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Optically Active *cis*-Dianiono(tetraamine)chromium(III) Complexes. IV. The $Cr(ox)(AA)_2^+$ (AA = en, pn, tn) Systems

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The preparations of the racemic [Cr(ox)(AA)$_2$]-ClO$_4$ salts (AA = en, RS-pn and tn) are described. These have been resolved by the method of racemic modifications using the monohydrogen dibenzoyl-(+)-tartrate anion and the less soluble diastereoisomerides have been assigned to the Δ absolute configuration on the basis of the measured circular dichroism spectra.

Introduction

Salts of the $Cr(ox)(en)_2^+$ cation were first prepared by Werner [1] and his students from the red, water-insoluble double salt $[Cr(ox)(en)_2][Cr(ox)_2(en)]$ [2]. Werner [1] was able to resolve the bromide salt by fractional crystallisation of the racemate seeded with crystals of the optically active Co(III) analog, but numerous attempts by Werner and Mathieu [3] to resolve the complex by the method of racemic modification [4], failed. The most direct method to prepare the optically active cation, so far developed, is by oxalate anation of the optically active *cis*-$CrCl_2(en)_2^+$ cation [5–7]. Recently, Vaughn and Walkwitz [8] have successfully used optically active $Co(EDTA)^-$ as a resolving agent [9].

In this paper we describe a simple and direct method for the resolution of the $Cr(ox)(en)_2^+$ cation using the monohydrogen dibenzoyl(+)-tartrate anion [10]. We also describe the preparation, properties and resolution of $[Cr(ox)(RS\text{-}pn)_2]ClO_4$ and $[Cr(ox)(tn)_2]ClO_4$.

Experimental

Dibenzoyl-(+)-tartaric acid was purchased from Aldrich and used as supplied. A pH 3.7 buffer was made by dissolving one mol of each of sodium formate and formic acid in water and diluting to one litre. *trans*-$[CrCl_2(tn)_2]ClO_4$ was prepared as described previously [11, 12]. The cation exchange resin, Zeolit 225C, SRC 6, 52–100 mesh, 2% cross linked, supplied in the Na^+ form, was used in a 7 × 1 cm diameter column and pre-washed with 1 *M* HCl under slight positive pressure. Absorption and elution flow rates were 3–4 ml/min. ORD, CD and visible absorption spectra were measured using a JASCO ORD/CD-5 recording spectropolarimeter.

CAUTION: Although we have experienced no difficulty with the perchlorate salts described here, these should be regarded as potentially explosive and treated with care.

Oxalatobis(1,2-diaminoethane)chromium(III) Perchlorate, ΔΛ-[Cr(ox)(en)$_2$]ClO$_4$

Oxalic acid dihydrate (0.435 mol, 55 g) was suspended in 200 ml of water and sodium dichromate dihydrate (0.065 mol, 18.5 g) was added in small portions (*care, effervescence*). The solution was heated on a steam bath until effervescence ceased (10–15 min) and ethylenediamine (0.25 mol, 15 g anhydrous or 17 g monohydrate) in water (200 ml) was added. $NaClO_4 \cdot H_2O$ (0.5 mol, 70 g) was then added and steam bath heating was continued for 2–3 hours, during which time $[Cr(ox)(en)_2]ClO_4$ contaminated with $[Cr(ox)(en)_2][Cr(ox)_2(en)]$ and $Na_2C_2O_4$ slowly deposited. The solution was cooled to room temperature and the impure product removed by filtration. The original mother liquor was returned to the steam bath to give, on evaporation, three further crops of impure product. The final volume was about 100 ml. The crude mixture was suspended in water (50 ml) and slurried to a thin paste. HCl (50 ml, 12 *M*) and $HClO_4$ (10 ml, 60%) were then added and the mixture warmed to about 50 °C. The slurry slowly cleared to give a red violet solution with the simultaneous deposition of orange crystals. The product was filtered from the ice cooled solution and washed with ice water, 2-propanol and ether and air dried. This was recrystallised from 80° water (pre-heated, 60 ml/g) followed by filtration and $NaClO_4 \cdot H_2O$ (3g/g) addition. The total yield of recrystallised material was 8.5 g. This material is sufficiently pure for resolution and analytically pure material is obtained by one further recrystallisation from 80 °C water with $NaClO_4 \cdot H_2O$ addition.

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Oxalatobis(RS-1,2-diaminopropane)chromium(III) Perchlorate, ΔΛ-[Cr(ox)(R,S-pn)$_2$] ClO$_4$

This was prepared similarly to the 1,2-diaminoethane analog. In this case the complex is more soluble and is only slowly deposited. Crops were collected at intervals over several weeks at room temperature. The main contaminant is $Na_2C_2O_4$, but two recrystallisations from 80 ℃ water with the addition of $NaClO_4 \cdot H_2O$, followed by ice cooling, are sufficient to give the analytically pure material as an orange microcrystalline powder. *Anal.* $[Cr(ox)(pn)_2]ClO_4 \cdot H_2O$, $CrC_8H_{22}N_4O_9Cl$, F.W. = 405.7. Calcd., C, 23.3; H, 5.77; N, 13.6%. Found, C, 23.7; H, 5.46; N, 13.8%.

Oxalatobis(1,3-diaminopropane)chromium(III) Perchlorate, ΔΛ-[Cr(ox)(tn)$_2$] ClO$_4$

The above method was not satisfactory for 1,3-diaminopropane, but the complex can be prepared as follows. *trans*-$[CrCl_2(tn)_2]ClO_4$ (3 g) was added to a solution of NaOH (1.5 g) in water (80 ml) and warmed until a clear red-pink solution formed (*ca.* 5 min, 30°). Solid $H_2C_2O_4 \cdot 2H_2O$ (1.5 g) was added in small portions and orange crystals of the diaqua deposited as the pH dropped. The temperature was raised (60 ℃) and all the solids dissolved to give a magenta coloured solution. $NaClO_4 \cdot H_2O$ (10 g) was then added and orange crystals of the product (1.5–2 g) deposited on ice cooling. These were collected by filtration and washed with isopropanol and ether. One recrystallisation from water with the addition of $NaClO_4 \cdot H_2O$ gave the product as clear orange plates. *Anal.* $[Cr(ox)(tn)_2]ClO_4$, $CrC_8H_{20}N_4O_8Cl$, F.W. = 387.7. Calcd., C, 24.8; H, 5.12; N, 14.4%. Found, C, 24.7; H, 5.52; N, 13.8%.

Resolution of ΔΛ-[Cr(Ox)(AA)$_2$] ClO$_4$

Dibenzoyl-(+)-tartaric acid (2 g) was suspended in 60 ℃ water (50 ml) and LiOH (*ca.* 0.75 g) added in small portions. When all the acid had dissolved, the pH was adjusted to about 7 (indicator paper) with formic acid. The orange perchlorate salt (2 g) was dissolved in 50 ml of the formate–formic acid buffer solution and 25 ml of water at 60 ℃. Without delay, the warm solution of the resolving agent was added to the warm complex solution and the less soluble diastereoisomeride commenced to crystallize immediately. The solution was allowed to cool spontaneously to room temperature and the precipitate (1.5–2 g) was collected by filtration 10–15 min after mixing the reagents. $NaClO_4 \cdot H_2O$ (10 g) was added to the mother liquor (cooled in ice), but only in the case of AA = en was any perchlorate salt deposited (0.4 g, 63% optically pure). 2-Propanol, and then ether was used to wash the isolated solids, which were air dried.

Isolation of the (–)$_{589}$-Cr(ox)(AA)$_2^+$ Cations

Typically, 100 mg of the $H(BzO)_2$-(+)-tatrate salt was suspended in 5 ml of dimethylformamide and 2–3 drops of 3 *M* HCl added to give a clear orange solution. This was then diluted with 20–25 ml of water and the solution was run through the cation exchange resin column. An orange band formed at the top of the resin which was then washed with three bed volumes of water. The complex cation was eluted with 50 ml of 1 *M* HCl, the first 5–10 ml of colourless effluent being discarded. ORD, CD and visible absorption spectra were recorded as soon as possible (5 cm cells) as the AA = en complex, at least, slowly decomposes via Cr–N bond rupture in acid solution [13, 14]. Complex ion concentrations were estimated from the visible absorption spectral parameters.

Results and Discussion

The preparation of the perchlorate salts of the $Cr(ox)(RS\text{-}pn)_2^+$ and $Cr(ox)(tn)_2^+$ cations is described. The former, using a method previously applied to the preparation of *cis-β*-Cr(ox)(trien)$^+$ [15, 16] and the latter by the reaction sequence

$$\textit{trans}\text{-}CrCl_2(tn)_2^+ \xrightarrow{OH^-} Cr(OH)_2(tn)_2^+ \xrightarrow{H_2C_2O_4}$$

$$Cr(tn)_2(OH_2)_2^{3+} \xrightarrow[C_2O_4^{2-}]{\text{heat}} Cr(ox)(tn)_2^+$$

Absorption spectral parameters for these previously unreported cations are listed in Table I. The spectral parameters for the $Cr(ox)(en)_2^+$ and $Cr(ox)(RS\text{-}pn)_2^+$ are very similar, but those for the $Cr(ox)(tn)_2^+$, while still characteristic of a Cr(III) oxalato tetraamine, are more similar to $Cr(ox)(NH_3)_4^+$. In particular, the absorption maximum at ~370 nm is more intense than that at ~500 nm, for these latter two cations.

The complex cations have been resolved by the method of racemic modification using the hydrogen dibenzoyl-(+)-tartrate anion. Brubaker and Schaefer [10] first reported the use of the Li$^+$ or Na$^+$ salts of $H(BzO)_2$-(+)-tart– as a resolving agent in coordination chemistry and were able to resolve a series of $Co(ox)(N_4)^+$ complexes. We have modified the procedure to allow the direct use of the water insoluble acid, without prior isolation of the monohydrogen salt, by using a sodium formate–formic acid buffer at pH = 3.7 as the solvent.

In all cases, the less soluble $[Cr(ox)(N_4)]$-$[H(BzO)_2$-(+)-tart], which precipitated from the buffer solution, had a negative CD at ~480 nm. A similar situation is observed in the Co(III) systems [10] but no attempt has been made here to establish isomorphism. The optically impure perchlorate salt

TABLE I. Visible Absorption Spectral Parameters for some $Cr(ox)(N_4)^+$ Cations.

N_4	Solvent	λ_{max} (ϵ)	λ_{min} (ϵ)	λ_{max} (ϵ)	λ_{min}, nm (ϵ, M^{-1} cm^{-1})	Ref.
$(NH_3)_4$	0.2 M H^+	503 (64)	430 (17)	375 (83)		a
	1.0 M H^+	501 (59.5)		373 (74.8)		b
	c	501 (58)	429 (11.8)	373 (73)		d
	c	500 (57.5)		375 (70.6)		e
$(en)_2$	1.0 M H^+	493 (91)		371 (87)		f
	1.0 M H^+	496 (91)	426 (19)	372 (85)		b
	0.2 M H^+	496 (91)		372 (85)		g
	c	496 (89)	428 (25)	375 (83)		h
$(pn)_2$	H_2O	494 (92)	425 (18)	370 (89)	328 (23)	i
$(tn)_2$	H_2O	494 (72)	425 (14)	369 (94)	325 (17)	i

[a] M. B. Davies, J. W. Lethbridge and M. S. Mirrlees, *J. Inorg. Nucl. Chem., 35,* 3354 (1973). [b] R. Davies and R. B. Jordan, *Inorg. Chem., 10,* 2432 (1971). [c] Solvent not stated, but presumably water. [d] O. Nor and A. G. Sykes, *J. Chem. Soc. Dalton,* 1232 (1973). [e] E. Kyuno, M. Kamada and N. Takana, *Bull. Chem. Soc. Japan, 40,* 1848 (1967). [f] J. A. Broomhead, N. Kane-Maguire and I. Lauder, *Inorg. Chem., 10,* 955 (1971). [g] M. B. Davies, J. W. Lethbridge and O. Nor, *J. Chromatog., 68,* 231 (1972). [h] M. B. Davies, *J. Inorg. Nucl. Chem., 38,* 2251 (1976). [i] This research.

TABLE II. ORD and CD Spectral Parameters for some Δ-$(-)_{589}$-$Cr(ox)(AA)_2^+$ Cations.[a]

CD Spectra[d]

AA	λ ($\Delta\epsilon$)	λ ($\Delta\epsilon$)	λ ($\Delta\epsilon$)	λ ($\Delta\epsilon$)	λ ($\Delta\epsilon$)
en[b]	480 (−2.12)	392 (0)	365 (+0.16)	345 (0)	330 (−0.07)
pn	480 (−2.39)	388 (0)	365 (+0.16)	346 (0)	330 (−0.05)
tn	478 (−1.51)	393 (0)	362 (+0.11)		

ORD Spectra[e]

AA	λ [M]	λ [M]	λ [M]	λ [M]	λ [M]	λ [M]	λ [M]
en[c]	589 (−1230)	525 (−3190)	488 (0)	445 (+4370)	390sh (3000)	353 (+2000)	320sh (+2640)
pn	589 (−1330)	528 (−3440)	492 (0)	449 (+5010)	390sh (+3360)	355 (+1440)	325sh (+3100)
tn	589 (−630)	518 (−1970)	489 (0)	448 (+3360)	390sh (+2280)	355 (+1860)	

[a] From the less soluble $H(BzO)_2$-(+)-tart$^-$ salt. Solvent is 1 M HCl. [b] See also S. Kaizaki, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Japan, 43,* 1100 (1970) and Ref. 5. [c] See also T. Burer, *Helv. Chim. Acta, 46,* 242 (1963) and Ref. 8. [d] $\Delta\epsilon$ (M^{-1} cm^{-1}). [e] [M] (° M^{-1} m^{-1}).

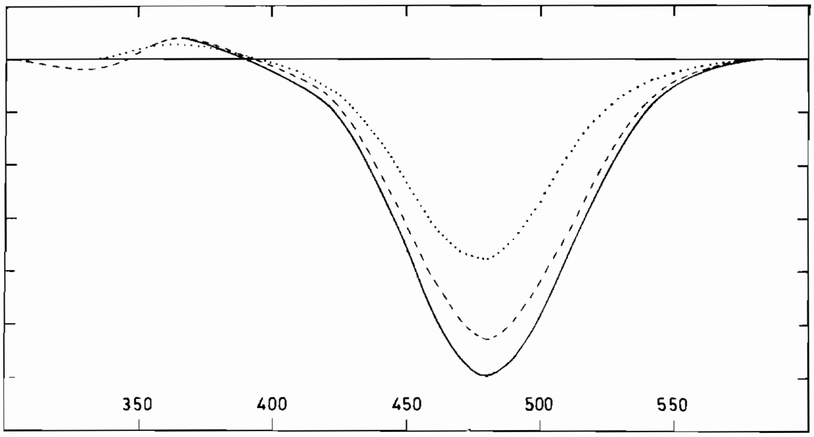

Fig. 1. Circular dichroism spectra of Δ-$(-)_{589}$-$\mathrm{Cr(ox)(tn)_2^+}$ (·····), Δ-$(-)_{589}$-$\mathrm{Cr(ox)(en)_2^+}$ (– – –) and Δ-$(-)_{589}$-$\mathrm{Cr(ox)((+)\text{-}S\text{-}pn)_2^+}$ (———) in 1 *M* HCl at room temperature. Each ordinate division corresponds to $\Delta\epsilon = \pm 0.4\ M^{-1}\ \mathrm{cm}^{-1}$.

of the more soluble diastereoisomeride was isolated from the filtrate, in the case of $\mathrm{Cr(ox)(en)_2^+}$, but for the RS-pn and tn analogs the filtrate solutions were too dilute to obtain crystalline enantiomeric perchlorates. Our qualitative observations suggest that the perchlorate salts of the enantiomers are more soluble than those of the racemates.

The less soluble diastereoisomerides are insoluble in water and the optically active cations were separated from the anion by ion exchange techniques. Table II lists the ORD and CD spectral parameters for these $(-)_{589}$-$\mathrm{Cr(ox)(AA)_2^+}$ cations derived from the less soluble diastereoisomerides. Qualitatively, the chiroptical parameters for the three cations are similar and characterised by a negative CD at ~480 nm. There are some minor differences in the CD of the $(-)_{589}$-$\mathrm{Cr(ox)(tn)_2^+}$ cation, when compared with the en and pn analogues, in that the negative CD associated with the ~370 nm chromophore is absent (Fig. 1). There is also a reduction in CD intensity for this cation, a not uncommon situation for tn complexes [17, 18]. The CD and ORD intensity differences between the $(-)_{589}$-$\mathrm{Cr(ox)(en)_2^+}$ and $(-)_{589}$-$\mathrm{Cr(ox)(pn)_2^+}$ cations suggest that the potentially asymmetric pn ligand may also be resolved. Resolution of $\Delta\Lambda$-$(-)_{589}$-$\mathrm{Cr(ox)((+)\text{-}S\text{-}pn)_2^+}$ [19] gives Δ-$(-)_{589}$-$\mathrm{Cr(ox)(S\text{-}pn)_2^+}$ with chiroptical parameters identical to those given by resolution of $\Delta\Lambda$-$\mathrm{Cr(ox)(R,S\text{-}pn)_2^+}$ described here. The internal stereochemical arrangement of the two pn ligands relative to each other remains unknown, but the two possible combinations in a Δ-$\mathrm{Cr(ox)(S\text{-}pn)_2^+}$ configuration have the C-methyl groups in positions well remote from the coordinated oxalate.

The $(+)_{589}$-$\mathrm{Cr(ox)(en)_2^+}$ cation has been assigned to the Λ absolute configuration [20] by McCaffery *et al.* [5] and Kaizaki *et al.* [17]. Thus, the $(-)_{589}$ cations associated with the less soluble $\mathrm{H(BzO)_2}$-(+)-tart$^-$ anion are assigned to the Δ configuration. These assignments are in complete agreement with those made for the analogous $(-)_{589}$-$\mathrm{Co(ox)(AA)_2^+}$ complexes (AA = en, tn) by Brubaker and Schaefer [10] on a comparison of the published CD spectra, and are in accord with the empirical correlation for $\mathrm{CrX_2(en)_2^+}$ complexes ($X \neq Cl$) proposed earlier [21].

We note that the cations of the less soluble $\mathrm{H(BzO)_2(+)}$-tart$^-$ salts of all the $\mathrm{M(ox)(N_4)^+}$ complexes so far resolved have the Δ-absolute configuration. Nevetheless, it would be unwise [22] to make assignments of absolute configuration solely on this basis.

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9 Abbreviations used: en = $\mathrm{NH_2CH_2CH_2NH_2}$, pn = $\mathrm{NH_2CH(CH_3)CH_2NH_2}$, tn = $\mathrm{NH_2(CH_2)_3NH_2}$, ox = $\mathrm{C_2O_4^{2-}}$, EDTA = $\mathrm{[CH_2N(CH_2CO_2^-)_2]_2}$, $\mathrm{H_2(BzO)_2}$-(+)-tart = dibenzoyl-(+)-tartaric acid.
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