

## Chromium(III) Complexes with Mixed Ethylenediamine/ Trimethylenediamine Coordination Spheres and their Optical Activity

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$[\text{Cr en}_{3-n} \text{tn}_n]^{3+}$  ( $n=0, 1, 2, 3$ ) have been prepared and resolved in the form of their bromides by means of nitro-(+)<sub>D</sub>-camphor. The circular dichroism of the complexes in the spectral region from 16.5 to ca. 43.5 kK have been measured, and values of the dipole strength and the rotatory strength of their "first" absorption band have been calculated. It is concluded that (+)<sub>D</sub>-[Cr en<sub>3</sub>tn]<sup>3+</sup> and (+)<sub>D</sub>-[Cr en<sub>2</sub>tn<sub>2</sub>]<sup>3+</sup> have the same absolute configuration, *A*, as (+)<sub>D</sub>-[Cr en<sub>3</sub>]<sup>3+</sup> and (-)<sub>D</sub>-[Cr tn<sub>3</sub>]<sup>3+</sup>.

The optical activity of the "first" absorption band ( $450 \text{ nm} < \lambda_{\text{max}} < 500 \text{ nm}$ ) of tris(diamine) chelate complexes of Co(III) and Cr(III) has been the topic of a very considerable number of studies by various authors.<sup>1</sup> One attractive feature of these complexes is the relative experimental ease with which well defined changes in the environment of the central ion can be brought about by suitable ligand substitutions and their influence upon the optical activity studied and compared to results of theoretical treatments.

Within a series of such complexes in which the geometry of the immediate environment of the central atom is kept constant the variations in rotatory strength of the first absorption band follow the variation in absorption intensity of that band. This may be interpreted by means of the expression

$$R_{\text{ba}} \propto |\vec{\mu}_e| \cdot |\vec{\mu}_m| \cos v$$

for the rotatory strength,  $R_{\text{ba}}$ , of an absorption band caused by the electronic transition,  $b \leftarrow a$ , associated with the induced electric and magnetic dipole moments,  $\vec{\mu}_e$  and  $\vec{\mu}_m$ ,  $v$  being the angle between the dipole moments. The absorption bands under consideration in the case of the Co(III) and Cr(III) complexes are electrically forbidden and magnetically allowed; they are

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generally believed to gain their intensity through vibronic coupling. Thus, in a series of tris(diamine) complexes  $\vec{\mu}_m$  would be approximately constant. If  $v$  is assumed to depend mainly on the geometry of the immediate surroundings of the central ion  $\cos v$  would hardly be expected to vary in a series of complexes like  $^* [M en_3]^{3+}$ ,  $[M(+)_D-pn_3]^{3+}$  and  $[M(+)_D-2,3 bn_3]^{3+}$ , provided the methyl groups are substituted into equatorial positions with respect to the five-membered metal-diamine rings, whereby the conformation of these rings is left unchanged. The substitution, however, influences the intensity of the absorption band as expressed, *e.g.* by the dipole strength of the transition

$$S_{ba} \propto |\vec{\mu}_e|^2$$

and this explains the variation in rotatory strength with absorption intensity.

A different type of influence could be expected – and is actually observed<sup>1</sup> – when substitutions are made such that the conformation of the metal chelate rings is altered as in complexes with *i*-bn or *m*-2,3-bn as ligands (ring conformation influenced by the presence of axial methyl groups) and when the metal chelate ring size is altered as in complexes with *tn* as a ligand.

Whereas this “ring size” effect – the difference between rotatory strengths of *en* and the corresponding *tn* complexes – has been observed a long time ago<sup>2,3</sup> for the pure tris(diamine) complexes of Co(III) and Cr(III), a systematic investigation of the mixed *en/tn* complexes has only recently been undertaken in our laboratory. Preliminary results of the investigation of the Co(III) complexes have been reported;<sup>4</sup> the Cr(III) complexes will be described in the following.

## EXPERIMENTAL

### Preparations

Dimethylsulfoxide (DMSO) is a convenient reaction medium for the preparation of tris(diamine) chromium(III) complexes,<sup>1,5</sup> and we have used it for the preparation of the pure as well as the mixed complexes, the latter being reported here for the first time.

$(\pm)$ -[Cr *en*<sub>3</sub>]Cl<sub>3</sub>.aq has been prepared before by reacting anhydrous CrCl<sub>3</sub> with dry ethylenediamine.<sup>6,7</sup> In this work the following modification has been used: To a suspension of 5–100 g anhydrous CrCl<sub>3</sub> in 10 times its weight of DMSO is added twice the equivalent amount of ethylenediamine, and the mixture is heated to 50–60°C and vigorously stirred for 1 h. The volume is doubled by adding ethanol, and the mixture is cooled in ice for half an hour and filtered. The precipitate is washed with ethanol, dissolved in water at 25°C and reprecipitated by addition of ethanol. Yield about 60 %.

$(\pm)$ -[Cr *en*<sub>2</sub>*tn*]Cl<sub>3</sub>.aq. To a suspension of 5–20 g *cis*-[Cr *en*<sub>2</sub>Cl<sub>2</sub>]Cl (crude product prepared after Rollinson and Bailar<sup>8</sup>) in 10 times its weight of DMSO 5 times the equivalent amount of 1,3-diaminopropane is added, and the mixture is vigorously stirred at 50–60°C for 1 h. The volume is doubled by adding ethanol, the mixture is cooled in ice for half an hour and filtered. The precipitate is washed with ethanol, dissolved in water at 25°C and reprecipitated by addition of ethanol. The product thus formed is contaminated by small amounts of  $(\pm)$ -[Cr *en* *tn*<sub>2</sub>]Cl<sub>3</sub> and must be purified by fractional precipitation with ethanol from aqueous solution. Yield *ca.* 35 % based on [Cr *en*<sub>3</sub>]Cl<sub>3</sub>, the starting material for the preparation of *cis*-[Cr *en*<sub>2</sub>Cl<sub>2</sub>]Cl.

\* The following abbreviations will be used: *en*, 1,2-diaminoethane; *pn*, 1,2-diaminopropane; 2,3-*bn*, 2,3-diaminobutane (optically active and *meso* forms); *i*-*bn*, 1,2-diamino-2-methylpropane; and *tn*, 1,3-diaminopropane.

( $\pm$ )-[Cr en  $tn_2$ ]Cl<sub>3</sub>.aq. A suspension of 5–50 g anhydrous CrCl<sub>3</sub> in 10 times its weight of DMSO is prepared. Ethylenediamine and 1,3-diaminopropane are added in the molar ratio CrCl<sub>3</sub>:en:tn=1:1:5, and the mixture is vigorously stirred at 50–60°C for 1 h. Precipitating with ethanol (cooling in ice) yields a crude product (contaminated by ( $\pm$ )-[Cr en<sub>2</sub>tn]Cl<sub>3</sub>), which is purified by fractional precipitation with ethanol from aqueous solution at 25°C. Yield about 45 %.

( $\pm$ )-[Cr  $tn_3$ ]Cl<sub>3</sub>.aq has previously been prepared from anhydrous CrCl<sub>3</sub> and a dried solution of 1,3-diaminopropane in ether.<sup>7</sup> In this work the salt has been prepared as follows: To 5–100 g anhydrous CrCl<sub>3</sub> suspended in 10 times its weight of DMSO is added twice the equivalent amount of 1,3-diaminopropane, and the mixture is stirred at 50–60°C for 2 h. Ethanol is added, the mixture is cooled in ice and filtered. The precipitate is washed with ethanol, dissolved in water at 25°C and reprecipitated by addition of ethanol. Yield about 55 %.

### Characterization and analysis

A paperchromatographic method developed<sup>4</sup> for the separation of the analogous Co(III) complexes proved applicable also to the system of Cr(III) complexes. Development of the chromatogram must take place in the absence of light; by subsequent exposure to daylight the colour of the spots changes from yellow to purple. The chromatograms were developed by means of the following mixture: Phenol saturated with water (90 % phenol): 30 volumes, 1-butanol: 14 vols., pyridine: 14 vols., benzene: 14 vols., acetone: 14 vols., water: 4 vols., acetic acid (80 %): 7 vols., which caused the ions [Cr en<sub>3</sub>]<sup>3+</sup>, [Cr en<sub>2</sub>tn]<sup>3+</sup>, [Cr en  $tn_2$ ]<sup>3+</sup>, and [Cr  $tn_3$ ]<sup>3+</sup> to descend with the relative velocities 1.0:1.5:2.0:2.3. The method has been used for controlling the purity of the mixed complexes. In a mixture of the tris-diamine complexes the limit of detection of each complex is ca. 5 %.

X-Ray powder photographs. Well developed, large crystals of the racemic chlorides were prepared by evaporating saturated aqueous solutions at 25°C. To prevent hydrolysis the evaporation must be carried out in darkness. The crystals were washed with ethanol, dried in air at 25°C and kept in darkness in well closed bottles. X-Ray powder photographs of the material thus prepared were taken to decide whether mixtures of pure complexes or pure, mixed complexes were present. The diagrams (Fig. 1) show that the latter assumption is correct.

Thermogravimetry. The water content and the equivalent weight of the racemic chlorides were determined by means of a thermobalance (Linseis). The water evaporates

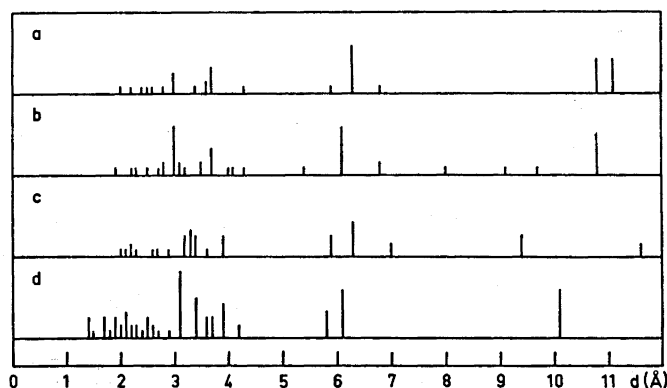


Fig. 1. X-Ray powder diagrams of racemic chlorides. (CoK $\alpha$  radiation.) The height indicates the relative intensities. a. ( $\pm$ )-[Cr  $tn_3$ ]Cl<sub>3</sub>; b. ( $\pm$ )-[Cr en  $tn_2$ ]Cl<sub>3</sub>; c. ( $\pm$ )-[Cr en<sub>2</sub>tn]Cl<sub>3</sub>; d. ( $\pm$ )-[Cr en<sub>3</sub>]Cl<sub>3</sub>.

below 120°C, and the anhydrous salts are stable until *ca.* 190°C. Heating the complexes to 500–600°C yields pure Cr<sub>2</sub>O<sub>3</sub>. The water content is not well defined and depends on the previous treatment (*cf.* Ref. 9). Thus the crystalline salts give off water in dry air and take up water in humid air. The equivalent weights are calculated for the dry salts and shown in Table 1.

Table 1. Water content and equivalent weight (per Cr) of racemic chlorides.

Anhydrous salt	Mol ratio H <sub>2</sub> O:Cr in salt hydrate	Equiv.w. of anhydrous salt	
		exp.	theor.
(±)-[Cr en <sub>3</sub> ]Cl <sub>3</sub>	1.5–3.9	339	339
(±)-[Cr en <sub>2</sub> tn]Cl <sub>3</sub>	2.0–3.8	351	353
(±)-[Cr en tn <sub>2</sub> ]Cl <sub>3</sub>	2.8–3.1	368	367
(±)-[Cr tn <sub>3</sub> ]Cl <sub>3</sub>	1.0–2.6	378	381

### Resolution

The optically active bromides were prepared from the chromatographically pure racemic chlorides by fractional crystallization of the camphor-nitronates, a method introduced by Werner<sup>10</sup> for [Cr en<sub>3</sub>]<sup>3+</sup>.

(+)<sub>D</sub>-[Cr en<sub>3</sub>]Br<sub>3</sub>.aq. Aqueous solutions of (±)-[Cr en<sub>3</sub>]Cl<sub>3</sub> and the (+)<sub>D</sub>-sodium salt of α-nitro-(+)<sub>D</sub>-camphor are mixed, whereby (+)<sub>D</sub>-[Cr en<sub>3</sub>](NO<sub>2</sub>-(+)<sub>D</sub>-camph)<sub>3</sub> is precipitated.<sup>2</sup> Treatment of the precipitate with hydrobromic acid and ethanol yields (+)<sub>D</sub>-[Cr en<sub>3</sub>]Br<sub>3</sub>.aq. By repeated resolution a product of constant optical activity is obtained. Pure (-)<sub>D</sub>-[Cr en<sub>3</sub>]Br<sub>3</sub>.aq was obtained from the first mother liquor by fractional precipitation with hydrobromic acid and ethanol.

(+)<sub>D</sub>-[Cr en<sub>2</sub>tn]Br<sub>3</sub>.aq. Mixing aqueous solutions of (±)-[Cr en<sub>2</sub>tn]Cl<sub>3</sub> and the (+)<sub>D</sub>-sodium salt of α-nitro-(+)<sub>D</sub>-camphor and treating the precipitate with hydrobromic acid and ethanol yields (+)<sub>D</sub>-[Cr en<sub>2</sub>tn]Br<sub>3</sub>.aq. Repeated resolution gives a product of constant activity. Attempts at preparing pure (-)<sub>D</sub>-[Cr en<sub>2</sub>tn]Br<sub>3</sub> have not been successful.

(+)<sub>D</sub>-[Cr en tn<sub>2</sub>]Br<sub>3</sub>.aq and (-)<sub>D</sub>-[Cr tn<sub>3</sub>]Br<sub>3</sub>.aq were obtained in complete analogy to (+)<sub>D</sub>-[Cr en<sub>2</sub>tn]Br<sub>3</sub>.aq. Similarly, attempts at isolating the antipodes were unsuccessful.

### Analytical control of the optically active bromides

The paperchromatographic method previously mentioned may be used for the bromides too. The optically active bromides proved chromatographically pure. Results of elemental analysis are listed in Table 2.

Table 2. Elemental analysis of optically active bromides.<sup>a</sup>

Sample (dried at 120°C)	% Cr		% C		% H		% N		% Br	
	found	theor.	found	theor.	found	theor.	found	theor.	found	theor.
(+) <sub>D</sub> -[Cr en <sub>3</sub> ]Br <sub>3</sub>	10.98	11.02	15.16	15.25	5.12	5.08	17.82	17.80	50.30	50.85
(+) <sub>D</sub> -[Cr en <sub>2</sub> tn]Br <sub>3</sub>	—	10.70	17.20	17.28	5.38	5.35	17.54	17.28	49.41	49.38
(+) <sub>D</sub> -[Cr en tn <sub>2</sub> ]Br <sub>3</sub>	10.62	10.40	18.82	19.20	5.70	5.60	16.57	16.80	47.36	48.00
(-) <sub>D</sub> -[Cr tn <sub>3</sub> ]Br <sub>3</sub>	—	10.12	20.36	21.01	6.05	5.84	16.18	16.34	45.65	46.69

<sup>a</sup> By Preben Hansen, Kem. Lab. II, H. C. Ørsted Inst., Copenhagen.

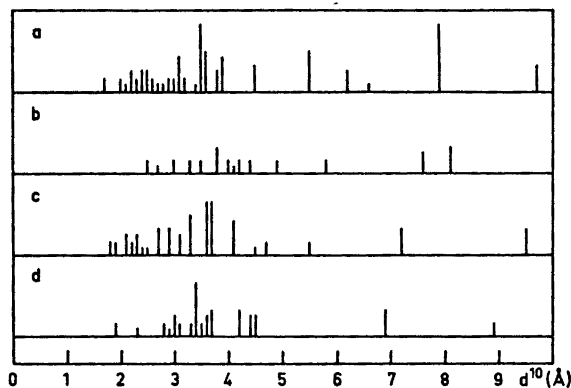


Fig. 2. X-Ray powder diagrams of active bromides. (CoK $\alpha$  radiation.) The height indicates the relative intensities. a.  $(-)_D$ -[Cr  $tn_3$ ]Br $_3$ ; b.  $(+)_D$ -[Cr  $en\ tn_2$ ]Br $_3$ ; c.  $(+)_D$ -[Cr  $en_2\ tn$ ]Br $_3$ ; d.  $(+)_D$ -[Cr  $en_3$ ]Br $_3$ .

The water content and equivalent weight have been determined by means of the thermobalance. Additionally the water content has been determined by drying at 120°C for 24 h. The results are listed in Table 3.

X-Ray powder diagrams are shown in Fig. 2. Attempts at preparing large crystals of the active salts for this purpose have not been successful. Trying to crystallize an optically active salt invariably resulted in the crystallization of the racemic compound, because the velocity of racemization in aqueous solution exceeds the velocity of crystallization. The X-ray powder photographs, therefore, have been made directly from the microcrystalline products of the resolution.

### Measurements

By means of a Cary 14 spectrophotometer absorption spectra have been recorded at 25°C in the range of 230–800 nm. The circular dichroism has been measured on a Roussel-Jouan Dichrographe in the range 230–600 nm. The results are shown in Fig. 3.  $(-)_D$ -[Cr  $en_3$ ]Br $_3$  within experimental uncertainty yielded precisely the mirror image of the CD curve shown for the  $(+)_D$  enantiomer. The sign of the optical rotation at  $D = 589$  nm has been determined by means of a Perkin-Elmer Polarimeter 141.

Table 3. Water content and equivalent weight (per Cr) of active bromides.

Anhydrous salt	Mol ratio H $_2$ O:Cr in salt hydrate		Equiv.w. of anhydrous salt	
	thermogr.	drying	exp.	theor.
$(+)_D$ -[Cr $en_3$ ]Br $_3$	0.6	0.6	470	472
$(+)_D$ -[Cr $en_2\ tn$ ]Br $_3$	0.2	0.2	485	486
$(+)_D$ -[Cr $en\ tn_2$ ]Br $_3$	3.1	3.0	502	500
$(-)_D$ -[Cr $tn_3$ ]Br $_3$	1.3	1.0	512	514

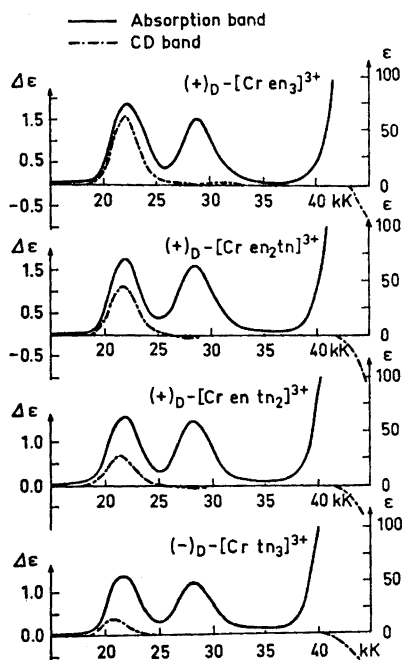


Fig. 3. Absorption and CD spectra of *ca.* 0.01 M aqueous solutions of act.- $[\text{Cr en}_{3-n} \text{tn}_n] \text{Br}_3$  ( $n = 0, 1, 2, 3$ ).

## DISCUSSION

It should be pointed out that for  $(+)\text{D}-[\text{Cr en}_3]^{3+}$  the CD curve obtained by us deviates somewhat from that earlier published by Mathieu<sup>11</sup> and generally accepted (*e.g.* by Landolt-Börnstein, Gmelin, and in Ref. 1) as correct. The main differences are the peculiar shape of the "first" CD band, and the fact that the CD remains positive throughout the spectral range studied including the range of the second, weakly optically active absorption band at *ca.* 28 kK where earlier measurements indicated a negative value. The continuous curve obtained by us is in fact not inconsistent with Mathieu's experimental results obtained at single wavelengths only; but we cannot explain the difference in sign. Iodide ions are known to influence the second absorption band of  $[\text{Cr en}_3]^{3+}$ , and as Mathieu's measurements were performed on the iodide we have repeated our measurements using the iodide in concentrations similar to those used by Mathieu. We have also checked that our measurements were performed before the effect of aquotisation is seen, and having furthermore obtained identical results (of opposite sign) for the  $(-)\text{D}$ -enantiomer we must conclude that our results are correct.

It has been suggested<sup>12</sup> that the rotatory strength of the "first" absorption band of a mixed tris(diamine) complex could be considered as approximately equal to the sum of three contributions, one from each of the metal chelate rings. Some quantities calculated for the purpose of testing this hypoth-

Table 4. Maximum values, wave-numbers and half widths for the "first" bands of absorption and circular dichroism of act.-[Cr en<sub>3-n</sub>tn<sub>n</sub>]<sup>3+</sup>Br<sub>3</sub>.

Optically active ion	"First" band of absorption			Band of circular dichroism		
	$\epsilon_{\max}$	$\nu_{\max}$ kK	$\Delta\nu_{\frac{1}{2}}$ kK	$(\epsilon_1 - \epsilon_r)_{\max}$	$\nu_0$ kK	$\Delta\nu_{\frac{1}{2}}$ kK
(+) <sub>D</sub> -[Cr en <sub>3</sub> ] <sup>3+</sup>	75.0	21.84	3.38	1.60	21.88	2.81
(+) <sub>D</sub> -[Cr en <sub>2</sub> tn] <sup>3+</sup>	71.0	21.65	3.38	1.17	21.84	2.83
(+) <sub>D</sub> -[Cr en tn <sub>2</sub> ] <sup>3+</sup>	60.0	21.60	3.34	0.71	21.33	2.86
(-) <sub>D</sub> -[Cr tn <sub>3</sub> ] <sup>3+</sup>	56.1	21.51	3.28	0.38	20.79	2.43

esis are given in Table 5. The dipole strength,  $S$ , and the total rotatory strength,  $\sum R_{\text{obs}}$ , are obtained from the areas of the absorption bands and the CD bands, respectively, as

$$S = 9.18 \times 10^{-39} \int \frac{\epsilon}{\nu} d\nu \text{ e.s.u.}$$

$$\sum R_{\text{obs}} = 2.29 \times 10^{-39} \int \frac{(\epsilon_1 - \epsilon_d)}{\nu} d\nu \text{ e.s.u.}$$

which for Gaussian absorption and CD bands transform to

$$S = 9.77 \times 10^{-39} \frac{\epsilon_{\max} \Delta\nu_{\frac{1}{2}}}{\nu_{\max}} \text{ e.s.u.}$$

$$\sum R_{\text{obs}} = 2.45 \times 10^{-39} (\epsilon_1 - \epsilon_r)_{\max} \frac{\Delta\nu_{\frac{1}{2}}}{\nu_0} \times 10^{40} \text{ Biot}$$

The values of  $S$  and  $\sum R_{\text{obs}}$  given in Table 5 have been calculated using this approximation. Numerical values of the band parameters are given in Table 4.

The rotatory strengths of the mixed complexes,  $\sum R_{\text{calc}}$ , are calculated from the data for the pure complexes according to three different schemes. The results in column I were obtained by simple linear interpolation between  $\sum R_{\text{obs}}$  of the pure complexes. The results in column II were obtained according to the scheme suggested in Ref. 1, in which the suggestion by Moffitt,<sup>13</sup> that only a part,  $S_{\text{act}}$ , of the observed dipole strength contributes to the optical

Table 5. Apparent values of dipole and rotatory strengths of the "first" absorption band of [Cr en<sub>3-n</sub>tn<sub>n</sub>]<sup>3+</sup> (as the bromide in ca. 10<sup>-2</sup> M aqueous solution).

Optically active ion	$S \times 10^{38}$ e.s.u.	$S_{\text{act}} \times 10^{38}$ e.s.u.	$\sum R_{\text{obs}}$ Biot	$\chi \times 10^{21}$ e.s.u.	$\sum R_{\text{calc}}$ Biot		
					I	II	III
(+) <sub>D</sub> -[Cr en <sub>3</sub> ] <sup>3+</sup>	11.34	5.13	5.04	1.285	—	—	—
(+) <sub>D</sub> -[Cr en <sub>2</sub> tn] <sup>3+</sup>	10.83	4.62	3.72	—	3.72	3.72	3.70
(+) <sub>D</sub> -[Cr en tn <sub>2</sub> ] <sup>3+</sup>	9.06	2.85	2.33	—	2.41	2.09	2.26
(-) <sub>D</sub> -[Cr tn <sub>3</sub> ] <sup>3+</sup>	8.36	2.15	1.09	0.43	—	—	—

activity, is combined with an attempt at taking into consideration the (non-linear) variation of the dipole strength caused by the stepwise substitution of en by tn. In this scheme

$$S_{\text{act}} = S - S_{[\text{Cr}(\text{NH}_3)_6]^{3+}} = S - 6.21 \times 10^{38} \text{ e.s.u.}$$

$$\sum R_{\text{calc}} = [(3 - n)\chi_{\text{en}} + n\chi_{\text{tn}}] \sqrt{S_{\text{act}}/3} \quad (n \text{ being the number of tn ligands per Cr})$$

$$\chi = \sum R_{\text{obs}}/3 \sqrt{S_{\text{act}}/3}$$

The results in column III were obtained using the latter scheme but substituting  $S$  for  $S_{\text{act}}$ , *i.e.* disregarding the suggestion by Moffitt. In this case – in contrast to the case of the analogous Co(III) complexes – these schemes yield rather similar results all of which are in fairly good agreement with the observed values of the rotatory strength.

The same absolute configuration,  $A$ , has been ascribed to  $(+)_D\text{-}[\text{Cr en}_3]^{3+}$  and  $(-)_D\text{-}[\text{Cr tn}_3]^{3+}$ .<sup>1,9</sup> The regular variation of the rotatory strength within the series of complexes considered in the present paper indicates that also  $(+)_D\text{-}[\text{Cr en}_2\text{tn}]^{3+}$  and  $(+)_D\text{-}[\text{Cr en tn}_2]^{3+}$  possess this configuration. This is in accordance with the result of applying the solubility criterion to the complex salts of  $\alpha$ -nitro- $(+)_D$ -camphor.

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