Inorganica Chimica Acta, *157* (1989) 33–43

Diamine-*N*,*N*′-diacetatochromate(III) Complexes with Oxalate and Malonate Anions. Crystal Structure of $(-)_{589}$-[Co(en)$_2$(C$_2$O$_4$)]$\frac{1}{N}$$(-)_{546}$-[Cr(1,3-pdda)(mal)]·H$_2$O

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(Received July 13, 1988)

Abstract

The *uns-cis*-[Cr(1,3-pdda)(L)]$^-$ complexes (1,3-pdda = 1,3-propanediamine-*N*,*N*′-diacetate; L = oxalate or malonate) were prepared and resolved. The corresponding *s-cis*-[Cr(edda)L]$^-$ complexes (edda = ethylenediamine-*N*,*N*′-diacetate) have been partially resolved. The infrared absorption and circular dichroism (CD) spectra are reported. Rotational strengths of the *uns-cis*-[Cr(1,3-pdda)(L)]$^-$ complexes decrease with increasing chelate ring size of the bidentate anionic ligands. $(-)_{589}$-[Co(en)$_2$(C$_2$O$_4$)]*uns-cis*-$(-)_{546}$-[Cr(1,3-pdda)(mal)]·H$_2$O crystallizes in the space group $P2_1$ of the monoclinic crystal system with $a = 7.832(3)$, $b = 14.207(6)$, $c = 10.801(3)$ Å, $\beta = 98.46(3)°$ and $Z = 2$. In the anionic chromium complex, the six-membered diamine ring assumes the stable chair conformation; the equatorial glycinate ring is puckered; and the axial glycinate ring is in the 'envelope' conformation. The absolute configuration of the chromium complex ion is ΔΔΔΛ.

Introduction

The chromium(III) ion can be expected to form several isomeric complexes with edda type ligands as shown in Fig. 1 (edda = ethylenediamine-*N*,*N*′-diacetate; L can be one bidentate ligand or two monodentate ligands occupying the 5th and 6th coordination positions). These isomers are now commonly referred to as symmetrical-*cis*; unsymmetrical-*cis*; or *trans*, with the appropriate abbreviations shown in Fig. 1 [1]. The format for describing the various chelate rings formed in these kinds of complex ions has been credited to Weakliem and Hoard who applied it originally to the ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetatocobaltate(III) ion [2]. The ethylenediamine (en) ring is referred to as the E ring; the axially coordinated glycinate ring as the R ring; and the equatorially coordinated ring as the G ring. It is assumed that the G rings in these kinds of complexes are more strained than the R rings because the ring angle sum of the latter is closer to the expected value for a five-membered chelate ring with glycinate. The G rings are usually observed to be puckered while the R rings are observed to be more planar than the Gs and referred to as having an 'envelope' conformation.

The edda$\frac{1}{N}$Co(III) complexes have been prepared in both the *uns-cis* and *s-cis* geometries [3–18], but it has been suggested that the *s-cis* geometry of chelated edda is probably the more stable of the two because the *s-cis* complexes form in greater abundance [8, 16]. Similar results were obtained for the corresponding Cr(III) complexes that were studied [19, 20]. One rationale generally accepted to explain this circumstance is the difference in angle strain between a G ring and an R ring [18].

The ligands 1,3-propanediamine-*N*,*N*′-diacetate (1,3-pdda) and ethylenediamine-*N*,*N*′-di-3-propionate (eddp) are O–N–N–O type ligands similar to edda except that both can form six-membered chelate rings (diamine for the 1,3-pdda and carboxylate for the

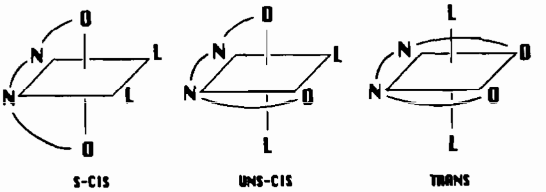

Fig. 1. The possible geometric isomers of a [ML$_2$(linear tetradentate)]$^{n\pm}$ complex.

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eddp ligand). Until recently, 1,3-pdda and eddp complexes were prepared only in the *uns-cis* geometry with Co(III) [21–25] (except where L = ethylenediamine) [23] and Cr(III) [26], but Bianchini *et al.* [27] have now reported the synthesis and characterization of all three isomers of the difluorocomplexes of Cr(III) with 1,3-pdda. That the *uns-cis* complex should form in preference to the *s-cis*, or indeed that the *trans* complex forms at all, appears to be inconsistent when the comparisons are made to the corresponding edda complexes, because the favored isomer here is almost always the *s-cis*. Furthermore, it is interesting to note that the coordination sphere of Cr(III) is larger than that of Co(III) so the effects caused by strain are expected to be enhanced in the case of Cr(III).

In this paper, we report the results of work aimed at trying to understand these apparent inconsistencies. We report and discuss the circular dichroism (CD) spectra of various 1,3-pdda and edda complexes with the Co(III) and Cr(III) ions. It has been well documented that information about a molecule's chiroptical properties can be an important source of insight regarding its stereochemistry. The CD spectra of complex ions can be affected by factors such as coordination geometry or the size of chelate rings. For example, it has been shown that the *s-cis*-[Co(edda)(L)]$^{n\pm}$ complexes are relatively insensitive to changes in the coordinated atoms or the ring size of the bidentate ligand, L. The CD spectra of the corresponding *uns-cis* complexes, however, show great changes depending on the chelate ring size formed by the bidentate ligand and whether the coordinated atoms of L are, N,N; N,O; or O,O [21, 22]. In addition, it was shown that the central chelate ring size of *uns-cis* complexes of edda and 1,3-pdda and the ring size of the bidentate ligands affects the shape of CD spectra in the same fashion. Rotational strengths decrease with increasing chelate ring size for the bidentate ligands and for the larger diamine ring of the framework of the 1,3-pdda complexes compared to those of edda [22]. The Cr(III) chromophore is different but comparable to that of Co(III) which has been the object of most of the chiroptical studies on metal complexes. It is, therefore, important to determine the reliability of applying theoretical tenets used for one system to describe another.

We report the infrared, absorption and CD spectral data as well as the crystallographic results for the following Cr(III) complexes: *s-cis*-[Cr(edda)(C_2O_4)]$^-$, *s-cis*-[Cr(edda)(mal)]$^-$, *uns-cis*-[Cr(1,3-pdda)(C_2O_4)]$^-$ and *uns-cis*-[Cr(1,3-pdda)(mal)]$^-$ (mal = malonate).

Experimental

1,3-Propanediamine-*N,N′*-diacetic acid dihydrochloride, $H_2$1,3-pdda·2HCl, was prepared by the method of Igi and Douglas [21]. Ethylenediamine-*N,N′*-diacetic acid, H_2edda, and other reagents obtained commercially were used without further purification.

Optical isomers are identified by the sign of the optical rotation at a wavelength, λ [$(+)_\lambda$ or $(-)_\lambda$] or by the sign of the lowest energy CD band, [(+) or (−)]. The chirality of the complex ion is assigned Δ or Λ according to IUPAC rules [28].

Preparation and Resolution of Potassium uns-cis-1,3-Propanediamine-N,N′-diacetatooxalatochromate(III) Monohydrate, Kuns-cis-[Cr(1,3-pdda)(C_2O_4)]·H_2O

A mixture of chromium chloride hexahydrate, $CrCl_3 \cdot 6H_2O$ (6.66 g, 2.50×10^{-2} mol) in 20 ml of water was added to 80 ml of an aqueous solution of $H_2$1,3-pdda·2HCl (6.58 g, 2.50×10^{-2} mol) and KOH (5.61 g, 0.100 mol) with heating and stirring. The resulting mixture was stirred and heated (*ca.* 90 °C) an additional 2 h by which time the solution became red–violet. A 4.60 g (2.50×10^{-2} mol) quantity of $K_2C_2O_4 \cdot H_2O$ in 30 ml of water was then added to the red–violet solution, and heating and stirring were continued for another 4 h. During the heating, the volume of this solution diminished but was maintained at *ca.* 30 ml by the addition of hot water when necessary. The solution was allowed to stand overnight in a refrigerator. The crystals of K*uns-cis*-[Cr(1,3-pdda)(C_2O_4)]·H_2O were collected on a filter, washed with ethanol, then ether and air dried. Yield: 6 g (60%). The complex was recrystallized from hot water. *Anal.* Calc. for K[Cr(1,3-pdda)(C_2O_4)]·H_2O, $KCrC_9H_{14}O_9N_2$ (FW = 385.31): C, 28.05; H, 3.66; N, 7.27. Found: C, 28.14; H, 3.85; N, 7.26%.

Resolution was accomplished by dissolving 1.93 g (5.00×10^{-3} mol) of K*uns-cis*-[Cr(1,3-pdda)(C_2O_4)]·H_2O in 10 ml of water and converting it to the corresponding silver salt via cationic exchange chromatography. To the resulting eluate was added 1.82 g (5.00×10^{-3} mol) of $(-)_{589}$-[Co(en)$_2$(C_2O_4)]Br·H_2O, and the suspension was warmed to *ca.* 60 °C for 30 min with stirring. The AgBr was filtered and washed with 5 ml of warm water. The filtrate and washings were combined, concentrated to *ca.* 12 ml and left to stand at room temperature overnight. The less soluble diastereoisomer, $(-)_{589}$-[Co(en)$_2$(C_2O_4)]$\frac{1}{N}(-)_{546}$-[Cr(1,3-pdda)(C_2O_4)]·$3H_2O$ was removed by filtration, washed with ethanol, then ether and air dried (*ca.* 0.9 g). The more soluble diastereoisomer, (*ca.* 0.85 g) $(-)_{589}$-[Co(en)$_2$(C_2O_4)]$\frac{1}{N}(+)_{546}$-[Cr(1,3-pdda)(C_2O_4)]·$4H_2O$ was isolated by allowing the filtrate to stand in a refrigerator for 6 h. Both diastereoisomers were recrystallized from small amounts of water at room temperature to constant values of optical rotation. Aqueous solutions (0.100%) gave $[\alpha]_{546} = -1585°$ ($[M]_{546} = -10290°$)

and $[\alpha]_{546}$ = +512° ($[M]_{546}$ = +3417) for the less and more soluble diastereoisomers, respectively. *Anal.* Calc. for $(-)_{589}$-[Co(en)$_2$(C$_2$O$_4$)]$\frac{1}{N}$$(-)_{546}$-[Cr(1,3-pdda)(C$_2O_4$)]·3H$_2$O, $\mathrm{CoCrC_{15}H_{34}O_{15}N_6}$, FW = 649.39: C, 27.74; H, 5.27; N, 12.94; H$_2$O, 8.32. Found: C, 27.31; H, 5.84; N, 12.92; H$_2$O, 7.40%. Calc. for $(-)_{589}$-[Co(en)$_2$(C$_2$O$_4$)]$\frac{1}{N}$$(+)_{546}$-[Cr(1,3-pdda)(C$_2O_4$)]·4H$_2$O, $\mathrm{CoCrC_{15}H_{36}O_{16}N_6}$, FW = 667.40: C, 26.99; H, 5.44; N, 12.59; H$_2$O, 10.79. Found: C, 27.34; H, 5.53; N, 12.73; H$_2$O, 9.80%.

The optical isomers of the [Cr(1,3-pdda)(C$_2$O$_4$)]$^-$ complex were obtained by dissolving each of the diastereoisomers in water and passing the solutions through a cation-exchange column in the K$^+$ form. The eluates were evaporated to dryness at room temperature. $[\alpha]_{546}$ = ±1730° in 0.100% solutions. *Anal.* Calc. for K$(-)_{546}$-*uns-cis*-[Cr(1,3-pdda)(C$_2$O$_4$)]·H$_2$O, $\mathrm{KCrC_9H_{14}O_9N_2}$, FW = 385.31: C, 28.05; H, 3.66; N, 7.27. Found: C, 28.30; H, 3.62; N, 7.39%. After recrystallization from warm water, the optical isomers slowly lost their optical activity. The specific rotations decreased from ±1730° to zero after standing in aqueous solution at room temperature for 7 days.

Preparation and Resolution of Barium uns-cis-1,3-Propanediamine-N,N'-diacetatomalonatochromate(III) Octahydrate, Bauns-cis-[Cr(1,3-pdda)(mal)]$_2$·8H$_2$O

A mixture of chromium chloride hexahydrate, CrCl$_3$·6H$_2$O (6.66 g, 2.50 × 10^{-2} mol) in 20 ml of water was added to an 80 ml aqueous solution of H$_2$1,3-pdda·2HCl (6.58 g, 2.50 × 10^{-2} mol) and KOH (5.61 g, 0.100 mol) with heating and stirring. Heating to about 90 °C was continued with stirring for 2 h by which time the solution became distinctly red–violet. A 30 ml aqueous solution containing 2.60 g (2.50 × 10^{-2} mol) of malonic acid plus 2.80 g (5.00 × 10^{-2} mol) of KOH was then added to the red–violet solution and heating and stirring continued for a further 4 h. During the heating, the volume was reduced to *ca.* 50 ml and maintained at this level by the addition of warm water. The reaction mixture was cooled, filtered off, and then added to a 5 × 30 cm column containing Dowex 1-X8 (200–400 mesh) anion-exchange resin in the Cl$^-$ form. The column was washed with H$_2$O and eluted with 0.05 M BaCl$_2$ solution (*ca.* 0.5 ml/min). One only band (red–violet) developed, and after elution, the resulting solution was desalted by passing it through a G-10 Sephadex column (2.5 × 40 cm). The eluate was concentrated to a volume of 8 ml on a water bath and allowed to stand in a refrigerator overnight. The crystals of Ba*uns-cis*-[Cr(1,3-pdda)(mal)]$_2$·8H$_2$O were collected by filtration, washed with ethanol, then ether and air dried. Yield: *ca.* 4.5 g. After adding ethanol to the filtrate and cooling, more of the complex was obtained (~1 g). The complex loses all of its water of crystallization when stored over anhydrous CaCl$_2$ for 4 days. *Anal.* Calc. for Ba[Cr(1,3-pdda)(mal)]$_2$, $\mathrm{BaCr_2C_{20}H_{28}O_{16}N_4}$, FW = 821.79: C, 29.23; H, 3.43; N, 6.82. Found: C, 28.66; H, 3.88; N, 7.04%.

Resolution was accomplished by dissolving 2.41 g (2.50 × 10^{-2} mol) of Ba*uns-cis*-[Cr(1,3-pdda)(mal)]$_2$·8H$_2$O in 10 ml of water and converting it to the corresponding silver salt via cationic exchange chromatography. A 1.82 g (5.00 × 10^{-3} mol) quantity of $(-)_{589}$-[Co(en)$_2$(C$_2$O$_4$)]Br·H$_2$O was added to the eluate after it was warmed to 60 °C. The AgBr was filtered, washed with 2 ml of warm water, and the filtrate in combination with the wash was allowed to stand in a refrigerator overnight. The less soluble diastereoisomer, $(-)_{589}$-[Co(en)$_2$(C$_2$O$_4$)]$\frac{1}{N}$-$(-)_{546}$-[Cr(1,3-pdda)(mal)]·H$_2$O, was removed by filtration, washed with ethanol, then ether and air dried. Yield 1.4 g. This diastereoisomer was recrystallized from warm water to a constant value of optical rotation. A 0.100% aqueous solution gave $[\alpha]_{546}$ = −1380° ($[M]_{546}$ = −8660°).

The filtrate was evaporated to a volume of 2 ml and placed in a refrigerator for 2 h. A mixture of diastereoisomers was removed by filtration, and ethanol was added to the filtrate which was then returned to the refrigerator to stand overnight. Crystals of the more soluble diastereoisomer were filtered off and recrystallized, as above, using warm water to a constant $[\alpha]_{546}$ = +148° and $[M]_{546}$ = +1008° for 0.100% solutions. *Anal.* Calc. for $(-)_{589}$-[Co(en)$_2$(C$_2$O$_4$)]$\frac{1}{N}$$(-)_{546}$-[Cr(1,3-pdda)(mal)]·H$_2$O, $\mathrm{CoCrC_{16}H_{32}O_{13}N_6}$, FW = 627.40: C, 30.63; H, 5.14; N, 13.40. Found: C, 31.19; H, 4.97; N, 14.13%. Calc. for $(-)_{589}$-[Co(en)$_2$(C$_2$O$_4$)]$\frac{1}{N}$$(-)_{546}$-[Cr(1,3-pdda)(mal)], $\mathrm{CoCrC_{16}H_{30}O_{12}N_6}$, FW = 609.37: C, 31.53; H, 4.96; N, 13.79. Found: C, 31.19; H, 4.97; N, 14.13%[*]. Calc. for $(-)_{589}$-[Co(en)$_2$(C$_2$O$_4$)]$\frac{1}{N}$$(+)_{546}$-[Cr(1,3-pdda)(mal)]·4H$_2$O, $\mathrm{CoCrC_{16}H_{38}O_{16}N_6}$, FW = 681.43: C, 28.20; H, 5.62; N, 12.33; H$_2$O, 10.57. Found: C, 28.50; H, 5.46; N, 12.30; H$_2$O, 11.89%.

The barium salts of the enantiomers were obtained using cation-exchange chromatography. The eluates were evaporated to small volumes and crystallization was effected in each case by the addition of ethanol to the solutions with cooling. The crystals were removed by filtration, washed with ethanol, then ether and air dried. Aqueous solutions (0.100%) of these enantiomers gave $[\alpha]_{546}$ = ±1050°. After standing 10 days at room temperature, aqueous solutions were optically inactive. The enantiomers crystallize with eight waters of crystallization but lose all of the water when dried over anhydrous CaCl$_2$ for several

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[*] The X-ray crystallographic results indicate that the diastereoisomer crystallizes with one water of crystallization, and elemental analysis suggests that this water molecule is lost in the drying process prior to the elemental analysis.

days. *Anal.* Calc. for Ba(–)$_{546}$-*uns-cis*-[Cr(1,3-pdda)(mal)]$_2$·8H_2O, $BaCr_2C_{20}H_{44}O_{24}N_4$, FW = 965.91: C, 24.87; H, 4.59; N, 5.80; H_2O, 14.92. Found: C, 25.10; H, 4.55; N, 5.87; H_2O, 13.94%.

Preparation and Resolution of Potassium s-cis-Ethylenediamine-N,N'-diacetatooxalatochromate(III) Monohydrate, Ks-cis-[Cr(edda)C$_2$O$_4$]·H$_2$O

This complex was prepared according to a published procedure [19].

Partial resolution was achieved using any of the several resolving agents: (–)$_{589}$-[Co(en)$_2$(C_2O_4)]$^+$, (–)$_{589}$-[Co(en)$_2$(NO_2)$_2$]$^+$, (–)$_{589}$-[Co(*S*-argH)$_2$(NO_2)$_2$]$^+$ and (–)$_{589}$-strychnine (*S*-argH = *S*-arginine).

A 0.74 g (2.0×10^{-3} mol) quantity of K*s-cis*-[Cr(edda)(C_2O_4)]·H_2O was dissolved in 10 ml of water, and the resulting solution was passed through a cation-exchange column in the H^+ form. An equivalent amount of (–)$_{589}$-strychnine (0.67 g, 2.0×10^{-3} mol) was added to the eluate with heating (50 °C) and stirring for 30 min. The mixture was then filtered off, and the filtrate was diluted to 50 ml and allowed to stand in the refrigerator for several days. The diastereoisomer (0.4 g) of lesser solubility, (–)$_{589}$-[strychnineH]$\frac{1}{N}$(–)$_{589}$-[Cr(edda)(C_2O_4)]·xH_2O, was collected by filtration, washed with ethanol, then ether and air dried. An aqueous solution of this diastereoisomer loses its optical activity within a half-hour after dissolution. A solution of the enantiomer K(–)$_{589}$-[Cr(edda)(C_2O_4)]·xH_2O was obtained by quickly passing the aqueous solution of the diastereoisomer through a cation-exchange column, but this solution lost all optical activity within a half-hour.

Preparation and Resolution of Potassium s-cis-Ethylenediamine-N,N'-diacetatomalonatochromate(III) Trihydrate, Ks-cis-[Cr(edda)(mal)]·3H$_2$O

This complex was prepared according to a published procedure [19].

Partial resolution was achieved by dissolving 0.84 g (2.0×10^{-3} mol) of K*s-cis*-[Cr(edda)(mal)]·3H_2O in a small amount of water and passing the resulting solution through a cation-exchange column in the H^+ form. A 0.67 g (2.0×10^{-3} mol) quantity of (–)$_{589}$-strychnine was added to the eluate which was then heated to 50 °C for 30 min with stirring. The mixture was then filtered, and the filtrate was concentrated to about 2 ml. Acetone (8 ml) was added and the resulting solution was allowed to stand in a refrigerator for several days. The crystals of the less soluble diastereoisomer, (–)$_{589}$-strychnineH$\frac{1}{N}$(–)$_{589}$-[Cr(edda)(mal)]·2H_2O, were filtered off, washed with acetone, then ether and air dried (0.5 g). $[\alpha]_{589} = -242°$ in a 0.1% aqueous solution. The diastereoisomer in water loses its optical activity within a half hour after recrystallization. *Anal.* Calc. for (–)$_{589}$-strychnineH–(–)$_{589}$-[Cr(edda)(mal)]·2H_2O, $CrC_{30}H_{39}O_{12}N_4$, FW = 699.66: C, 51.50; H, 5.62; N, 8.00. Found: C, 52.02; H, 5.69; N, 8.56%.

The (–)$_{589}$-enantiomer of the complex ion with K^+ as the counter ion was obtained by passing a solution of the strychnine diastereoisomer through a cation-exchange column in the K^+ form. The eluate was evaporated to dryness within 30 min. A 0.1% aqueous solution gave $[\alpha]_{589} = -370°$. In 6 h the rotation diminishes to zero. *Anal.* Calc. for K(–)$_{589}$-*s-cis*-[Cr(edda)(mal)]·2H_2O, $KCrC_9H_{16}O_{10}N_2$, FW = 403.34: C, 26.80; H, 4.00; N, 6.94. Found: C, 26.55; H, 4.41; N, 7.27%.

Physical Measurements

The $[\alpha]_\lambda$ values were measured in a 1 dm tube at 20 °C using a Perkin-Elmer SP Polarimeter. Infrared spectra were recorded on a Perkin-Elmer 197 Infracord Spectrophotometer using KBr pellets. Electronic absorption spectra were recorded on a Varian SuperScan 3 recording spectrophotometer using aqueous solutions that were typically 1.00 to 7.00×10^{-3} M. The circular dichroism spectra were recorded at room temperature with a Jobin–Yvon Dichrographe III using a xenon arc source. Elemental analyses for carbon, hydrogen and nitrogen were performed by the Microanalytical Laboratory, Department of Chemistry, Faculty of Science, University of Belgrade.

An X-ray analysis was performed on a deep orange crystal of (–)$_{589}$-[Co(en)$_2$(C_2O_4)]$\frac{1}{N}$(–)$_{546}$-[Cr(1,3-pdda)(mal)]·H_2O that was allowed to grow slowly from an aqueous solution. A crystal of approximate dimensions $0.40 \times 0.30 \times 0.16$ mm was cut from a large block and used for data collection. Accurate cell constants and a crystal orientation matrix were determined on an Enraf-Nonius CAD-4 diffractometer by least-squares refinement of the setting angles of 25 reflections with $20° < 2\theta < 30°$. Intensity data were collected by the $\omega/2\theta$ scan method using monochromatized radiation in the range $4° < 2\theta < 50°$. The intensities of three reflections, chosen as standard, were monitored every 2 h of exposure time and showed no significant variation. The intensities of 4656 reflections (Friedel pairs) were measured, of which 2092 had $I > 3\sigma^2(I)$, where $\sigma^2(I) = S + 2B + [0.004(S - B)]^2$, S = scan count, and B = time-averaged background count. Data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied [29]. The crystal data and experimental details are given in Table 1.

The structure was solved by direct methods (MULTAN '82) [30] and refined by full-matrix least-squares calculations with anisotropic temperature factors for the non-hydrogen atoms. A difference Fourier synthesis revealed all hydrogen atoms that

TABLE 1. The Δ-(–)$_{589}$-[Co(en)$_2$(C$_2$O$_4$)]–ΔΔΔΛ-(–)$_{546}$-*uns-cis*-[Cr(1,3-pdda)(mal)]·H_2O Crystal Data Summary

Formula	$C_{16}H_{32}N_6O_{13}CoCr$
M	627.3
Space group	$P2_1$
Cell dimensions	
a (Å)	7.832(3)
b (Å)	14.207(6)
c (Å)	10.801(3)
β (°)	98.46(3)
V (Å)	1189(2)
Z	2
D (g cm^{-1})	1.753
Crystal size (mm)	0.40 × 0.30 × 0.16
λ (Mo Kα) (Å)	0.71073
μ (cm^{-1})	12.18
Temperature for data collection (K)	293
Scan method	$\omega/2\theta$
Scan speed (°/min)	0.90–2.35
ω scan width (°)	(0.70–0.35 tan *θ*)
Data collection range (2*θ*) (°)	4–50
Min. and max. absorption correction factors	0.926, 0.999
Octants of data collected	$h, 0 \rightarrow 9; k, -16 \rightarrow 16; l, -12 \rightarrow 12$
No. data collected	4656
No. data used, [$I > 3\sigma(I)$]	2092
R for merged data, on *F*s	0.020
$R_f = \Sigma[\|F_o\| - \|F_c\|]/\|F_o\|$	0.027
$R_w = [\Sigma\Delta^2/\Sigma w F_o^2]^{1/2}$ [a]	0.037
(Δ/σ)max in last cycle	<0.05
Δρ in final ΔF map (e Å^{-3})	0.35
GOF	1.032

[a] $w = [\sigma^2|F_o| + (0.060|F_o|)^2]^{-1}$.

were included in the refinement at fixed positions from the ΔF map and an overall isotropic temperature factor. The refinement converged with $R = 0.027$ and $R_w = [\Sigma w\Delta^2/\Sigma w F_o^2]^{1/2} = 0.037$, where $w = [\sigma^2(F_o) + 0.060 F_o^2]^{-1}$. At the conclusion of the refinement, maximum shift/e.s.d. for parameters was less than 0.05 and the difference electron density map was essentially featureless. Atomic scattering factors were assigned according to Cromer and Mann [31] (non-hydrogen) and Stewart *et al.* [32] (hydrogen atoms) with allowance made for anomalous dispersion [33]. The computer programs used in this study were from the Enraf-Nonius Structure Determination Package [34] and ORTEP [35]. Final fractional coordinate and equivalent isotropic thermal parameters with e.s.d.s are given in Table 2. See also 'Supplementary Material'.

TABLE 2. Fractional Coordinates and Equilibrium Isotropic Thermal Parameters for Δ-(–)$_{589}$-[Co(en)$_2$(C$_2$O$_4$)]–ΔΔΔΛ-(–)$_{546}$-*uns-cis*-[Cr(1,3-pdda)(mal)]·H_2O [a]

Atom	*x*	*y* [b]	*z*	*B* (Å^2)[c]
Co	0.08060(4)	0.61890	0.72787(3)	1.491(6)
Cr	–0.42854(5)	0.55894(4)	1.26214(4)	1.558(8)
O(1)	–0.2893(3)	0.6394(2)	1.3857(2)	2.31(4)
O(2)	–0.1925(3)	0.7836(2)	1.4261(3)	3.27(6)
O(3)	–0.3981(3)	0.3124(2)	1.4388(2)	3.20(5)
O(4)	–0.3300(3)	0.4420(2)	1.3411(2)	2.29(4)
O(5)	–0.5749(3)	0.4900(2)	1.1306(2)	2.53(5)
O(6)	–0.6240(4)	0.4049(3)	0.9575(3)	4.57(7)
O(7)	–0.0853(4)	0.5253(4)	1.0242(3)	5.82(9)
O(8)	–0.2493(3)	0.5721(2)	1.1561(2)	2.58(5)
O(9)	0.2725(3)	0.5782(2)	0.6496(2)	2.13(4)
O(10)	0.2531(3)	0.6673(2)	0.8557(2)	2.22(4)
O(11)	0.5560(3)	0.5781(3)	0.6813(2)	3.43(6)
O(12)	0.5376(3)	0.6648(3)	0.9122(2)	3.45(6)
N(1)	–0.5322(3)	0.6867(2)	1.1960(2)	2.08(5)
N(2)	–0.6067(3)	0.5393(2)	1.3820(2)	1.79(5)
N(3)	0.0740(4)	0.7394(2)	0.6418(3)	2.31(5)
N(4)	–0.1021(3)	0.6702(2)	0.8132(3)	2.10(5)
N(5)	–0.0846(3)	0.5585(3)	0.6020(3)	2.16(5)
N(6)	0.0802(3)	0.4991(2)	0.8169(2)	1.99(5)
C(1)	–0.2980(4)	0.7282(3)	1.3675(3)	2.23(6)
C(2)	–0.4456(4)	0.7640(3)	1.2743(3)	2.45(7)
C(3)	–0.7243(4)	0.6945(3)	1.1795(3)	2.41(6)
C(4)	–0.7987(4)	0.6699(3)	1.2977(3)	2.61(7)
C(5)	–0.7870(4)	0.5660(3)	1.3334(3)	2.32(6)
C(6)	–0.5950(4)	0.4388(3)	1.4226(4)	2.78(7)
C(7)	–0.4297(4)	0.3928(3)	1.3993(3)	2.12(6)
C(8)	–0.5269(5)	0.4436(3)	1.0420(3)	2.79(7)
C(9)	–0.3367(6)	0.4332(4)	1.0381(4)	4.22(9)
C(10)	–0.2111(4)	0.5155(3)	1.0741(3)	2.68(7)
C(11)	0.4204(4)	0.5971(3)	0.7131(3)	2.24(6)
C(12)	0.4103(4)	0.6473(3)	0.8405(3)	2.22(6)
C(13)	–0.0062(5)	0.8087(3)	0.7151(4)	2.83(7)
C(14)	–0.1620(4)	0.7613(3)	0.7536(3)	2.63(7)
C(15)	–0.0535(5)	0.4563(3)	0.6096(4)	3.02(7)
C(16)	–0.0400(5)	0.4320(3)	0.7435(4)	3.27(8)
O(W1)	–0.1161(4)	0.7530(3)	1.0719(3)	4.63(7)

[a] Standard deviations in the least significant figures are given in parentheses. [b] The *y* coordinate of Co was fixed to define the origin. [c] $B_{eq} = 4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

The absolute configuration of ΔΔΔΛ-(–)$_{546}$-[Cr(1,3-pdda)(mal)]$^-$ was determined by accepting that the absolute configuration of (–)$_{589}$-[Co(en)$_2$(C$_2$O$_4$)]$^+$ is Δ as determined previously [36].

Results and Discussion

Infrared Spectroscopy

Infrared spectra of the complexes reported here were measured to help determine the coordination geometry of the 1,3-pdda ligand. The measured vibrational energies of the carboxylate groups verify that they are all coordinated rather than present as carboxylic acid groups or free carboxylate ions [37–39]. Infrared absorption in the carboxylate carbonyl region has been useful also in distinguishing geometrical isomers of aminopolycarboxylic acid complexes [26, 40, 41], with the asymmetric stretching frequencies being particularly useful for distinguishing between *s-cis* and *uns-cis* isomers. The K*s-cis*-$[Cr(edda)(C_2O_4)]\cdot H_2O$ and K*s-cis*-$[Cr(edda)(mal)]\cdot 3H_2O$ complexes show single asymmetric stretching frequencies of the coordinated edda ligand at 1640 and 1635 cm^{-1}, respectively. A single absorption frequency is observed in each case because of the equivalence of the carbonyl groups required by C_2 symmetry [19]. Each of the *uns-cis*-(1,3-pdda) complexes shows two bands in this region (1650 and 1684 cm^{-1} for K*uns-cis*-$[Cr(1,3\text{-}pdda)(C_2O_4)]\cdot H_2O$ and 1615 and 1660 cm^{-1} for Ba*uns-cis*-$[Cr(1,3\text{-}pdda)(mal)]_2\cdot 8H_2O$), as expected because the glycinate chelate rings are nonequivalent (R and G) for the *uns-cis* isomers.

Visible Absorption Spectra

The visible absorption spectra for *uns-cis*-$[Cr(1,3\text{-}pdda)(L)]^-$, where L = oxalate or malonate, are shown in Fig. 2 (Table 3). The corresponding data measured for the $[Cr(edda)(L)]^-$ complexes of known *s-cis* configuration are given for comparison [19]. The important spin-allowed d–d electronic transitions of a Cr(III) ion in a strong electric field of octahedral symmetry have been characterized as $^4A_{2g} \rightarrow {}^4T_{2g}$ (at lower energy) and $^4A_{2g} \rightarrow {}^4T_{1g}$ at higher energy. The *uns-cis*-1,3-pdda-Cr(III) complexes have C_1 symmetry. Furthermore, a holohedrized complex such as *cis-N*-$[Cr(N_2)(O_4)]$ has symmetry no higher than C_2. Therefore, as many as six electronic absorption components (spin-allowed) can be expected from the original $^4T_{2g}(O_h)$ and $^4T_{1g}(O_h)$ electronic states, although these are never observed.

The spectral results, specifically the two symmetrical bands, suggest that both the *uns-cis*-$[Cr(1,3\text{-}pdda)(L)]^-$ and the *s-cis*-$[Cr(edda)(L)]^-$ complexes, have effectively pseudo-octahedral symmetry. The energy level splitting diagram of the lowest spin-allowed transitions for different symmetries of $[Cr(N_2)(O_4)]$ type complexes [42], obtained from both ligand field theory [43] or the orbital angular overlap model [44], shows that the splitting of the $^4T_{2g}(O_h)$ level is larger for the *trans-N* than for the *cis-N* configuration. For example, the splitting of the first band measured for the *cis-N*-$[Cr(ida)_2]^-$ (ida = iminodiacetate, O–N–O type ligand) is smaller by a factor of two than that observed for a similar *trans-N* complex [42]. The lower energy spin-allowed bands of the *cis-N*-$[Cr(N_2)(O_4)]$ type complexes are expected to show no splitting so absorption spectra are not expected to show a clear distinction between *s-cis* and *uns-cis* complexes.

TABLE 3. Absorption and Circular Dichroism Spectral Data of Diammine-*N,N'*-diacetatochromate(III) Complexes with Oxalate and Malonate Anions

Complex	Absorption		Circular dichroism	
	ν^a	ϵ	ν^a	$\Delta\epsilon$
Δ-$(-)_{546}$-*uns-cis*-$[Cr(1,3\text{-}pdda)(C_2O_4)]^-$	19.30	108	17.76	+0.90
			20.00	−2.93
			22.22(sh)	−0.30
	25.57	93	24.63	+0.75
			25.57	+0.81
Δ-$(-)_{546}$-*uns-cis*-$[Cr(1,3\text{-}pdda)(mal)]^-$	19.34	94	17.67	+0.76
			19.84	−1.76
			22.22(sh)	−0.15
	25.70	68	25.19	+0.56
			25.77	+0.50
Δ-$(-)_{589}$-*s-cis*-$[Cr(edda)(C_2O_4)]^{-\,b}$	18.72	88		− (dominant)
				+
	25.44	74		−
				−
Δ-$(-)_{589}$-*s-cis*-$[Cr(edda)(mal)]^{-\,bc}$	18.53	69	18.48	-1.05^d
			21.27	$+0.35^d$
	25.06	53	23.86	-0.03^d
			25.51	$+0.05^d$
			27.85	-0.09^d

[a] In units of cm^{-1} × 10^{-3}. [b] Partial resolution. [c] Absorption spectral data taken from ref. 19. [d] Value approximate because of partial resolution.

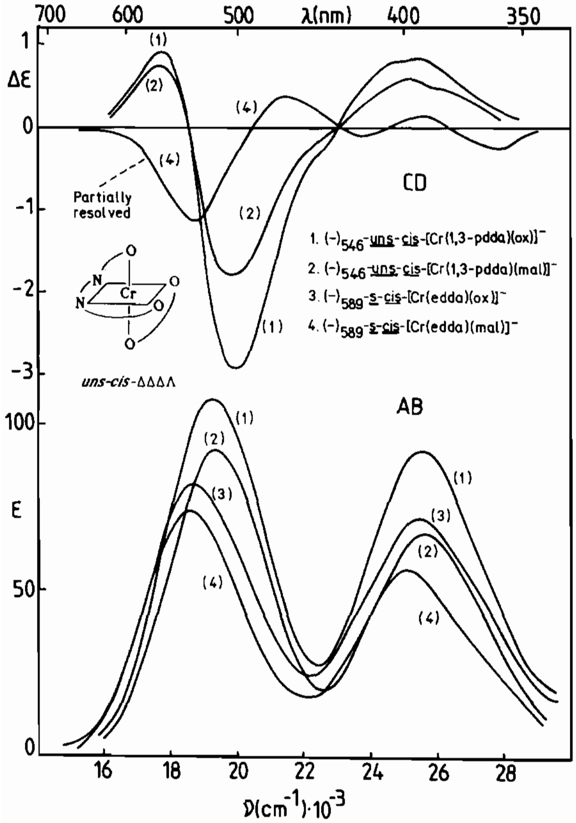

Fig. 2. Absorption and circular dichroism spectra of the diamine-*N,N'*-diacetatochromate(III) complexes with oxalate and malonate anions.

The molar absorptivities of the 1,3-pdda complexes (Table 3, Fig. 2) are higher than those of the corresponding *s-cis*-edda complexes [19]. This was noted also for the corresponding Co(III)–edda complexes [8, 15, 17]. The higher intensities of the 1,3-pdda complexes are consistent with the lower symmetry of the *uns-cis* isomers.

The 1,3-pdda ligand has been shown to exert a weaker ligand field than the edda ligand [21], therefore one could reasonably expect that the *s-cis* isomers of the 1,3-pdda complexes should give spectra whose first absorption bands are located at lower energies than those of the corresponding *s-cis*-edda complexes. The fact that the first absorption bands of the 1,3-pdda complexes are located at higher energies than those of the corresponding *s-cis*-edda complexes is an additional indication that these complexes contain the 1,3-pdda ligand in a different coordination geometry (*uns-cis*).

Circular Dichroism Spectra and Absolute Configuration

The CD spectra of the *uns-cis*-1,3-pdda and *s-cis*-edda Cr(III) complexes are shown along with their absorption spectra in Fig. 2. The spectral data are listed in Table 3.

That the enantiomers of these complexes racemized in solution in diffuse laboratory light at room temperature was noted earlier in 'Experimental'. The enantiomers of the *uns-cis*-1,3-pdda-Cr(III) complexes were observed to racemize more slowly than the corresponding *s-cis*-edda complexes, and were therefore isolable in the solid state. All attempts to isolate K(−)$_{589}$-*s-cis*-[Cr(edda)(C_2O_4)] in the solid state were unsuccessful, but the isolation of the solid K(−)$_{589}$-*s-cis*-[Cr(edda)(mal)] was possible because complete racemization required about 6 h at room temperature.

The CD spectra of the complexes shown, as usual, exhibit greater resolution of the spectral components than the corresponding absorption spectra. By comparison of the positions of the CD peaks and shoulders with the absorption band maxima, there are indications of the presence of three CD components in both regions of the spin-allowed d–d absorption bands for all of the complexes in Fig. 2. The complete removal of the degeneracy of both triplet states (O_h parentage) is expected for the actual symmetry of these complexes. Comparable results are routinely obtained for similar and corresponding Co(III) complexes when the bidentate ligand occupying the fifth and sixth octahedral coordination positions is malonate [15, 24, 46]. The three components are not resolved when oxalate replaces the malonate ligand [15, 22, 45].

The contributions to chirality by the arrangement of chelate rings (referred to as the configurational effect) and by the asymmetric nitrogen donor atoms can be expected to have major effects on the measured CD intensities of these chiral complexes. The *s-cis* complexes have three chelate ring pairs that produce enantiomers whose chiralities are either ΛΛΛ or ΔΔΔ, whereas the *uns-cis* complexes have four chelate ring pairs that produce enantiomers whose chiralities are either ΛΛΛΔ (net Λ) or ΔΔΔΛ (net Δ) [28, 46]. Empirical correlations between absolute configurations and CD spectra have been based on work done with $[Co(en)_3]^{3+}$ and related complexes [47, 48]. The correlations have been extended to Cr(III) complexes based on the great spectral similarities of d^3 and low-spin d^6 complexes [48–50]. The dominant CD peak in the first absorption band region usually determines the net CD sign for this lower energy transition of O_h parentage. The dominant or net CD sign of the lower energy transition (O_h) of the (+)$_{546}$-isomers of bis(oxalato)diamine complexes of the *cis*-$[Cr(N_2)(O_4)]$-type is positive and these were assigned the Λ configuration [51].

The empirical correlation of absolute configuration and CD sign has been extended to aminopolycarboxylic acid complexes of Co(III) and Cr(III). Often D_{4h} is a better idealized model than D_3, requiring correlations between complexes with D_{4h} symmetry and those with D_3 symmetry. The correlation with the sign of a dominant CD peak sometimes fails because of variations in the relative intensities of the CD peaks. In such cases with actual C_2 symmetry, the lowest energy CD peak has been assigned as $A_g \rightarrow E_g(D_{4h})$ parentage and its sign has been used for empirical correlations [41, 52], with support from results of studies of chiral complex ions made with stereospecific ligands [41, 53] or from results of X-ray crystallographic studies [54]. Complexes of Co(III) [5, 6, 7, 12–18] and Cr(III) [19, 20] with edda and those with 1,3-pdda ligands have been interpreted based upon some lower symmetry derived from idealized D_{4h} symmetry.

Both asymmetric nitrogen donors for the *uns-cis*-1,3-pdda or *s-cis*-edda complexes are forced to adopt the same absolute configuration, *i.e.* *RR* or *SS* (according to the Cahn–Prelog–Ingold rule). Certain authors have suggested that the *uns-cis*-1,3-pdda complexes as the *uns-cis*-edda complexes can have nitrogen donors with mixed configurations [21], but this is only possible with the highly puckered ethylenediamine backbone of the edda ligand with *uns-cis* coordination. An examination of Dreiding molecular models of the Cr(III) ion with the *uns-cis* coordinated 1,3-pdda ligand shows that the diamine chelate ring has the stable chair conformation which then precludes the possibility of nitrogen donors with mixed configurations. Furthermore, a *s-cis* coordinated 1,3-pdda ligand would probably contain a diamine chelate ring with a twist-boat conformation, but again the mixed configurations of nitrogen donors is precluded. The chair conformation of the six-membered diamine chelate ring has both nitrogen donors with axial bonds pointing in the same direction so that axial coordination of glycinate rings emanating from the donor nitrogens to opposite ends of the octahedron is impossible.

It has been suggested that for the *s-cis*-edda-Co(III) complexes asymmetric nitrogen donor atoms make significant contributions to the rotatory strengths of individual peak intensities in CD spectra [12, 14]. Although the net vicinal effect from this source is expected to be small, the two T_{1g} components, which are of opposite sign, have very high intensities. The sign of the vicinal contribution for the low energy component is positive for the *S* configuration about the nitrogens and negative for the *R* configuration. Thus, this vicinal effect is expected to reinforce the effect of the configuration of the chelate rings on the rotatory strength for these kinds of complexes. And again, because the Cr(III) chromophore is so qualitatively similar to the Co(III) chromophore, one should expect the same effect for the related Cr(III) complexes.

In the first absorption band region for the *uns-cis*-1,3-pdda–Cr(III) oxalato and malonato complexes, there is a dominant peak with a negative sign and probably comes from the $^4B_{2g}$ state in D_{4h} symmetry. The band at lower energy can be traced to the ^4E_g state in D_{4h} symmetry. The CD intensities of these complexes, expressed in terms of major peaks or net rotational strengths, decrease from oxalate to malonate, with increasing size of the dicarboxylate chelate ring. This decrease in intensities has also been observed in the corresponding *uns-cis*-1,3-pdda–Co(III) complexes and could be attributable to the higher expected strain in the more rigid oxalate chelate ring compared to that of the malonate chelate ring [22].

The CD spectra of *s-cis*-[Co(edda)L]$^{n\pm}$ are remarkably similar considering that L can be diamine [13], dicarboxylate ion [15] or amino acid [5]. The spectra of the Λ complexes in the lower energy absorption band region are characterized by a dominant positive peak at slightly lower energy than the absorption maxima and a negative peak at about the energy of the higher energy shoulder of the absorption band. The CD spectra of the *uns-cis* edda complexes of Co(III) [7, 15–17, 21] show significant variation depending on the ligating atoms and ring size of L. The CD spectra of the corresponding Co(III) complexes of 1,3-pdda are similar to those of the edda complexes, but with distinct differences. The CD spectrum [22] of Λ-*uns-cis*-[Co(1,3-pdda)(mal)]$^-$ shows three well-defined peaks in the region of each absorption band. Under the lower energy absorption band, the dominant positive peak (near the energy of the absorption maximum) is flanked by negative peaks. The intensity of this dominant CD peak increases for the corresponding oxalato complex and is even greater for the carbonato complex [22]. In both of these cases, the negative CD peaks under the first absorption band disappear.

There is a great similarity between the CD spectra of corresponding complexes of Co(III) and Cr(III). The similarity includes the Co(III) and Cr(III) complexes *s-cis*-[M(edda)(mal)]. The $(-)_{589}$-*s-cis*-[Cr(edda)(mal)]$^-$ ion (Fig. 2) can be assigned the Δ configuration based on the dominant (net) positive CD peak in the lower energy absorption band region. The CD spectrum in the lower energy absorption band region of *uns-cis*-[Cr(1,3-pdda)(mal)]$^-$ (Fig. 2) differs from that of the corresponding Co(III) complex in that there is a shoulder of the same sign as the dominant peak on the higher energy side. In the case of *uns-cis*-[Cr(1,3-pdda)(C_2O_4)]$^-$ all CD peaks have greater intensity than those of the malonato complex. The dominant peak in the oxalato complex does not cancel the lower energy negative peak as in the case of *uns-cis*-[Co(1,3-pdda)(C_2O_4)]$^-$. The dominant negative CD peak in the lower energy absorption band for the $(-)_{546}$-*uns-cis* complexes in Fig. 2 gives the Δ configuration based on comparison to spectra of Co(III) complexes.

The Crystal Structure of Δ*-(−)*$_{589}$*-[Co(en)*$_2$*(*C_2O_4*)]−* $\Delta\Delta\Delta\Lambda$*-(−)*$_{546}$*-uns-cis-[Cr(1,3-pdda)(mal)]·*H_2O

The ORTEP drawing of $(-)_{546}$-[Cr(1,3-pdda)mal]$^-$ is shown in Fig. 3. Important bond lengths and angles for this anion are listed in Tables 4 and 5. The corresponding bond length and bond angle tables for the cation, Δ-$(-)_{589}$-[Co(en)$_2$(C_2O_4)]$^+$, have been omitted from this report because similar data have been reported elsewhere [36]. Table 2, however, lists the fractional coordinates and thermal positional parameters for all the atoms constituting the diastereoisomer. The coordination geometry for the holohedrized [Cr(N_2)(O_4)] complex is approximately octahedral, and the Cr−N and Cr−O distances are nearly the same as those found in similar complexes [27, 55–57]. The crystal structure analysis confirms the *uns-cis* geometry of the 1,3-pdda ligand. The diamine ring is in the thermodynamically favored chair conformation, the R ring is in the envelope conformation, the G ring is puckered, and the malonate chelate ring is in the boat conformation. The R ring is significantly more planar than the G ring which is fairly typical of aminopolycarboxylate complexes of this type.

There is expected to be significant van der Waals' interaction between the axial hydrogen atom of C(4) and the hydrogen atom of C(2) that points to it. That these two hydrogen atoms can come within each other's van der Waals' radius probably explains why the *uns-cis* geometry is preferred to the *s-cis*. The

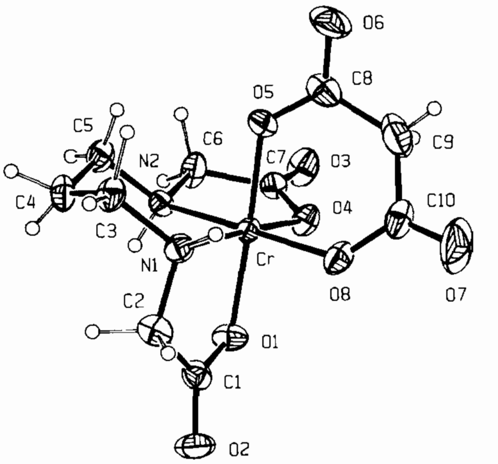

Fig. 3. ORTEP drawing and labeling scheme for $\Delta\Delta\Delta\Lambda$-$(-)_{546}$-*uns-cis*-[Cr(1,3-pdda)(mal)]$^-$. All atoms except hydrogens are drawn at the 50% probability level.

TABLE 4. Crystallographic Bond Lengths (Å) of $\Delta\Delta\Delta\Lambda$-$(-)_{546}$-*uns-cis*-[Cr(1,3-pdda)(mal)]$^-$

Cr–O(1)	1.962(2)
Cr–O(4)	1.973(3)
Cr–O(5)	1.953(2)
Cr–O(8)	1.947(2)
Cr–N(1)	2.072(3)
Cr–N(2)	2.057(3)
O(1)–C(1)	1.278(5)
O(2)–C(1)	1.245(4)
O(3)–C(7)	1.230(5)
O(4)–C(7)	1.280(4)
O(5)–C(8)	1.264(5)
O(6)–C(8)	1.229(5)
O(7)–C(10)	1.199(5)
O(8)–C(10)	1.264(5)
N(1)–C(2)	1.488(5)
N(1)–C(3)	1.493(4)
N(2)–C(5)	1.482(4)
N(2)–C(6)	1.492(5)
C(1)–C(2)	1.505(4)
C(3)–C(4)	1.519(5)
C(4)–C(5)	1.525(6)
C(6)–C(7)	1.505(5)
C(8)–C(9)	1.504(6)
C(9)–C(10)	1.541(7)

TABLE 5. Crystallographic Bond Angles (°) of $\Delta\Delta\Delta\Lambda$-$(-)_{546}$-*uns-cis*-[Cr(1,3-pdda)(mal)]$^-$

O(1)–Cr–O(4)	93.1(1)	Cr–O(1)–C(1)	117.3(2)	C(3)–C(4)–C(5)	114.8(3)
O(1)–Cr–O(5)	174.5(1)	Cr–O(4)–C(7)	116.4(2)	N(2)–C(5)–C(4)	110.9(3)
O(1)–Cr–O(8)	88.1(1)	Cr–O(5)–C(8)	127.1(2)	N(2)–C(6)–C(7)	112.6(3)
O(1)–Cr–N(1)	82.8(1)	Cr–O(8)–C(10)	128.0(3)	O(3)–C(7)–O(4)	124.8(3)
O(1)–Cr–N(2)	90.7(1)	Cr–N(1)–C(2)	109.1(2)	O(3)–C(7)–C(6)	118.7(3)
O(4)–Cr–O(5)	92.4(1)	Cr–N(1)–C(3)	116.3(2)	O(4)–C(7)–C(6)	116.5(3)
O(4)–Cr–O(8)	93.7(1)	C(2)–N(1)–C(3)	112.3(3)	O(5)–C(8)–O(6)	125.1(4)
O(4)–Cr–N(1)	174.6(1)	Cr–N(2)–C(5)	116.2(2)	O(5)–C(8)–C(9)	118.6(3)
O(4)–Cr–N(2)	82.6(1)	Cr–N(2)–C(6)	107.3(2)	O(6)–C(8)–C(9)	116.2(4)
O(5)–Cr–O(8)	91.0(1)	C(5)–N(2)–C(6)	111.3(3)	C(8)–C(9)–C(10)	121.1(4)
O(5)–Cr–N(1)	91.7(1)	O(1)–C(1)–O(2)	122.0(3)	O(7)–C(10)–O(8)	122.4(4)
O(5)–Cr–N(2)	90.6(1)	O(1)–C(1)–C(2)	117.1(3)	O(7)–C(10)–C(9)	120.7(4)
O(8)–Cr–N(1)	98.6(1)	O(2)–C(1)–C(2)	120.9(4)	O(8)–C(10)–C(9)	116.9(3)
O(8)–Cr–N(2)	176.1(1)	N(1)–C(2)–C(1)	111.8(3)		
N(1)–Cr–N(2)	93.9(1)	N(1)–C(3)–C(4)	112.8(3)		

s-cis geometry would force a twist boat conformation of the diamine chelate ring, but significant nonbonded interactions still remain from hydrogen atoms of both R rings to the hydrogen atoms of carbons making up the diamine chelate ring. Forming at least one G ring, even though the angle strain is greater than that of an R ring, reduces some of this nonbonded interaction of the hydrogen atoms on carbons of different rings and also allows the diamine chelate ring to form the favored chair conformation. Bianchini *et al.* [27] have shown that *trans*-[Cr(1,3-pdda)F_2]$^-$ also has the propanediamine ring in the more stable chair conformation, but with two equatorially coordinated G rings. Perhaps both the *trans* geometry and the *uns-cis* geometry for these complexes are thermodynamically more stable than the *s-cis* geometry for the propanediamine backbone. The *s-cis* geometry appears to be the most stable of the three when edda is used as the tetradentate ligand.

The absolute configuration of the chiral Cr(III) complex ion determined in this crystallographic study is described as ΔΔΔΛ which is also suggested by a consideration of the CD spectrum. Both donor nitrogens have the *S* configuration as expected for this ΔΔΔΛ configuration.

Supplementary Material

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

Acknowledgements

The authors are grateful to the Serbian Research Fund for financial support. They also thank Dr Franc Gubensek (Josef Stefan Institute, Ljubljana, Yugoslavia) for measurement of the CD spectra used in this study.

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