

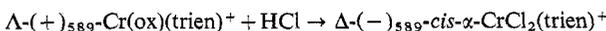
## The Configuration of the Cr(ox)(trien)<sup>+</sup> Cation

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### Abstract

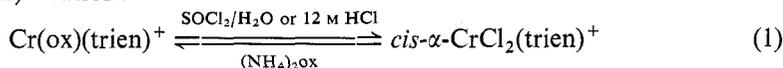
On the basis of the inversion reaction



the oxalato complex is now believed to have the *cis-β* configuration, rather than the previously suggested *cis-α*.

### Introduction

Salts of the Cr(ox)(trien)<sup>+</sup> cation (which necessarily has the *cis* configuration) were first described in 1966,<sup>1</sup> and since that time this complex has been used in various kinetic<sup>2</sup> and synthetic studies.<sup>3</sup> The complex was originally assigned the *cis-α* configuration<sup>1</sup> on the basis of its infrared spectrum and the ready interconversion to the *cis-α*-CrCl<sub>2</sub>(trien)<sup>+</sup> cation:<sup>1,3</sup>



However, Fordyce *et al.*<sup>3</sup> observed that under anhydrous conditions the forward reaction yielded *cis-β*-CrCl<sub>2</sub>(trien)<sup>+</sup> which rapidly isomerized to the *cis-α* dichloro complex in the presence of low concentrations of water.

As part of a continuing study of optically active chromium(III) amine complexes<sup>4-6</sup> we have prepared optically active Cr(ox)(trien)<sup>+</sup> and we now report the chiroptical changes that occur during the forward reaction (1).

### Experimental

Triethylenetetraamine (Fluka) and (+)-dibenzoyltartaric acid monohydrate (Aldrich) were used as supplied. [Cr(ox)(trien)] Br·H<sub>2</sub>O was prepared as described previously.<sup>1</sup>

#### Resolution of the Cr(ox)(trien)<sup>+</sup> Cation

Cr(ox)(trien)<sup>+</sup> decomposes in acidic media through Cr-N bond rupture with a half-life of about 50 min at 298 K,<sup>2</sup> so all operations during the resolution procedure should be performed expeditiously.

<sup>1</sup> House, D. A., and Garner, C. S., *J. Am. Chem. Soc.*, 1966, **88**, 2156.

<sup>2</sup> Veigel, J. M., *Inorg. Chem.*, 1968, **7**, 69.

<sup>3</sup> Fordyce, W. A., Sheridan, P. S., Zinato, E., Ricciari, P., and Adamson, A. W., *Inorg. Chem.*, 1977, **16**, 1154.

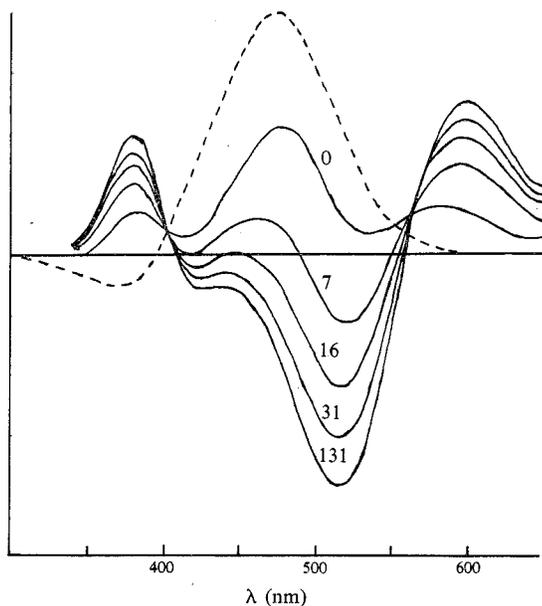
<sup>4</sup> House, D. A., *J. Inorg. Nucl. Chem.*, 1973, **35**, 3103.

<sup>5</sup> Kindred, I. J., and House, D. A., *J. Inorg. Nucl. Chem.*, 1975, **37**, 1359.

<sup>6</sup> Kindred, I. J., and House, D. A., *J. Inorg. Nucl. Chem.*, 1975, **37**, 1320.

The bromide salt (2 g) was ground in a large mortar with 50 ml of 1.0 mol dm<sup>-3</sup> sodium formate/formic acid buffer (pH 3.7) and 25 ml H<sub>2</sub>O until all the solid dissolved (c. 5 min). (+)-Dibenzoyltartaric acid (H<sub>2</sub>dbt) monohydrate (2 g) was suspended in 50 ml of warm (313 K) water and LiOH (c. 0.75 g) was added in small portions until all the solid had dissolved. The final pH was adjusted to below 8 (indicator paper) with formic acid. The still warm solution of the resolving agent was added to the room-temperature solution of the oxalato bromide and the less soluble diastereoisomeride (2 g) immediately precipitated. After 2-min stirring, the precipitate was removed from the mother liquor by filtration, and NaClO<sub>4</sub>·H<sub>2</sub>O (10 g) was added to the mother liquor to precipitate (during 10 min, ice cooling) the optically impure perchlorate salt (1 g) of the more soluble diastereoisomeride. Both precipitates were washed with propan-2-ol and then ether, and air-dried.

*Spectral parameters.*—(±)-Cr(ox)(trien)<sup>+</sup>:<sup>2</sup> λ<sub>max</sub> 495 nm (ε 147 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>), λ<sub>min</sub> 420 (33.7), λ<sub>max</sub> 370 (104). Δ(-)<sub>589</sub>-[Cr(ox)(trien)] [Hdbt], c.d. (10% dimethylformamide, 90% water): [Δε]<sub>482</sub> -1.92 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>, [Δε]<sub>395</sub> 0, [Δε]<sub>358</sub> +0.23. Λ-(+)<sub>589</sub>-[Cr(ox)(trien)] ClO<sub>4</sub>, c.d. (H<sub>2</sub>O): [Δε]<sub>482</sub> +0.92, [Δε]<sub>395</sub> 0, [Δε]<sub>358</sub> -0.11; 48% optically pure based on the (-)<sub>589</sub> data. Λ-(+)<sub>589</sub>-[Cr(ox)(trien)] ClO<sub>4</sub>, o.r.d. (H<sub>2</sub>O): [M]<sub>589</sub> +270° mol<sup>-1</sup> dm<sup>3</sup> m<sup>-1</sup>, [M]<sub>525</sub> +562, [M]<sub>495</sub> 0, [M]<sub>450</sub> -1240, giving [M]<sub>589</sub> -560 for the Δ(-)<sub>589</sub> enantiomer.



**Fig. 1.** --- C.d. spectrum of Λ-(+)<sub>589</sub>-*cis*-β-[Cr(ox)(trien)] ClO<sub>4</sub> in H<sub>2</sub>O. — C.d. spectral changes of the same complex, after 0, 7, 16, 31 and 131 min in 12 mol dm<sup>-3</sup> HCl at room temperature, to give Δ(-)<sub>589</sub>-*cis*-α-CrCl<sub>2</sub>(trien)<sup>+</sup>.

*Λ-(+)<sub>589</sub>-cis-α-Dichloro(triethylenetetraamine)chromium(III) Chloride*

Δ(-)<sub>589</sub>-[Cr(ox)(trien)] [Hdbt] (1 g) was moistened with SOCl<sub>2</sub> and a few drops of water were added. The orange slurry rapidly turned to a purple oil. The excess of SOCl<sub>2</sub> was allowed to evaporate at room temperature (1–2 h) and the oil triturated with methanol. The resulting blue powder was collected by filtration, washed with methanol, and air-dried. The infrared spectrum of the product agreed with the published data for *cis*-α-[CrCl<sub>2</sub>(trien)] Cl.<sup>1,3</sup>

*Spectral parameters.*—(±)-*cis*-α-CrCl<sub>2</sub>(trien)<sup>+</sup> (0.1 mol dm<sup>-3</sup> HCl):<sup>1,3,7</sup> λ<sub>max</sub> 534 (95.5), λ<sub>min</sub> 455 (28.5), λ<sub>max</sub> 396 (86.7). Λ-(+)<sub>589</sub>-*cis*-α-CrCl<sub>2</sub>(trien)<sup>+</sup>, c.d. (0.1 mol dm<sup>-3</sup> HCl): [Δε]<sub>600</sub> -0.77, [Δε]<sub>558</sub> 0, [Δε]<sub>515</sub> 1.24, [Δε]<sub>495</sub> 0.15, [Δε]<sub>425</sub> 0.19, [Δε]<sub>405</sub> 0, [Δε]<sub>379</sub> -0.55, [Δε]<sub>320</sub> 0. Λ-(+)<sub>589</sub>-*cis*-α-CrCl<sub>2</sub>(trien)<sup>+</sup>, o.r.d. (0.1 mol dm<sup>-3</sup> HCl): [M]<sub>650</sub> -400, [M]<sub>619</sub> 0, [M]<sub>589</sub> +1300, [M]<sub>555</sub> +2660, [M]<sub>505</sub> 0, [M]<sub>470</sub> -1230, [M]<sub>440</sub> -943, [M]<sub>405</sub> -1480, [M]<sub>370</sub> 0, [M]<sub>355</sub> +257, [M]<sub>325</sub> 0.

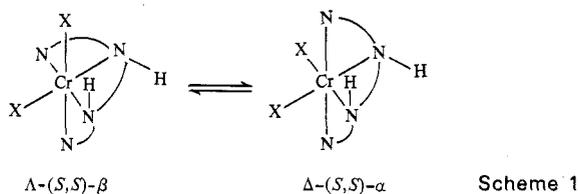
<sup>7</sup> Hsu, C. Y., and Garner, C. S., *Inorg. Chim. Acta*, 1967, **1**, 17.

### Instrumentation

All spectra were measured on a JASCO ORD/CD-5 recording spectropolarimeter.

### Results and Discussion

The  $(\pm)$ -Cr(ox)(trien)<sup>+</sup> cation has been resolved by use of the monohydrogen (+)-dibenzoyltartrate anion.<sup>8</sup> The  $(-)$ <sub>589</sub>-Cr(ox)(trien)<sup>+</sup> cation isolated as the less soluble diastereoisomeride has a large negative c.d. at 482 nm, and is assigned the  $\Delta$  absolute configuration on the basis of a comparison with the c.d. spectra of analogous Co<sup>III</sup> complexes.<sup>8</sup> We note that all the less soluble diastereoisomerides of M(ox)(N<sub>4</sub>)<sup>+</sup> cations (M = Co,<sup>8</sup> Cr<sup>9</sup>) so far isolated with this optically active anion have been assigned to the  $\Delta$  configuration: N<sub>4</sub> = (en)<sub>2</sub>, ((RS)-pn)<sub>2</sub>, (tn)<sub>2</sub>, (trien), (2,3,2-tet), (3,2,3-tet).



Although the absolute configuration can be readily assigned, it is not possible to distinguish between the *cis*- $\alpha$  and *cis*- $\beta$  trien configurations on the basis of the c.d. spectral parameters.<sup>8,10</sup> Reaction of  $\Lambda$ -(+)<sub>589</sub>-Cr(ox)(trien)<sup>+</sup> with concentrated HCl results in the formation of  $\Delta$ -(-)<sub>589</sub>-*cis*- $\alpha$ -CrCl<sub>2</sub>(trien)<sup>+</sup> (Fig. 1). The absolute configuration of this latter cation was established by comparison of the c.d. spectrum with that reported for the analogous Co<sup>III</sup> complex.<sup>10</sup> Inversions of this type are rare in coordination chemistry<sup>11</sup> and the present example is significant in that it is one of the few reported examples to take place in acidic solution.<sup>3</sup> It is not possible for a  $\Lambda$ -*cis*- $\beta$   $\rightleftharpoons$   $\Delta$ -*cis*- $\alpha$  change to occur without proton inversion, but a  $\Lambda$ -*cis*- $\beta$   $\rightleftharpoons$   $\Delta$ -*cis*- $\alpha$  change can be readily envisaged (Scheme 1). As proton inversions in acidic solution are unlikely, we suggest that the starting Cr(ox)(trien)<sup>+</sup> cation has the *cis*- $\beta$  configuration, as the *cis*- $\alpha$  configuration for the resulting dichloro product is now well established.<sup>1,3,12</sup>

### Acknowledgments

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<sup>8</sup> Brubaker, G. R., and Schaefer, D. P., *Inorg. Chem.*, 1971, **10**, 968.

<sup>9</sup> Yang, D., and House, D. A., *Inorg. Chim. Acta*, in press.

<sup>10</sup> Sargeson, A. M., and Searle, G. H., *Inorg. Chem.*, 1965, **4**, 45.

<sup>11</sup> Basolo, F., and Pearson, R. G., 'Mechanisms of Inorganic Reactions' 2nd Edn, p. 265 (John Wiley: New York 1967).

<sup>12</sup> Buckingham, D. A., and Jones, D., *Inorg. Chem.*, 1965, **4**, 1387.