α-cis*-[Co(edda)$(OH_2)_2$]$^+$ and *β-cis*-[Co$(NO_2)_2$(edda)]$^-$. Splitting of the G ring proton resonances is also evident. In neutral D_2O the peaks at 3.48 and 3.40 ppm are assigned to the inner peaks of an AB quartet and the shoulder at 3.44 ppm to an upfield resonance due to the R ring H_B protons. In acidic D_2O peaks are present at 3.55, 3.47, 3.42 and 3.37 ppm and as N–H coupling does not produce significant splitting of the R ring H_B proton resonances[8] it can be concluded that the G ring proton resonances have been split.

When a sample of K*β-cis*-[Co(CO_3)(edda)]·H_2O was dissolved in 1*M* DNO_3 (which converts the carbonato to the diaqua complex) it gave a pmr spectrum which, after amine proton exchange, was indistinguishable from the spectrum obtained by dissolving *β-cis*-[Co(edda)$(OH_2)_2$]ClO_4 in D_2O. When K*β-cis*-[Co(CO_3)(edda)]·H_2O was dissolved in cold D_2O and immediately (before the second carbonato species could form) treated with excess acid the spectrum was again indistinguishable from that obtained by dissolving *β-cis*-[Co(edda)$(OH_2)_2$]ClO_4 in D_2O. However if a D_2O solution of K*β-cis*-[Co(CO_3)(edda)]·H_2O was allowed to stand for five minutes (so that an equilibrium mixture of the two *β-cis* carbonato isomers formed) and then treated with excess acid, the spectrum shown in Figure 11 resulted. Clearly this solution contains two species. As for the carbonato isomers complete assignment of the spectrum is difficult. An AB quartet (4.26, 3.97, 3.42 and 3.13 ppm) is assigned to the R ring protons of the new species. The peak at 3.48 ppm must belong to the G ring protons but a complete assignment is not possible. When a solution containing the two species is allowed to stand for 24 hr the spectrum changes until it becomes identical with one obtained from a solution of the solid diaqua complex.

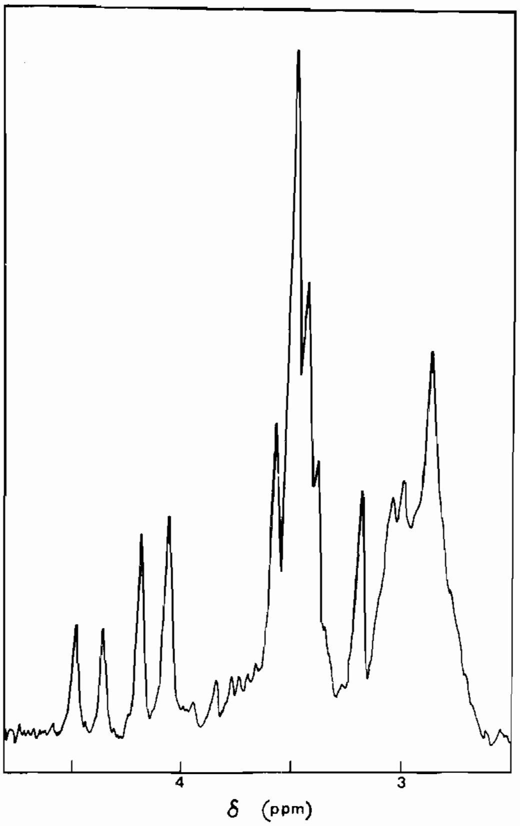

Figure 10. Pmr spectrum of *β-cis*-[Co(edda)$(OH_2)_2$]$^+$ in 0,1*M* DNO_3.

When a solution of *β-cis*-[Co(edda)$(OH_2)_2$]$^+$ is treated with excess sodium bicarbonate the resultant solution has a spectrum identical with that in Figure 8, that is the solution contains both forms of *β-cis*-[Co(CO_3)(edda)]$^-$. This is expected as alkaline conditions facilitate interconversion between the *β-cis*-(*SR,RS*) and *β-cis*-(*SS,RR*) forms.

Pmr indicates that the solid *β-cis*-[Co(edda)$(OH_2)_2$]ClO_4 isolated consists of one form which is also the more stable in aqueous solution. It was not possible to establish which isomer this is on the basis of the pmr spectra but the x-ray structure determination indicates it is the *β-cis*-(*SR,RS*) racemate.

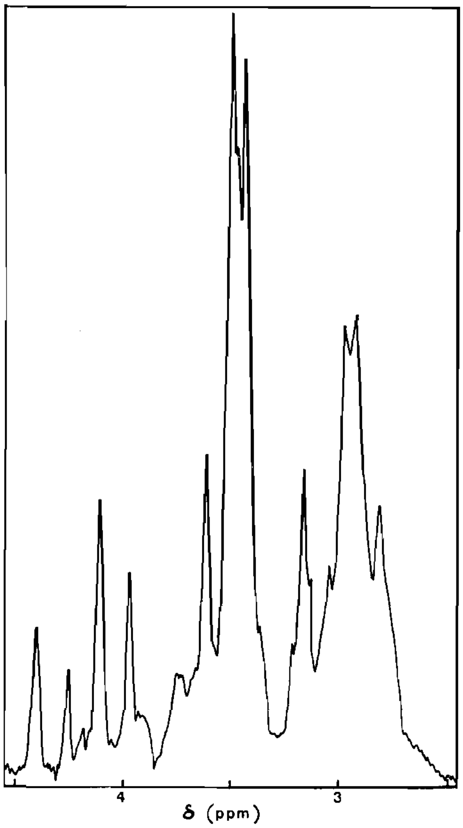

Figure 11. Pmr spectrum of aged (5 min) β-cis-$[Co(CO_3)(edda)]^-$ in D_2O after acidification (that is of a mixture of β-cis-(SR,RS) and β-cis-(SS,RR)-$[Co(edda)(OH_2)_2]^+$.

C. Optical Rotatory Dispersion Spectra

Sargeson and Searle[9] ascertained the absolute configuration of some α-cis- and β-cis-$[CoX_2(trien)]^{n+}$ complexes by relating their RD and CD curves through those of the bisethylenediamine analogues to those of Λ-$[Co(en)_3]^{3+}$. The optical isomers of both the α-cis and β-cis forms can be related to Λ- and Δ-$[CoX_2(en)_2]^{n+}$ and hence Λ and Δ-$[Co(en)_3]^{3+}$ by elimination of the central ethylene bridge. A dominant positive Cotton Effect for the long wavelength visible absorption band was indicative of a Λ configuration. This has been given theoretical support for complexes of C_2 symmetry.[49] The α-cis trien complexes are of C_2 symmetry but the β-cis complexes possess C_1 symmetry. However the R.D. curves of the β-cis complexes were similar to those of the α-cis and bisethylenediamine complexes and approximate C_2 symmetry was assumed.

The R.D. curves of the α-cis-$[CoX_2(edda)]^{\pm}$ complexes are shown in Figure 12. All the curves are of the same form and show displacements constistent with the positions of the ligands in the spectrochemical series. The complexes possess C_2 symmetry and the

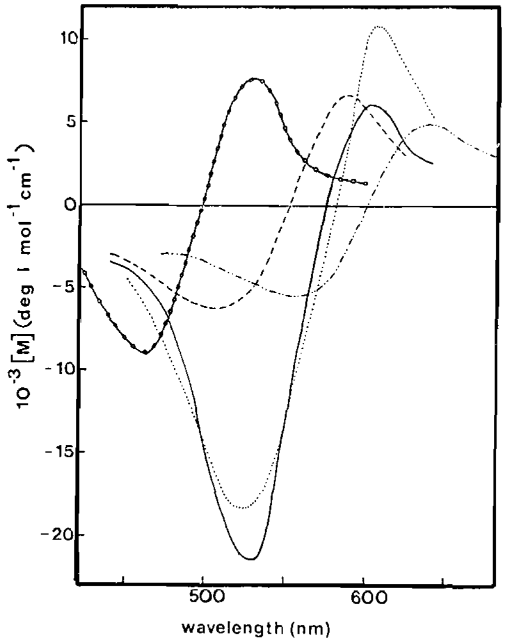

Figure 12. R.D. spectra of Λ-α-cis-$[CoX_2(edda)]^{\pm}$ complexes. ——— $[Co(mal)(edda)]^-$. ----------- $[Co(edda)(OH_2)_2]^+$. ······· $[Co(CO_3)(edda)]^-$ —··—··— $[CoCl_2(edda)]^-$. -o-o-o-o- $[Co(NO_2)_2(edda)]^-$

positive Cotton Effects are therefore diagnostic of a Λ configuration. Van Saun and Douglas[2] have made similar assignments of absolute configuration for the carbonato and malonato complexes by a comparison of their C.D. curves with those reported by Legg *et al.*[5] on other edda complexes. Additional evidence for the assignment is furnished by a combined pmr, R.D. and C.D. study of the optical isomers of a series of complexes containing the asymmetric tetradentate ligands ethylenediamine-N,N'-di-L-α-propionate(LL-eddp) and ethylenediamine-N,N'-di-D-α-propionate(DD-eddp).[33] The absolute configurations of these complexes were assigned unequivocally from an analysis of the pmr spectra and a knowledge of the absolute configuration of the ligand. The R.D. and C.D. data reported showed the α-cis isomers assigned the Λ configuration exhibited a dominant positive Cotton Effect for the low energy visible absorption band. As edda and eddp are both tetradentate O–N–N–O ligands it seems certain that for analogous species a dominant positive Cotton Effect in the long wavelength visible absorption band will indicate the Λ configuration.

The R.D. curves of the β-cis isomers assigned a Λ configuration are shown in Figure 13. A dominant positive Cotton Effect associated with the low energy visible absorption band is attributed to a Λ absolute configuration on the following grounds. The R.D. curves are of the same general form as was observed for the α-cis isomers, the α-cis- and β-cis-$[CoX_2(trien)]^{n+}$

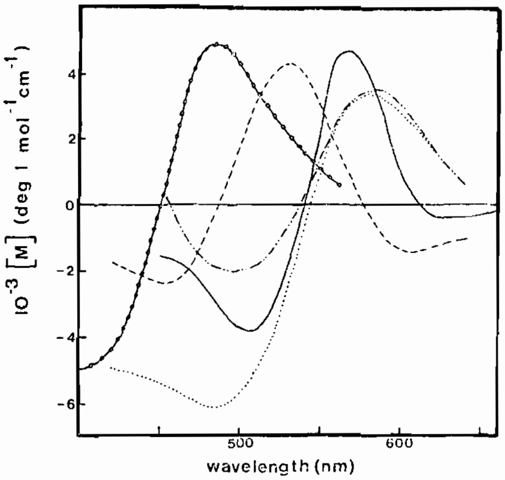

Figure 13. R.D. spectra of Λ-β-*cis*-$[CoX_2(edda)]^{\pm}$ complexes. ——— $[Co(mal)(edda)]^-$; ----------- $[Co(edda)(OH_2)_2]^+$; ······· $[Co(CO_3)(edda)]^-$; —··—··— $[CoCl_2(edda)]^-$; -o-o-o-o- $[Co(NO_2)_2(edda)]^-$

systems,[9] and the bisethylenediamine complexes.[11] In view of the similarity of the edda and trien chelate systems it is reasonable that in β-*cis*-$[CoX_2(edda)]^{\pm}$ complexes a dominant positive Cotton Effect should be associated with a Λ configuration. Legg and Douglas,[50] on the basis of a ring pairing method for relating the absolute configurations of octahedral chelate complexes of different symmetries, have predicted a dominant positive Cotton Effect would be associated with a Λ configuration in β-*cis*-$[CoX_2(edda)]^{\pm}$ complexes. Further evidence for the assignment is provided by the observation of a negative Cotton Effect for $\Delta\beta$-*cis*-$[Co(LL\text{-}eddp)(en)]^+$, the absolute configuration of which was established from a pmr study together with a knowledge of the absolute configuration of the ligand.[33]

The absolute magnitude of the Cotton Effect is clearly smaller for the β-*cis* than for the α-*cis* isomers. This effect was also observed in the trien system and was attributed[9] to the lower symmetry of the β-*cis* isomers.

Further evidence for the assignment of a common absolute configuration to complexes with similar R.D. curves was provided by a series of experiments based on reactions normally observed to occur with retention of configuration.[9,11,51] The reactions:

$$[CoCl_2(edda)]^- \xrightarrow{Hg^{2+},\ H_3O^+} [Co(edda)(OH_2)_2]^+$$

$$[Co(edda)(OH_2)_2]^+ \xrightarrow{HCO_3^-} [Co(CO_3)(edda)]^-$$

$$[Co(edda)(OH_2)_2]^+ \xrightarrow{NO_2^-} [Co(NO_2)_2(edda)]^-$$

$$[Co(CO_3)(edda)]^- \xrightarrow{H_3O^+} [Co(edda)(OH_2)_2]^+$$

all occur with retention of configuration, confirming that those complexes assigned a Λ configuration (within the α-*cis* or β-*cis* series) did in fact share a common configuration.

An attempt to show that Λ-β-*cis*-(*SS*)- and Λ-β-*cis*-(*SR*)-$[Co(edda)(OH_2)_2]^+$ had distinct R.D. spectra by comparing the spectra of an acidified solution of NaΛ-*B*-*cis*-(*SR*)-$[Co(CO_3)(edda)]\cdot 3H_2O$ with that of an aqueous solution acidified after equilibration of the Λ-β-*cis*-(*SR*) and Λ-β-*cis*-(*SS*) isomers was unsuccessful.

D. X-ray Structural Investigation

The x-ray structural investigation referred to earlier shows the β-*cis*-$[Co(edda)(OH_2)_2]ClO_4$ to be the Λ-β-*cis*-(*SR*), Δ-β-*cis*-(*RS*) racemate. This, together with the pmr evidence, establishes the solid β-*cis* carbonato complex isolated to be the (*SR,RS*) racemate. As the dichloro complexes were prepared in acidic conditions from the carbonato complexes (a medium normally giving retention of configuration at *sec*-N atoms) it seems certain that these salts are also (*SR, RS*) racemates.

The configurations of the asymmetric *sec*-N atoms in the β-*cis* dinitro and malonato complexes cannot be stated with certainty at this stage.

E. Stability of Edda Complexes

In this work no evidence was found for the *trans* configuration of edda. This is similar to the trien system,[20,52] where only *cis* configurations are stable in aqueous solution. This confirms that the existence of three coplanar consecutive linked chelate rings is associated with considerable strain.

Legg *et al.*[3,5,6] found that the α-*cis* configuration of edda was favoured almost exclusively where the remaining two positions were chelated diamine ligands. This was thought due to the greater non-bonding interactions between the amine ligand protons and edda in the β-*cis* isomers. In the oxalato and malonato complexes these interactions are eliminated thus enhancing β-*cis* stability. Greater yields of β-*cis* were found but a pmr study showed the α-*cis* isomers to be more stable in D_2O.[4]

In this study α-*cis*-$[Co(edda)(OH_2)_2]^+$ was found to be more stable than the β-*cis* isomer in aqueous solution. In D_2O the α-*cis* and β-*cis* dinitro and carbonato isomers were of similar stability.

Thus the presence of two coplanar consecutive linked chelate rings in the β-*cis* isomers does not appear to be necessarily unstable compared with the α-*cis* configuration in these $[CoX_2(edda)]^{\pm}$ complexes. Other factors such as interatomic interactions, the nature of X, and solvation effects all seem likely to influence the relative stability of these isomers.

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