Chiral Metal Complexes.
20*. The Λ-β- to Δ-α-[Co(edda)CO₃]⁻ Inversion

MICHAEL A. COX, R. HUW GRIFFITHS, PETER A. WILLIAMS**

Department of Chemistry, University College, P.O. Box 78, Cardiff CF1 1XL, U.K.

and ROBERT S. VAGG**

School of Chemistry, Macquarie University, North Ryde, N.S.W. 2113, Australia

Received December 12, 1984

Abstract

The Δ-α- and Λ-β- forms of [Co(edda)CO₃]⁻ have been isolated as crystalline diastereoisomeric salts of the cation Δ-[Co(en)₂(ox)]⁺. When each salt is dissolved in 1.0 F aqueous Na₂CO₃ at 25 °C an isomeric equilibration process occurs between these species in which the Δ-α form predominates before the eventual racemisation of both anionic species. On proceeding to equilibrium the Λ-β-[Co(edda)CO₃]⁻ isomer is observed to invert its absolute configuration at the central metal ion in converting to the Δ-α stereoisomer. This is the first reported example of inversion–isomerisation involving the β → α transformation in a chiral complex containing a linear tetradentate.

Introduction

Most reported reactions showing inversion of metal ion absolute configuration in octahedral coordination compounds involve ligand substitution [1b]. However, we recently reported a series of Ru-(II) complexes containing three bidentate ligands which undergo an inversion–isomerisation process on exposure to light [2].

Certain reactions of complexes containing linear tetradentates were among the earliest examples of metal-ion inversion discovered, although these also involved substitution in the coordination sphere [3, 4]. Other related examples also are known [5]. The inversion-isomerisation of tetradentate complexes is somewhat more intriguing. There are four ways by which such inversions may proceed, these being the transformations α → α, α → β, β → α or β → β. Several examples of the latter, involving retention of β topology, have been reported by Fujii *et al.* [6]. These involve the complex β-[CoL-(S-aa)], where L is a tetradentate Schiff base and aa is an amino acidate anion. An α → β example has been reported recently [7], and in addition an α → α inversion could be envisaged during the reaction of Λ-α-[Co(R-picpn)Cl₂]⁺† with oxalate anion [8]. In the latter case an iodide salt containing four diastereoisomers of the cation [Co(R-picpn)-(ox)]⁺ was isolated, one of these being the Λ-α-form. Subsequently it was isomerised together with the other diastereoisomers to yield pure Δ-α-[Co(R-picpn)(ox)]⁺, which may be conveniently isolated as its perchlorate salt.

Octahedral inversion reactions involving a β → α topological change are extremely rare, and indeed only those involving substitution in the β-[Rh(S,S-eddp)Cl₂]⁻ ion have been reported [9]. Examples of β → α isomerisation are known, however, in which optically inactive complexes were employed [10]. We have found recently that under certain conditions the inversion-isomerisation process represented in (1) may be observed. This reaction, details

$$\Lambda\text{-}\beta\text{-}[Co(edda)CO_3]^-_{(aq)} \longrightarrow \Delta\text{-}\alpha\text{-}[Co(edda)CO_3]^-_{(aq)} \tag{1}$$
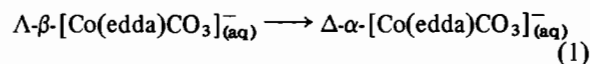
of which are reported below, represents the first example of β → α inversion-isomerisation, and completes the set of such reactions for complexes containing linear tetradentate ligands.

Experimental

Na₃[Co(CO₃)₃]·3H₂O [11] was reacted with eddaH₂ following the published procedure [12]

---

*Part 19 is ref. 1a.

**Authors to whom correspondence should be addressed.

---

†picpn represents 3-methyl-2,6-di-2-pyridyl-2,5-diaza-hexane; edda is the 1,2-diaminoethane-N,N'-diacetate dianion; S,S-eddp is the 1,2-diaminoethane-N,N'-di-S-propionate dianion; ox represents the oxalate dianion.

to yield $Na[Co(edda)CO_3] \cdot 3/2H_2O$. $[Co(en)_2$-$(ox)]Cl \cdot H_2O$ was prepared and resolved (as either the bromide or iodide salt) using a published method [13]. Δ-Λ-α-$K[Co(edda)CO_3] \cdot 4H_2O$ was prepared using the procedure of Van Saun and Douglas [14].

$\{\Delta$-$[Co(en)_2(ox)]\}\{\Lambda$-$\beta$-$[Co(edda)CO_3]\} \cdot 7H_2O$
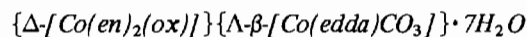
This diastereoisomeric salt was prepared using a procedure slightly modified from that reported by Jordan and Legg [15].

A mixture of Δ-$[Co(en)_2(ox)]I$ (4.00 g, 11 mmol) and silver acetate (1.84 g, 11 mmol) was finely ground, dissolved in water (22 cm^3) and the reaction mixture warmed on a water-bath at 50 °C for 15 min. The precipitated silver iodide was removed by filtration and washed with water (3 × 5 cm^3). To the combined filtrate and washings was added $Na[Co(edda)CO_3] \cdot 3/2H_2O$ (7.38 g, 22 mmol) and the mixture was heated with stirring at 50 °C until all the solids had dissolved. The solution was cooled in a current of air for an hour, during which time a deep-purple oil formed. This was dissolved by gentle warming and the reaction solution was placed in a refrigerator. Over four days a crop of purple crystals deposited. These were collected under suction, washed with ethanol, acetone, and dried at the pump. Yield: 1.95 g. $\Delta\epsilon_{557} = +14.0$ dm^2 mol^{-1}. Two recrystallisations from warm water did not lead to any change in optical activity. *Anal*: Calc. for $C_{13}H_{40}N_6O_{18}Co_2$: C, 22.7; H, 5.9; N, 12.2. Found: C, 22.6; H, 6.0; N, 12.4%. The filtrate from the first crop was stored in the refrigerator for an additional week, whereupon a second solid fraction (1.69 g) was collected as above. Two recrystallisations from water gave purple needles (0.95 g) with chiroptical properties identical to the first fraction.

$\{\Delta$-$[Co(en)_2(ox)]\}\{\Delta$-α-$[Co(edda)CO_3]\} \cdot 3H_2O$
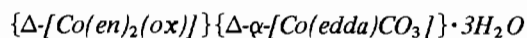
The preparation of this diastereoisomer was carried out using Δ,Λ-α-$K[Co(edda)CO_3] \cdot 4H_2O$ and Δ-$[Co(en)_2(ox)]I$ following the method of Van Saun and Douglas [14]. The yield of pure diastereoisomer was much lower than that reported (6% after two recrystallisations) and the magnitude of the CD spectrum of Δ-α-$[Co(edda)$-$CO_3]^-$ recorded in 1.0 F aqueous NaHCO$_3$ (*vide infra*) somewhat lower than the spectrum previously reported. The wavelengths of the extrema and null-dichroic points were the same, however. $\Delta\epsilon_{570} = -18.0$ dm^2 mol^{-1}. *Anal*: Calc. for C_{13}-$H_{32}N_6O_{14}Co_2$: C, 25.4; H, 5.3; N, 13.7. Found: C, 25.5; H, 5.4; N, 13.7%. Further recrystallisations did not increase the optical activity of the diastereoisomeric salt and attempts to isolate further product material from the reaction mixture gave crops containing only β-$[Co(edda)$-$CO_3]^-$.

Analyses were carried out by Mrs A. Dams in the Department of Chemistry, Cardiff. Electronic and CD spectra were recorded using a Perkin-Elmer SP800 spectrophotometer and a Jobin Yvon CNRS Dichrographe III instrument respectively.

Results and Discussion

A number of workers have commented on the lability of the isomeric forms of $[Co(edda)CO_3]^-$ in aqueous solutions [14, 15], and that an equilibrium mixture of α and β species which is present in solution may be isolated in the solid state [12, 16, 17]. We have observed that changes in the optical activity of the resolved α- and β-$[Co(edda)CO_3]^-$ ions in solution may be minimized by addition of bicarbonate ion, provided that a low temperature is maintained. Thus a known amount of $\{\Delta$-$[Co$-$(en)_2(ox)]\}\{\Lambda$-β-$[Co(edda)CO_3]\} \cdot 7H_2O$ was slurried with CM Sephadex® C-25 resin in the K$^+$ cycle in ice-cold water. The solution was filtered in the cold onto a previously weighed amount of NaHCO$_3$, the resin washed with ice-cold water and the filtrate and washings made up to volume so as to give a NaHCO$_3$ concentration of 1.0 F. Measurement of the CD spectrum of the resulting solution of Λ-β-$[Co(edda)CO_3]^-$ under these conditions gave values of $\Delta\epsilon_{556} = +23.0$ and $\Delta\epsilon_{384} = -8.8$ dm^2 mol^{-1}, respectively. These values compare favourably with those published previously for solutions in water alone of $\Delta\epsilon_{558} = +28.0$ and $\Delta\epsilon_{383} = -6.7$ dm^2 mol^{-1} [15].

In a similar fashion the spectrum of Δ-α-$[Co$-$(edda)CO_3]^-$ was recorded in 1.0 F aqueous NaHCO$_3$. Values for the extrema were $\Delta\epsilon_{555} = -32.0$, $\Delta\epsilon_{492} = +18.2$ and $\Delta\epsilon_{380} = -7.9$ dm^2 mol^{-1}. The shape, positions of extrema and null-dichroism points of the CD curve are the same as those reported by Van Saun and Douglas [14], but the magnitude is only about two-thirds of that previously reported. However, the α-isomer is quite labile in aqueous solutions and changes in CD prior to addition of bicarbonate may account for these discrepancies in CD values. Little change is evident in the CD spyctra of solutions of the resolved α- and β-complexes in 1.0 F aqueous NaHCO$_3$ at 0 °C during three hours. At elevated temperatures, however, solutions of both species react to give zero optical activity after a period of two days. The temperature of the reaction solutions studied here was 47 °C.

An entirely different pattern of reactivities for both α and β enantiomeric forms is observed, however, when their respective diastereoisomers formed with Δ-$[Co(en)_2(ox)]^+$ are dissolved in aqueous 1.0 F Na$_2$CO$_3$. Changes in optical activity, at least initially, are too rapid to record if the isolated enan-

tiomers of [Co(edda)CO$_3$]$^-$ are used, and so experiments were restricted to the diastereoisomeric salts mentioned above.

In Fig. 1 is shown the change in CD for a solution of {Δ-[Co(en)$_2$(ox)]}{Δ-α-[Co(edda)CO$_3$]}·3H$_2$O in
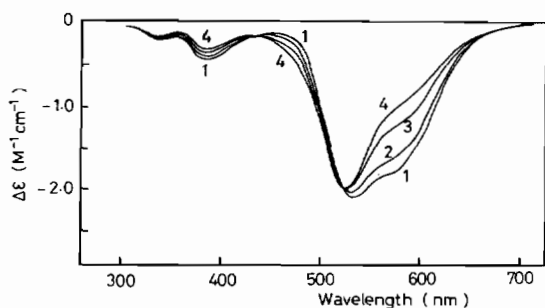
Fig. 1. Changes recorded in the CD spectrum of {Δ-[Co(en)$_2$-(ox)]}{Δ-α-[Co(edda)CO$_3$]}·3H$_2$O dissolved in aqueous 1.0 F Na$_2$CO$_3$ at 25 °C. (1) Immediately after dissolution; (2) after 10 min; (3) after 23 min; (4) after 40 min.

Fig. 2. Changes recorded in the CD spectrum of {Δ-[Co(en)$_2$-(ox)]}{Λ-β-[Co(edda)CO$_3$]}·7H$_2$O dissolved in aqueous 1.0 F Na$_2$CO$_3$ at 25 °C. (1) Diastereoisomeric salt in H$_2$O alone; subsequent spectra in 1.0 F Na$_2$CO$_3$; (2) after 12 min; (3) after 19 min; (4) after 26 min; (5) after 40 min; (6) after 54 min.

water at 25 °C. A decrease in the region of the spectrum due to the Δ-α-[Co(edda)CO$_3$]$^-$ ion is observed with time. Ultimately the CD spectrum of the Δ-[Co(en)$_2$(ox)]$^+$ counter-ion alone is observed. This particular observation is of some importance in that it is clear that the observed optical activity of the Co-edda complexes at equilibrium, and also during the course of the equilibration reaction, therefore is not generated by the presence of the cationic resolving agent in a fashion similar to that ascribed to the Pfeiffer effect [18].

However, when {Δ-[Co(en)$_2$(ox)]}{Λ-β-[Co-(edda)CO$_3$]}·7H$_2$O is dissolved in 1.0 F Na$_2$CO$_3$ an inversion of the absolute configuration of the anion is observed. Changes in the CD spectra in the early stages of the inversion process are shown in Fig. 2. This inversion process is evidenced by the change in sign of the low-energy band around 570 nm due to the anion. Ultimately these spectra too change to that of Δ-[Co(en)$_2$(ox)]$^+$ alone, and a racemic mixture of α- and β-[Co(edda)CO$_3$]$^-$ results. The observation of this particular inversion, the first example of inversion-isomerisation involving a β → α transformation in tetradentate complexes, provides some information on the associated mechanism. It indicates clearly that under the conditions selected reaction (1) above is faster than any involving planar intermediates which would result ultimately in a racemic mixture of α and β complexes.

We do not wish to imply that the mechanisms of the reactions overall can be described solely by reaction (1) or those involving planar intermediates. However, it should be noted that the eventual optical activity of the [Co(edda)CO$_3$]$^-$ anion in all of the solutions is zero, and that both α and β isomers are present. The detailed course of the reactions leading to
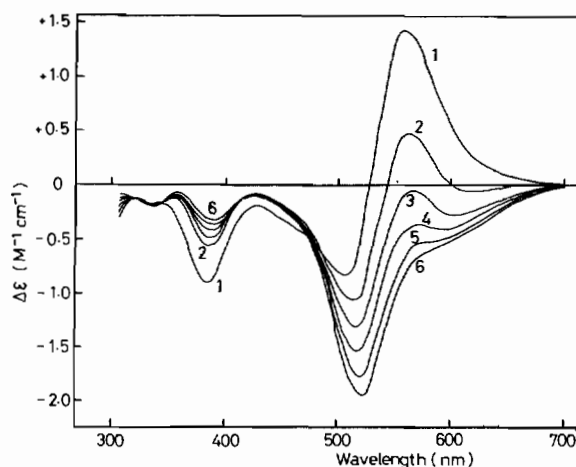
equilibrium is no doubt quite complex, as other workers have pointed out [19]. Notwithstanding this complexity it is clear that in the initial stage of reaction in aqueous Na$_2$CO$_3$ an overall inversion of absolute configuration does occur for the β-[Co(edda)CO$_3$]$^-$ ion, and that this occurs as a result of kinetic factors, in spite of the fact that the β-enantiomers are apparently the more thermodynamically stable.

References

1 (a) P. Jones, P. A. Williams and R. S. Vagg, *Inorg. Chim. Acta, 103,* 49 (1985);
  (b) F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions, 2nd edn.', Wiley, New York, 1967.
2 T. J. Goodwin, P. A. Williams, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 88,* 165 (1984), and refs. therein.
3 E. Kyuno, L. J. Boucher and J. C. Bailar, Jr., *J. Am. Chem. Soc., 87,* 4488 (1965).
4 E. Kyuno and J. C. Bailar, Jr., *J. Am. Chem. Soc., 88,* 1120 (1966).
5 A. M. Sargeson and G. H. Searle, *Inorg. Chem., 6,* 787 (1967).
6 Y. Fujii, Y. Kuwana, S. Takahashi, K. Shimizu and K. Hiroi, *Bull. Chem. Soc. Jpn., 55,* 2598 (1982), and refs. therein.
7 T. J. Goodwin, P. A. Williams and R. S. Vagg, *Inorg. Chim. Acta, 86,* L73 (1984).
8 J. A. Chambers, T. J. Goodwin, M. W. Mulqi, P. A. Williams and R. S. Vagg, *Inorg. Chim. Acta, 75,* 241 (1983).
9 M. E. Foss Sheridan, M.-J. Jun and C. F. Liu, *Inorg. Chim. Acta, 76,* L109 (1983).
10 P. F. Coleman, J. I. Legg and J. Steele, *Inorg. Chem., 9,* 937 (1970).
11 H. F. Bauer and W. C. Drinkard, *Inorg. Synth., 8,* 202 (1966).

12 L. J. Halloran, A. L. Gillie and J. I. Legg, *Inorg. Synth.*, *18*, 103 (1978).

13 W. T. Jordan and L. R. Froebe, *Inorg. Synth.*, *18*, 96 (1978).

14 C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, *8*, 115 (1969).

15 W. T. Jordan and J. I. Legg, *Inorg. Chem.*, *13*, 955 (1974).

16 P. J. Garnett and D. W. Watts, *Inorg. Chem.*, *8*, 2534 (1969).

17 P. J. Garnett and D. W. Watts, *Inorg. Chim. Acta*, *8*, 293 (1974).

18 P. Pfeiffer and K. Quehl, *Chem. Ber.*, *64*, 2667 (1931); *65*, 560 (1932).

19 G. Lapidus and G. M. Harris, *J. Am. Chem. Soc.*, *85*, 1223 (1963), and refs. therein.