

Induced Optical Activity in $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Co}(\text{en})_3^{3+}$ Upon Outer-Sphere Association With (+)Tartrate²⁻ and Other Chiral Anions

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It is reported that a chiral anion in an outer sphere position can induce circular dichroism in the $d-d$ transitions of an octahedral substitution inert transition metal complex. It is suggested that the anion must be preferentially orientated by chelatic bonding.

The CD spectra (light absorption spectra are also reported) of the outer sphere complexes between $\text{Co}(\text{NH}_3)_6^{3+}$ (I), (+)Co(en)₃³⁺ (II), (-)Co(en)₃³⁺ (III) and (+)tartrate²⁻ (IV) and (-)tartrate²⁻ (V) are discussed in terms of the following effects: A. CD due to preferential association of the chiral anion to one enantiomer in a racemic mixture if the CD of the enantiomers are changed upon the association. B. Induced CD by direct interaction between the chiral anion and the d -orbitals. C. Chiral medium effect, CD due to the different refractive indices, for left and right circularly polarised light, of the optically active solvent. D. CD caused by preferred conformation of inner chelatic ligands in the presence of the helical outer sphere ligand.

It is concluded that the effect C can be generally neglected, and that the CD differences between the outer sphere complexes II-IV and II-V (or III-IV and III-V) are due to a combination of B and D effects. The CD effect of I-IV (or I-V) is the B-type effect.

The maximum is observed at the same wavelength as the $^1A_{1g} \rightarrow ^1T_{1g}$ absorption band of I and is in I-IV and I-V -0.02 and +0.02 M⁻¹ cm⁻¹, respectively. These values are about 10 times lower than the corresponding CD effects observed with tartrate in the inner sphere.

The stability constants for the outer sphere complexes have been estimated from UV absorbance measurements. From the fact that the same constants were obtained under the conditions $C_M > C_L$ and $C_M < C_L$, it has been concluded that only one complex is formed. The stability constants for the complexes are: I-IV ($31 \pm 1 \text{ M}^{-1}$), II-IV and III-V ($26 \pm 2 \text{ M}^{-1}$), II-V and III-IV ($22 \pm 2 \text{ M}^{-1}$). The constants obtained from similar measurements on circular dichroism were considerably lower (e.g. that of II-IV, $16 \pm 3 \text{ M}^{-1}$) a fact which has not yet been possible to explain.

In the light of the current discussions on outer-sphere complexes,¹⁻¹⁰ if the bonding is purely a result of Coulombic attraction or if other forces also contribute, it has been considered pertinent to investigate cases where the outer sphere ligand has a quality that can make it possible to determine if the arrangement of the outer sphere ligands is random or not. In the recently studied system $\text{Co}(\text{en})_3^{3+} + \text{EDTA}^{2-}$ ^{11,12} where it could be shown that an observed spectroscopic effect was due only to outer sphere association, it was concluded that a preferential non-random association was the case. This conclusion was based upon the assumption that the dissymmetric (*i.e.* non-spherical) orbitals studied (E_a and A_2 , see Refs. 11, 12) should be equally perturbed on average if the perturbation was due to the outer sphere association and the latter was random. This is equivalent to saying that the "contact areas" of E_a and A_2 are equal—an eventual screening by the inner ligands is equally partitioned between the two orbitals.

A case which should provide information in the field discussed here is the association between a chiral metal complex and a chiral anion. Any differences (in stabilities) between two *semi-enantiomeric* systems (*e.g.* $(-)\text{Co}(\text{en})_3^{3+} + (+)\text{tartrate}^{2-}$ *contra* $(-)\text{Co}(\text{en})_3^{3+} + (-)\text{tartrate}^{2-}$) must be assigned to different arrangements at the associations. Such a system and its enantiomer (*e.g.* $(-)\text{Co}(\text{en})_3^{3+} + (+)\text{tartrate}^{2-}$ and $(+)\text{Co}(\text{en})_3^{3+} + (-)\text{tartrate}^{2-}$), however, are chemically equivalent.

The association between certain optically active species (*e.g.* $(+)\text{Co}(\text{en})_3^{3+} + (+)\text{tartrate}^{2-}$) has already been studied by Ogino¹³ who actually reports a difference between the "semienantiomeric" association constants. At the determination of the constants, however, Ogino used excess of ligand only, a method which might involve a considerable error due to the formation of more than one complex.¹² At the investigation here we have therefore also applied a method using the central ion in excess. The methods have been described elsewhere.¹²

Another purpose of this investigation has been to determine if a chiral ligand in an *outer sphere* position can induce optical activity (*i.e.* circular dichroism) into the $d-d$ -transitions of the metal ion. CD has been reported by Mason and Norman¹⁴ in the region of the absorption ${}^1A_{1g} - {}^1T_{1g}$ of $\text{Co}(\text{NH}_3)_6^{3+}$ when dissolved in $(+)\text{diethyltartrate}$, but the absorption intensity of the metal complex changed considerably (increase) in this medium, which should not be expected at an ordinary outer sphere complex formation. The nature of the "ligand" and the fact that it was used in excess also makes it difficult to assign the observed CD effect to discrete outer sphere complexes.

It should be noted that Bhatnagar and Kirschner,²⁰ who studied the compounds $[\text{Co}(\text{NH}_3)_4(+)\text{tartrate}]\text{ClO}_4$ (I), $[\text{Co}(\text{NH}_3)_5(+)\text{tartrate}]\text{ClO}_4$ (II), and $[\text{Co}(\text{NH}_3)_6]_2(+)\text{tartrate}_3$ (III), did not find any anomalous rotatory dispersion (\equiv Cotton effect) in the ligand field wavelength region of a solution of the last mentioned salt (III). They concluded therefore that to be able to give rise to a Cotton effect, it was necessary for the chiral ligand to be in the inner sphere and they suggested that the presence of anomalous rotatory dispersion was a criterion for inner sphere coordination. They also noted that with

tartrate as a bidentate ligand (I), the induced Cotton effect was noticeably greater than with tartrate as a monodentate ligand (II).

A purely induced CD effect (Cotton effect) can only be studied between a *non*-chiral chromophore (e.g. $\text{Co}(\text{NH}_3)_6^{3+}$) and a *non*-absorbing chiral species (e.g. (+)tartrate²⁻ in the visible), as, if one of the constituents possesses CD, the induced effect upon association may be inseparably mixed with a CD polarisation of the kind reported for (+)Co(en)₃³⁺ + EDTA²⁻.¹¹

The observations of Mason and Norman¹⁴ have actualized the question if an outer sphere coordination is the only possible explanation of the CD. As the absorption intensity of a chromophore depends on the refractive index of the medium surrounding the actual electronic transition, it might be suggested that any chromophore dissolved in an optically active medium, *i.e.* a medium having different refractive indices n_l and n_r for left and right circularly polarised light, should have different absorption for left and right circularly polarised light, *i.e.* should exhibit circular dichroism. This question will be further discussed (Discussion).

Though a large number of investigations have been performed concerning the circular dichroism spectra of transition metal complexes whose dissymmetry is caused by a helical arrangement of chelatic ligands around the central ion, complexes deriving their dissymmetry from chirality of the chelate ligands themselves have been relatively little studied.¹⁵ Some simple rules have been suggested, however, for the sign and magnitude of the induced Cotton effect in such complexes.^{16,17} Attempts have been made to relate the sign with the absolute configuration of the complex *via* the assignment of an "octant sign"¹⁶ of the type applied by Moffitt and co-workers to define the absolute configuration of organic carbonyl compounds,¹⁸ but it is questionable if there can ever be any general rule correlating the sign of the Cotton effect with the *octant sign*. For the magnitude of the Cotton effect there has long existed an empirical rule saying that a "strong" effect can be produced only if the chiral ligand is chelatically bonded to the metal ion.^{17,36} This criterion seems to be evident, at least from a tentative point of view, because with only *one* connecting link the chiral ligand can take practically any position in relation to the metal ion and in the overall sum different induced Cotton effects from different arrangements will cancel. Because of the lack of examples of CD of complexes with and without chelatic bonding of a certain ligand, however, this rule has not been proved to be general.

One of the principal difficulties when trying to apply an "octant sign - Cotton effect rule" on transition metal inner sphere complexes, is that of making the spectral assignments of the bands corresponding to the Cotton effects, especially if the symmetry is radically changed at the introduction of the chiral ligand.¹⁵ On the other hand, it might be suggested that, if it is really possible to induce CD from the outer sphere, the metal complex of high symmetry (e.g. $\text{Co}(\text{NH}_3)_6^{3+}$) might be used to indicate the conformation of a chiral outer sphere ligand, *via* the CD induced in the rigid inner sphere of high symmetry (O_h) when superimposed by a weak chiral field from an embracing outer sphere ligand.

METHODS

Absorption (and in applicable cases circular dichroism, *e.g.* for (+)Co(en)₃³⁺) has been measured on solutions with varying concentration C_M of the metal complex M and constant concentration C_L of outer sphere ligand L ($C_L < C_M$) or with varying C_L and constant C_M ($C_M < C_L$). These methods have been described before¹² but the first mentioned one will be briefly described.

If δ_A is the difference in absorption between the solutions (C_M, C_L) and ($C_M, C_L=0$), ϵ_M and ϵ_{ML} are the molar absorption coefficients for M and ML, respectively, and $\beta_1 = [ML]/[M][L]$ is the required stability constant,

$$C_M/\delta_A = \frac{1}{C_L(\epsilon_{ML} - \epsilon_M)} C_M + \frac{1}{\beta_1 C_L(\epsilon_{ML} - \epsilon_M)} + \frac{1}{\epsilon_{ML} - \epsilon_M}$$

Thus a straight line will be obtained if C_M/δ_A is plotted *versus* C_M (provided that the absorption of L can be neglected). β_1 is obtained as the ratio between the slope of the line and {the intercept - $1/(\epsilon_{ML} - \epsilon_M)$ }, $\epsilon_{ML} - \epsilon_M$ is given by the slope of the line, as C_L is known.

The absorption and circular dichroism measurements have been performed at wavelengths giving optimal differences δ_A and δ_{CD} (265.0 nm and 443.3 nm, respectively). The CD wavelength has also been chosen to provide $\Delta\epsilon_M = 0$, which makes it possible to use a differential method, described in Ref. 12. The value of ϵ_M was simply obtained from the absorbance of the solution ($C_M, C_L = 0$).

Circular dichroism has been studied of solutions of (+)Co(en)₃³⁺, (±)Co(en)₃³⁺ and Co(NH₃)₆³⁺ in the presence of some optically active anions with varying possibility of forming *chelatic* bonds (Table 4).

In view of the earlier experiences of the pH-dependence¹¹ and dependence on ionic strength¹² of the association degree of Co(en)₃³⁺ + EDTA²⁻, it has been considered important to briefly investigate the corresponding effects for the association with tartrate²⁻.

EXPERIMENTAL

The experimental details concerning the determinations of stability constants have been described before.¹² The absorption and the circular dichroism measurements were performed with a Zeiss PMQ II instrument and a Jouan Dichrograph Model B, respectively. The UV absorption spectra were recorded with a Cary Model 15 spectrophotometer. All cell-holders were thermostated to $25.00 \pm 0.05^\circ\text{C}$.

Tartrate²⁻ solutions were prepared from (-)tartaric acid (*p.a.*, BDH) and (+)tartaric acid (*p.a.*, Merck) by addition of two equivalents of sodium hydroxide. Camphorate²⁻, camphorsulphonate⁻, and alaninate⁻ were prepared in the corresponding way from (+)camphoric acid (*p.a.*, Aldrich), (+)camphor-10-sulphonic acid (*purum*, Fluka), and L(+)-alanine (Schuchardt), respectively. L(+)-Glutamic acid sodium salt (*p.a.*) was obtained from BDH. The rotations of 0.1 M solutions of the tartrate²⁻ enantiomers were found to be +0.520 and -0.520 deg dm⁻¹. Except for Co(NH₃)₆Cl₃ the preparation and the qualities of all other chemicals have been described before.¹² As it was found impossible, due to low solubility, to use a 0.03 M stock solution of Co(NH₃)₆(ClO₄)₃, the chloride was used instead (preparation in Ref. 21). Separate experiments with Co(NH₃)₆(ClO₄)₃ (prepared from the chloride by precipitation with conc. HClO₄) have also been performed to show that the chloride influence was of minor importance (*cf.* Fig. 6.)

Dipole strengths have been obtained from the absorption band areas of the spectra in Fig. 5. These spectra have been calculated from recorded spectra on solutions with $C_M=3.00$ mM, $C_L=20.0$ mM and $I=0.100$ M.

pH measurements were performed in order to show if any deprotonisation takes place in tartrate²⁻ when complexing with the metal complex ions. Though no pH changes could be detected, the inaccuracy due to the low stability constants makes the conclusion of no deprotonisation not completely reliable.

Qualitative CD studies have been performed with higher concentrations of M and L. No other effects or tendencies than the reported (Table 4) were observed. (Due to low solubility of the camphorate, this ligand could not be used in higher concentrations.)

It was observed that different molar absorption coefficients (at 265 nm) could be obtained with $\text{Co(en)}_3(\text{ClO}_4)_3$ prepared at different occasions. This must probably be assigned to strongly UV absorbing (organic) impurities. The large difference between certain absorption coefficients in Table 2 can probably be explained in the same way.

Table 1. Measured CD differences, δ_{CD} , between the solutions (C_M, C_L) and ($C_M, C_L=0$) for the case M=(-)Co(en)₃³⁺, L=(+)tartrate²⁻ and (-)tartrate²⁻ (δ_{-+} and δ_{--} , respectively). $C_L=4.00$ mM.

C_M (mM)	$+\delta_{--} \times 10^4$ (cm ⁻¹)	C_M/δ_{--} (M cm)	$+\delta_{-+} \times 10^4$ (cm ⁻¹)	C_M/δ_{-+} (M cm)
3.00	1.80 ± 0.10	16.7	1.20 ± 0.10	25.0
4.80	2.77	17.3	1.80	26.7
6.00	3.39	17.7	2.32	25.9
7.20	4.09	17.6	2.70	26.7
9.00	4.91	18.3	3.16	28.5
10.80	5.81	18.6	3.86	28.0
12.00	6.26	19.1	4.27	28.1
13.80	7.12	19.4	4.72	29.2
C_M/δ versus C_M slope (cm) intercept (M cm)		245 ± 14 16.04 ± 0.13		350 ± 61 24.34 ± 0.55

Table 2. Final results from UV absorption and CD measurements on solutions containing (+)Co(en)₃(ClO₄)₃ and Na₂(+)tartrate denoted ++, (+)Co... and Na₂(-)... denoted +-, etc. Number of measuring points is given in italics in the second column. The obtained values of ϵ_M and $\Delta\epsilon_M$ are 165 and 0 M⁻¹ cm⁻¹, respectively.

Method	Isomers of Co(en) ₃ ³⁺ and tartrate ²⁻	Absorbance at 265.0 nm		Circular dichroism at 443.3 nm	
		β_1 (M ⁻¹)	$\epsilon_{\text{ML}} - \epsilon_{\text{M}}$ (M ⁻¹ cm ⁻¹)	β_1 (M ⁻¹)	$\Delta\epsilon_{\text{ML}} - \Delta\epsilon_{\text{M}}$ (M ⁻¹ cm ⁻¹)
$C_M > C_L$	++ 9	26 ± 2	350 ± 30	17 ± 2	-0.95 ± 0.1
	+ - 9	23 ± 3	370 ± 30	12 ± 3	-0.8 ± 0.2
$C_L = 4.00_0$ mM	-- 8	29 ± 4	530 ± 40	16 ± 1	+1.02 ± 0.09
	- + 8	23 ± 4	610 ± 60	15 ± 2	+0.71 ± 0.09
$C_L > C_M$	++ 6	26 ± 3	350 ± 30	15 ± 1	-1.09 ± 0.05
	+ - 6	18 ± 2	420 ± 30	17 ± 3	-0.70 ± 0.08
$C_M = 2.97_3$ mM	++ and --	26 ± 2	350 ± 30	16 ± 3	- and + 1.0 ± 0.1
	+ - and - +	22 ± 2	390 ± 30	15 ± 3	- and + 0.7 ± 0.1

RESULTS

Table 2 presents the final results from UV absorbance measurements and differential CD measurements in the visible region on $\text{Co(en)}_3^{3+} + \text{tartrate}^{2-}$ solutions. Table 1 gives some examples of the CD measurements.

It is obvious (Table 2) that there is no great difference between the results obtained with excess of M and excess of L with $\text{M} = \text{Co(en)}_3^{3+}$ and $\text{L} = \text{tartrate}^{2-}$, contrary to the corresponding case with $\text{L} = \text{EDTA}^{2-}$, where the β_1 values obtained with excess of M were almost twice the values with excess of L.¹² This fact suggests that the predominating associate is the $[\text{Co(en)}_3]\text{tartrate}^+$ complex even at relatively high L concentrations.

The mean values of β^* obtained from the absorbance measurements are in good agreement with those reported by Ogino¹³ ($\beta_{++} = 26 \pm 2 \text{ M}^{-1}$ and $\beta_{-+} = 21 \pm 2 \text{ M}^{-1}$).¹³

The β values estimated from differential CD measurements, however, are considerably lower than these values. This discrepancy ** was also observed in the $\text{Co(en)}_3^{3+} + \text{EDTA}^{2-}$ case,¹² but has not yet been possible to explain. Fig. 1 gives examples on lines obtained from C_M/δ_{Abs} versus C_M and C_M/δ_{CD} versus C_M . As can be seen, the points correspond very well to straight lines,

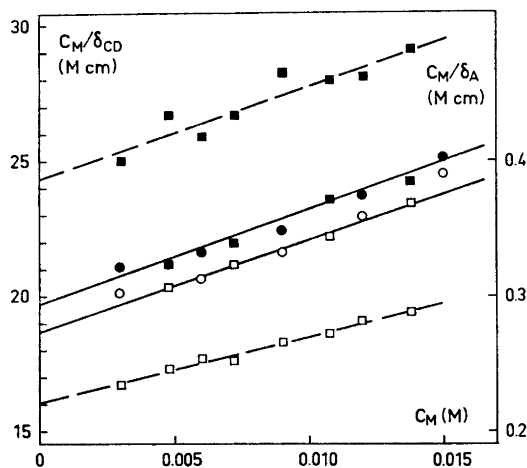


Fig. 1. C_M/δ plotted versus C_M ($C_M > C_L = 4.00_0 \text{ mM}$) for (+) and (-) Co(en)_3^{3+} combined with (+) and (-) tartrate, e.g. δ_{+-} corresponds to (+) $\text{Co(en)}_3^{3+} + (-)$ tartrate. Absorbance at 265 nm (+ + = \square and \circ , + - = \blacksquare and \bullet) and circular dichroism at 443.3 nm (- - = \square and - + = \blacksquare) are used.

* The enantiomeric equilibria, e.g. (+) $\text{Co(en)}_3^{3+} + (-)$ tartrate²⁻ $\rightleftharpoons \dots$ and (-) $\text{Co(en)}_3^{3+} + (+)$ tartrate²⁻ $\rightleftharpoons \dots$, have been considered equivalent from a chemical point of view, i.e. $\beta_{+-} = \beta_{-+}$ and $\beta_{++} = \beta_{--}$.

** It might be suspected that the difference is due to an erratic absorption measurement. A species exhibiting circular dichroism should not obey the Bouguer-Lambert-Beer law ($A = \log(I_0/I) = \epsilon lc$) but a law $A \approx \epsilon lc - 0.288 g^2(\epsilon lc)^2$ (see Ref. 22), where $g = (\epsilon_1 - \epsilon_2)/\epsilon$. However, as the g values of the active species will be small (3×10^{-3}), the departure will be negligible. Measurements on pure (+) $\text{Co(en)}_3(\text{ClO}_4)_3$ verify that so is the case.

It has also been checked that the CD deflection was proportional to c and l (for (+) Co(en)_3^{3+}).

even in the $-+$ case where the observed CD differences are considerably smaller than in the $--$ case (*cf.* Table 1.)

To more closely study the possible existence of an "induced CD" effect we concentrated on the couple $\text{Co}(\text{NH}_3)_6^{3+} - \text{L}$, where L is an optically active anion. In this case an apparent CD in the $d-d$ bands of cobalt could be caused only by the interaction with the d -orbitals from the dissymmetric field of the anion effected either by direct interaction with the orbitals (or with a dissymmetric electrostatic field) of the anion or by the formation of a chiral chelatic inner ligand *via* hydrogen bonding to two adjacent ammonia molecules. Table 4 shows the results of such experiments. CD has been found to appear in $\text{Co}(\text{NH}_3)_6^{3+}$ when complexing with (+)-10-camphorsulphonate⁻ and (+)tartrate²⁻ ions, which ligands also seem to be most fitted for the formation of chelatic bonding (the rigid (+)camphorate²⁻ ion appears for steric reasons to be unsuitable and the alaninate⁻ ion has only one negative group available or group suitable for hydrogen bonding and the amino group is not supposed to form any strong outer sphere bonds on cobaltamine complexes²⁶). 10-Camphorsulphonate⁻ and tartrate²⁻ are also the only anions, in the table, which produce strong negative effects on the CD maxima of the E_a and A_2 components of the CD spectrum of (+)Co(en)₃³⁺ (Table 4), a fact that indicates either a higher degree of association with these ligands, or a stronger polarizing power in the complex (or a combination of these effects).

The mapping down of the outer sphere complexation of $\text{Co}(\text{NH}_3)_6^{3+} + \text{tartrate}^{2-}$, necessary for obtaining the absolute CD of the associate, $\Delta\epsilon_{\text{ML}}$, is reported in Table 3. As with $\text{Co}(\text{en})_3^{3+}$ the results with $C_{\text{M}} > C_{\text{L}}$ and $C_{\text{M}} < C_{\text{L}}$ are approximately the same, indicating that only the 1:1 complex is of any importance. The high precision in the determination of β_1 is due mainly to a large difference between ϵ_{M} and ϵ_{ML} (Fig. 2).

Table 3. Results from UV absorption measurements at 265.0 nm on C_{M} M $\text{Co}(\text{NH}_3)_6^{3+} + C_{\text{L}}$ M (+)tartrate²⁻.
A = absorbance per unit length.

2.97 ₃ mM $\text{Co}(\text{NH}_3)_6\text{Cl}_3$				3.00 mM $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$				4.00 mM $\text{Na}_2(+)\text{tartrate}$ ($\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$)			
C_{L} (mM)	A (cm ⁻¹)	δ (cm ⁻¹)	C_{L}/δ (M cm)	C_{L} (mM)	A (cm ⁻¹)	δ (cm ⁻¹)	C_{L}/δ (M cm)	C_{M} (mM)	A (cm ⁻¹)	δ (cm ⁻¹)	C_{M}/δ (M cm)
0	0.029	0	—	0	0.0080	0	—	3.00	0.0510	0.0430	0.0698
10.00	0.110	0.066	0.151	10.00	0.0985	0.0855	0.117	4.50	0.0760	0.0640	0.0703
14.00	0.137	0.087	0.161	12.00	0.1115	0.0975	0.123	6.00	0.0975	0.0815	0.0736
16.00	0.147	0.094	0.170	14.00	0.1255	0.1105	0.127	7.50	0.1200	0.1000	0.0750
18.00	0.158	0.102	0.176	16.00	0.1830	0.1220	0.131	9.00	0.1395	0.1155	0.0779
20.00	0.169	0.110	0.182	18.00	0.149	0.1320	0.136	12.00	0.175	0.143	0.0839
22.00	0.178	0.116	0.190	20.00	0.159	0.141	0.142				
26.00	0.197	0.129	0.202								
$\beta_1 = 30.3 \pm 1.3 \text{ M}^{-1}$ $\epsilon_{\text{ML}} - \epsilon_{\text{M}} = 103 \pm 3 \text{ M}^{-1} \text{ cm}^{-1}$ $\epsilon_{\text{M}} = 10 \text{ M}^{-1} \text{ cm}^{-1}$				$\beta_1 = 27.9 \pm 1.4 \text{ M}^{-1}$ $\epsilon_{\text{ML}} - \epsilon_{\text{M}} = 139 \pm 5 \text{ M}^{-1} \text{ cm}^{-1}$ $\epsilon_{\text{M}} = 2.7 \text{ M}^{-1} \text{ cm}^{-1}$				$\beta_1 = 32 \pm 2 \text{ M}^{-1}$ $\epsilon_{\text{ML}} - \epsilon_{\text{M}} = 141 \pm 8 \text{ M}^{-1} \text{ cm}^{-1}$ $\epsilon_{\text{M}} = 2.7 \text{ M}^{-1} \text{ cm}^{-1}$			

Fig. 3 depicts the molar circular dichroism spectra and the absorption spectra of $[\text{Co}(\text{NH}_3)_6](+)\text{tartrate}^+$ and $[\text{Co}(\text{NH}_3)_6](-)\text{tartrate}^+$. The former spectra are obviously mirror-images of each other. The latter are identical with each other and the spectrum of $\text{Co}(\text{NH}_3)_6^{3+}$, thus proving that the *inner* coordination sphere is left unchanged.

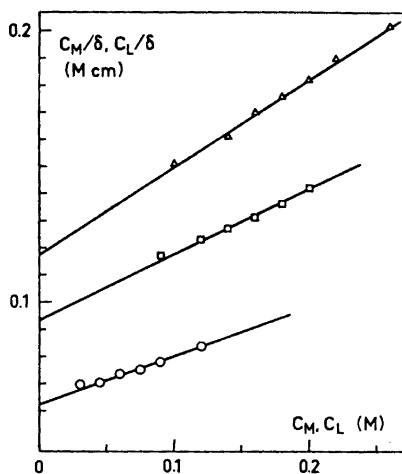


Fig. 2. Determination of the stability constant (β_1) of $[\text{Co}(\text{NH}_3)_6](+)\text{tartrate}^+$ from absorbance measurements at 265.0 nm (Table 3). C_L/δ plotted versus C_L ($\text{Co}(\text{NH}_3)_6\text{Cl}_3$ Δ , $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ \square) i.e. $C_L > C_M$. C_M/δ plotted versus C_M ($\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ \circ) i.e. $C_L < C_M$.

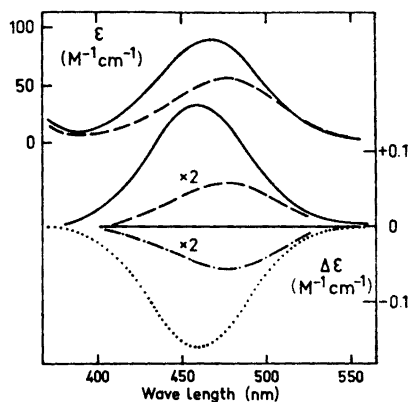


Fig. 3. Absorption spectra (above) of $\text{Co}(\text{en})_3^{3+}$ (—, $\epsilon_{\text{max}} = 88 \text{ M}^{-1} \text{ cm}^{-1}$ at 468 nm) and $\text{Co}(\text{NH}_3)_6^{3+}$ (---, $\epsilon_{\text{max}} = 57 \text{ M}^{-1} \text{ cm}^{-1}$ at 476 nm). Circular dichroism spectra (below) and absorption spectra (above) of $[(\pm)\text{Co}(\text{en})_3](-)\text{tartrate}^+$ (—) and $[\text{Co}(\text{NH}_3)_6](-)\text{tartrate}^+$ (---) and the circular dichroism spectra of the corresponding complexes with (+)tartrate²⁻ (....) and (-)tartrate²⁻ (-.-., respectively).

A determination has also been made of the CD induced in a racemic mixture of (+) and (-) $\text{Co}(\text{en})_3^{3+}$ by the presence of the (+)tartrate²⁻ ion. The CD of the hypothetical ion-pair $[(\pm)\text{Co}(\text{en})_3](+)\text{tartrate}^+$ has been calculated (Table 4, Fig. 3) (the mean of β_{+-} and β_{++} was used as a " β_{\pm} "). The remarkable difference between this CD and the effect in $[\text{Co}(\text{NH}_3)_6](+)\text{tartrate}^+$ is shown in Fig. 3. Both effects have negative signs for (+)tartrate (and positive for (-)tartrate).

The more pronounced CD of $[(\pm)\text{Co}(\text{en})_3](+)\text{tartrate}^+$ may have a simple explanation: as the (+)tartrate²⁻ ion has a preferentially higher degree of association to (+) $\text{Co}(\text{en})_3^{3+}$ than to (-) $\text{Co}(\text{en})_3^{3+}$ (Table 2), and $\Delta\epsilon_{\text{ML}}$ is more negative than $\Delta\epsilon_{\text{M}}$, a mixture of $(\pm)\text{Co}(\text{en})_3^{3+}$ and (+)tartrate²⁻ is actually expected to exhibit a negative CD even if the chiral outer sphere ligand did not introduce any additional dissymmetric effect in the interior of the complex ion.

Fig. 4. shows the CD spectra of (+)Co(en)₃³⁺ and (+)Co(en)₃(+)-tartrate, estimated from recorded spectra of a few solutions and the β₁ values obtained from *absorbance measurements* (Table 2). The fact that the absorbance measurements were used explains the disagreement with the Δε obtained from the differential CD measurements (Table 2).

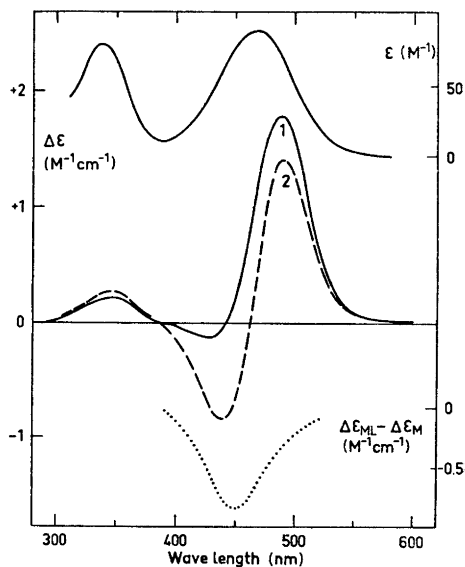


Fig. 4. Molar circular dichroism and absorption spectra of (+)Co(en)₃³⁺ and (+)[Co(en)₃](+)-tartrate⁺ in the "ligand field" range (Δε_M 1, Δε_{ML} 2, ε_M and ε_{ML} -). The difference Δε_{ML} - Δε_M is also depicted.

Since the tartrate itself gives rise to strong CD in the UV it has not been meaningful to resolve the CD spectra of its outer sphere complexes with Co(NH₃)₆³⁺ and Co(en)₃³⁺. However, the corresponding absorption spectra have been calculated (see Fig. 5). The nature of the spectrum of Co(en)₃(+)-tartrate⁺ is similar to that for the complex with EDTA²⁻,¹² *i.e.* it is a spectrum without any appreciable *inter* ionic charge transfer band and with approximately the same dipole strength* as in the free metal complex ion. The broadening of the band is interesting especially in view of the CD change reported in Fig. 4 where the maximum of Δε_{ML} - Δε_M is positioned at a wavelength considerably lower than the absorption maximum, thus suggesting an increased splitting of the components of the respective bands [E(C.T.) to longer wavelength, E_a (L.F.-band) to shorter wavelength]. A total shift of

$$* D_k \approx 0.918 \times 10^{-38} \int_0^{+\infty} \frac{\epsilon(\lambda)}{\lambda_{\max}} d\lambda \text{ erg cm}^{-3} \text{ molecule}^{-1} \text{ has been estimated, by assuming sym-}$$

metric (Gaussian) shapes of the bands, from the longer wavelength halves of the respective bands (see Fig. 5). The results will therefore exclude the additional band at shorter wavelengths due to transitions in the ligand. For Co(NH₃)₆³⁺, Co(NH₃)₆(+)-tartrate⁺, Co(en)₃³⁺ and Co(en)₃(+)-tartrate⁺ the dipole strength values 4.9×10^{-35} , 5.2×10^{-35} , 4.6×10^{-35} , and 4.4×10^{-35} erg cm⁻³ molecule⁻¹, respectively, were obtained.

the $E_a + A_2$ absorption band (*i.e.* a change in the ligand field parameter, Dq) is improbable as it should have to be of a magnitude observable in the ordinary absorption spectrum.

A comparison (Table 4) of the CD effects developed by (+)10-camphor-sulphonate⁻ and by tartrate²⁻ on $\text{Co}(\text{NH}_3)_6^{3+}$ and $(\pm)\text{Co}(\text{en})_3^{3+}$ shows that while the effects from the last mentioned anion differ considerably in magnitude, those of the first mentioned one do not. The strong CD of $(\pm)\text{Co}(\text{en})_3(+)$ -tartrate⁺ and the fact that the CD maxima in the other cases coincide with

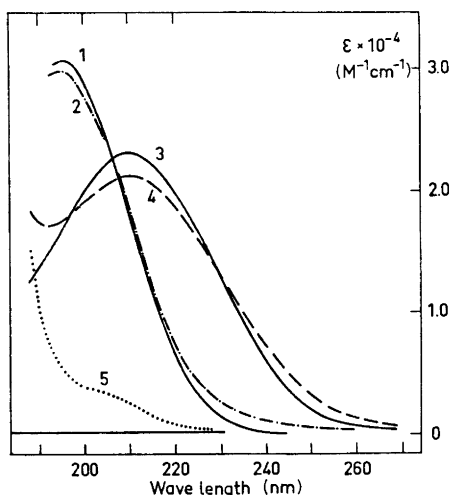


Fig. 5. Molar UV absorption spectra of the species $(+)\text{Co}(\text{en})_3^{3+}$ (3), $\text{Co}(\text{NH}_3)_6^{3+}$ (1), $[(+)\text{Co}(\text{en})_3](+)\text{tartrate}^+$ (4), $[(+)\text{Co}(\text{en})_3](+)\text{tartrate}^+$ (2) and $(+)\text{tartrate}^{2-}$ (5), $\times 10$. The maxima obtained: $\epsilon_{\text{max}}(\text{Co}(\text{en})_3^{3+}, 210 \text{ nm}) = 2.3_4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_{\text{max}}(\text{Co}(\text{NH}_3)_6^{3+}, 196 \text{ nm}) = 3.0_7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_{\text{max}}(\text{Co}(\text{en})_3(+)\text{tartrate}, 211 \text{ nm}) = 2.1_3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{\text{max}}(\text{Co}(\text{NH}_3)_6(+)\text{tartrate}, 196 \text{ nm}) = 2.9_7 \text{ M}^{-1} \text{ cm}^{-1}$.

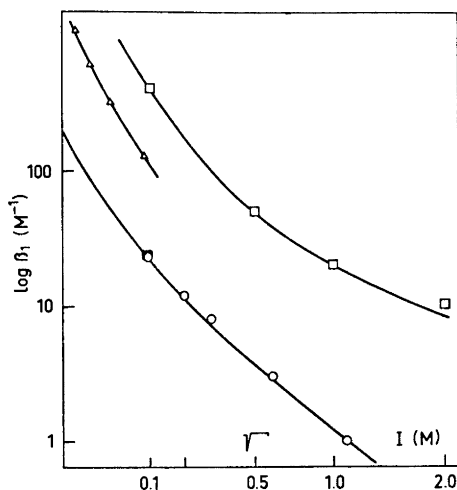


Fig. 6. Comparison of β_1 (log) versus the ionic strength $I(\sqrt{\quad})$ estimated in Table 5 for “ $[(\pm)\text{Co}(\text{en})_3](+)\text{tartrate}^+$ ” (O) with the corresponding dependence obtained for $[(\text{Co}(\text{NH}_3)_6]\text{SO}_4^+$ (Δ)²⁷ and for $(\text{Co}(\text{en})_3\text{EDTA}^+)$ (\square)¹².

the wavelengths of the absorption maxima, suggest that in this case the “induced CD” (the direct influence of the dissymmetric field of the anion on the d -orbitals of cobalt) is accompanied by a stronger effect * probably caused by a conformational change in the inner chelate rings to fit the conformation of the associated tartrate ion. This effect is probably of the same kind as the effects observed in visible CD and UV absorption and CD of $(+)\text{Co}(\text{en})_3^{3+}$ upon association with certain oxy-anions (*e.g.* EDTA^{2-} , $\text{S}_2\text{O}_3^{2-}$)^{3,11,12} but due to different fitting (giving different closeness of approach) with (+) and (-)-

* As will be shown later, the effect on CD by the preferential association⁺ is of minor importance.

Table 4. The influence on the CD of (+)Co(en)₃³⁺ and the CD of solutions of Co(NH₃)₆³⁺ and racemic Co(en)₃³⁺ in the presence of certain optically active anions. The ionic strength is about 0.2 M except in the tartrate case where it is 0.1 M. C_M=0.0120 M except in the tartrate solutions where C_M=0.00300 M. A zero CD recording denotes a CD less than 1 × 10⁻⁵ cm⁻¹. The wavelengths (nm) of the CD maxima are given in parenthesis.

Anion, L	C _L (mM)	M = (+)Co(en) ₃ ³⁺				M = Co(NH ₃) ₆ ³⁺		"M = (±)Co(en) ₃ ³⁺ "	
		CD(M _{Coen₃} ⁻¹ cm ⁻¹)		Effect		CD in ML		CD in ML	
		max 1	max 2	430 nm	490 nm	M _{Co(NH₃)₆} ⁻¹ cm ⁻¹	(M ⁻¹ cm ⁻¹)	M _{Coen₃} ⁻¹ cm ⁻¹	(M ⁻¹ cm ⁻¹)
None	0	-0.140 (428)	+1.800 (487)	0	0	0	-	0	-
Na(-) alaninate	128	-0.150 (429)	+1.821 (487)	-	+	0		0	
Na(-) glutamate	128	-0.191 (430)	+1.813 (487)	-	+	0		0	
Na(+)-10-camphor- sulphonate	128	-0.178 (429)	+1.768 (489)	-	-	-0.006 _s (480-490)		-0.011 (470)	
Na ₂ (+)cam- phorate	32	-0.204 (430)	+1.810 (487)	-	+	0		0	
Na ₂ (+)tartrate (I = 0.1 M)	20	-0.396 (434)	+1.675 (490)	-	-	-0.008 _s (480)	-0.02 ₃ (480)	-0.052 ₀ (459)	-0.16 ₅ (459)

tartrate²⁻ it renders different intensity (Table 2). That the effect is absent in the (±)Co(en)₃³⁺ + (+)-10-camphorsulphonate⁻ case may be referred either to an inability of the anion to produce any conformational change or to equal association, *i.e.* β₊₊ = β₋₊, due to equal fitting. The *non* rigid nature of the alkylsulphonate portion of the anion and the polarising power on the CD spectrum of (+)Co(en)₃³⁺ being not much weaker than that of (+)tartrate²⁻ make the second alternative probable and the first less probable, respectively.*

Due to small effects (in absorbance and CD) on mixing with the other anions in Table 4 it has not been possible to estimate the stability constants for the respective outer sphere complexes (except with glutamate⁻ where the absorbance measurements indicated a β of the order of 3 M⁻¹ with Co(NH₃)₆³⁺).

The study of the outer sphere complex Co(en)₃EDTA⁺¹² showed that the stability constant decreased rapidly with increasing ionic strength. Another observation was that the CD, Δε_M as well as Δε_{ML}, did not vary when changing the ionic strength. Thus the apparent dependence of the CD on the ionic strength should roughly reflect the corresponding dependence of the associa-

* Due to distortion of the conformation equilibria; for (+)Co(en)₃³⁺ kkk ← kkk' ← kk'k' ← k'k'k' with (+)tartrate²⁻ and for (-)Co(en)₃³⁺ the reverse, but less effectively. That the conformation k of ethylenediamine should be preferred with (+)tartrate²⁻ is indicated by the fact that β₊₊ > β₋₊. The conclusion is confirmed by comparing the CD spectra of (+)Co(d-pn)₃³⁺, (-)Co(d-pn)₃³⁺, (-)Co(l-pn)₃³⁺ and (+)Co(l-pn)₃³⁺ which may represent the configuration/conformation combinations M(C₃)(kkk), P(C₃)(kkk), P(C₃)(k'k'k') and M(C₃)(k'k'k'), respectively. In a mixture of these species the hypothetical change (+)Co(l-pn)₃³⁺ → (+)Co(d-pn)₃³⁺, (-)Co(l-pn)₃³⁺ → (-)Co(d-pn)₃³⁺ would just produce the effect visualized in Fig. 4 (dotted line).

Table 5. The dependence of CD of solutions of Co(en)_3^{3+} , $\text{Co(NH}_3)_6^{3+} + \text{tartrate}^{2-}$ on pH and ionic strength. The ionic strength dependence of β is roughly estimated by assuming a constant $\Delta\epsilon_{\text{ML}} = -0.16 \text{ M}^{-1} \text{ cm}^{-1}$ at 460 nm, on a hypothetical outer sphere complex $(\pm)\text{Co(en)}_3(+)\text{tartrate}^+$.

6.00 mM $\text{Co(NH}_3)_6\text{Cl}_3$, 20.00 mM $\text{Na}_2(+)\text{tartrate}$, $C \text{ M HClO}_4$, $\lambda = 480 \text{ nm}$						6.00 mM $(\pm)\text{Co(en)}_3(\text{ClO}_4)_3$, 20.00 mM $\text{Na}_2(+)\text{tartrate}$ $C \text{ M NaClO}_4$ $\lambda = 460 \text{ nm}$			
$I = 0.200 (\text{NaClO}_4)$			$I = 0.100 (\text{NaClO}_4)$						
C_{HClO_4} (mM)	pH	$-\text{CD} \times 10^5$ (cm^{-1})	C_{HClO_4} (mM)	pH	$-\text{CD} \times 10^5$ (cm^{-1})	C_{NaClO_4} (M)	I (M)	$-\text{CD} \times 10^5$ (cm^{-1})	" β " (M^{-1})
0	6.92	3.4	0	7.10	4.6	0	0.096	28.0	23
10	4.10	2.4	10	4.20	3.5	0.1	0.196	17.4	12
20	3.49	1.4	20	3.58	2.4	0.2	0.296	12.9	8
30	2.98	1.0	30	3.06	1.6	0.5	0.596	5.6	3
40	2.53	0	40	2.56	0.9	1.0	1.096	1.9	1

tion constant. Table 5 presents the results of CD measurements on solutions of $\text{Co(en)}_3^{3+} + (+)\text{tartrate}^{2-}$ and $\text{Co(NH}_3)_6^{3+} + (+)\text{tartrate}^{2-}$ at different pH and constant ionic strength. β values have been estimated for the hypothetical outer sphere complex $(\pm)\text{Co(en)}_3(+)\text{tartrate}^+$ (by using the computed CD in Table 4) and the dependence on the ionic strength is compared in Fig. 6 with some earlier results in this field.

DISCUSSION

We have above tentatively indicated the probable existence of the following CD effects in a solution containing an inactive (or a racemic mixture of a) transition metal complex and a chiral anion: A. CD due to preferential association to one enantiomer in a racemic mixture if $\Delta\epsilon_{\text{M}} \neq \Delta\epsilon_{\text{ML}}$. B. Induced CD by direct interaction between the anion and the orbitals taking part in the electronic transitions studied. C. Chiral medium effect. "CD artefact" due to different refractive indices, n_i and n_r , of the medium surrounding the chromophore. D. CD caused by changed conformation of the inner sphere ligands. The presence of a helical outer sphere ligand makes certain conformations preferred, chiral *per se*, of the inner sphere (chelatic) ligands.

"Effect A" should not be confused with the so called "Pfeiffer effect"³⁴ which is a not yet completely explained CD effect arising in solutions of certain metal complex racemates in the presence of certain optically active ions. One criterion on the complex is, namely, that it should be unstable towards racemisation. The present author feels, however, that one possible explanation of the "Pfeiffer effect" is a preferential association (of the type treated in this report) between the chiral anion and one enantiomer of the complex ions combined with the probable³⁵ stabilisation of the associates. The "Pfeiffer effects" observed if chiral cations (instead of anions) are added must be attributed to association due to van der Waals forces. (Instantaneous CD effects can be related to effect B.)

To check to what extent the magnitude of the $\Delta\varepsilon$ of “(\pm)Co(en)₃(\pm)tartrate⁺” of Table 4 (obtained by assuming equal concentrations of the $++$ and $-+$ complexes) is representative for an induced CD effect (B), we have compared it with the “true” $\Delta\varepsilon$ of this hypothetical compound, $(\Delta\varepsilon_{++} + \Delta\varepsilon_{-+})/2$. Any deviation from the last mentioned value should, according to the earlier discussion, be attributed to effect A. The recorded CD ($-0.052 \times 3.00 \times 10^{-3} \text{ cm}^{-1}$ at 459 nm, Table 4) =

$$\begin{aligned} & [(+)Co(en)_3(+)tartrate^+]\Delta\varepsilon_{++} + [(-)Co(en)_3(+)tartrate^+]\Delta\varepsilon_{-+} \\ & + [(+)Co(en)_3^{3+}]\Delta\varepsilon_{++} + [(-)Co(en)_3^{3+}]\Delta\varepsilon_{-+} \\ & \approx 10^{-3}\{0.51\Delta\varepsilon_{++} + 0.45\Delta\varepsilon_{-+} + 0.99(+0.62) + 1.05(-0.62)\} (\text{cm}^{-1}). \\ & (\beta_{++} = 26 \text{ M}^{-1}, \beta_{-+} = 22 \text{ M}^{-1}). \end{aligned}$$

If we assume that $\Delta\varepsilon_{-+}/\Delta\varepsilon_{++} = -0.7$ (according to Table 2 at 443.3 nm) also at 459 nm (*cf.* Fig. 4) the equation above yields the values -0.64 and $+0.45 \text{ M}^{-1} \text{ cm}^{-1}$ for $\Delta\varepsilon_{++}$ and $\Delta\varepsilon_{-+}$, respectively. Obviously the mean $((-0.64 + 0.45)/2 = -0.1 \text{ M}^{-1} \text{ cm}^{-1})$ is of the same magnitude as the $\Delta\varepsilon$ first estimated (-0.165 , Table 4), *i.e.* the effect A has no dominating influence.

The large difference between $|\Delta\varepsilon_{++}|$ and $|\Delta\varepsilon_{-+}|$ (or between $\Delta\varepsilon_{++}$ and $\Delta\varepsilon_{-+}$, see Table 2) can be assigned to a combination of several effects: effects with different signs in $\Delta\varepsilon_{++}$ and $\Delta\varepsilon_{-+}$ are the induced CD effects (B, negative and positive sign, respectively) and the CD due to changed conformation of inner ligand (D, negative and positive sign, respectively). An additional effect, suggested by a comparison of the values of $(\varepsilon_{ML} - \varepsilon_M)_{++}$ and $(\varepsilon_{ML} - \varepsilon_M)_{+-}$ with those of $(\Delta\varepsilon_{ML} - \Delta\varepsilon_M)_{++}$ and $(\Delta\varepsilon_{ML} - \Delta\varepsilon_M)_{+-}$ (350, 390 and -1.0 , $-0.7 \text{ M}^{-1} \text{ cm}^{-1}$, respectively), is that different steric fitting will give different intensity of the ordinary polarisation of CD (negative signs in both $\Delta\varepsilon_{++}$ and $\Delta\varepsilon_{-+}$) and C.T. absorption bands (of the kind observed at the association with almost any oxy-anion, *e.g.* EDTA²⁻).¹² One should thus like to suggest that this “fitting effect” amounts to about 25 % $\left(100 \frac{(390 - 350)/350}{(390 - 350)/350 + (1 - 0.7)/1}\right)$, while 75 % consists of the effects B and D above. Of course such an estimate can be wrong as, *e.g.*, the UV absorption intensity may vary with inner ligand conformation. The fact that ε_{+-} is larger than ε_{++} is, *e.g.*, confusing as the closest approach probably takes place in the $++$ case.

It can be shown that the so called “chiral medium effect” (C) can be ignored in the cases studied here. As this effect should depend only on the absorption of the solute and the difference $n_1 - n_r$ of the solvent at the wavelength used at the CD measurement, any solution devoid of CD and having absorption and optical activity of magnitudes defined by the experiments above, should prove this. Simple tests with concentrated sucrose solutions ($\alpha = 20^\circ \text{ dm}^{-1}$ at 600 nm implying a difference $n_1 - n_r = \lambda\alpha/\pi = 7 \times 10^{-7}$; α in radians) containing suitable chromophores (Methylene Blue, K₂Cr₂O₇, KCo(EDTA)) thus failed to exhibit any CD (*i.e.* $0 \leq |\text{CD}| < 10^{-5}$). The tests were performed on samples with absorbances lower than 2. With higher absorption, CD deflection could be recorded due to “instrumental artefacts”.^{28,20}

Under certain assumptions (Lorenz-Lorentz field) it can be shown²³ that the effect due to surrounding dielectric (with the refractive index n) can be expressed by $\alpha_{\text{solution}} = \alpha_{\text{gas}}(n^2 + 2)/3$ and $\Delta\epsilon_{\text{solution}} = \Delta\epsilon_{\text{gas}}(n^2 + 2)/3$ for optical rotation and circular dichroism, respectively. The corresponding correction for the absorption is $\epsilon_{\text{solution}} = \epsilon_{\text{gas}} [(n^2 + 2)/3]^2(1/n)$. While, following suggestions by Gans²⁴ and Kauzmann,²⁵ the optical rotational data are regularly presented in terms of field corrected specific rotation ("rotivity" = $[\alpha] \times 3/(n^2 + 2)$), a corresponding correction for ordinary absorption or circular dichroism is usually ignored. A "chiral medium CD",

$$A_1 - A_r = A \left[\left(\frac{n_1^2 + 2}{3} \right)^2 / n_1 - \left(\frac{n_r^2 + 2}{3} \right)^2 / n_r \right] = +4.4 \times 10^{-4}$$

should be expected in a solution, 0.020 M Malachite Green in (+)fenchon (with $d = 0.01$ cm, $A = 2.0$, $n = 1.5$ and $n_1 - n_r = 2.2 \times 10^{-4}$). In reality a feeble *negative* CD (-0.3×10^{-4}) was observed at the absorption maximum at 630 nm, so we can conclude that "effect C" is irrelevant.

The present investigation has shown, besides the existence of certain 1:1 outer sphere complexes, that a chiral ion in an outer sphere position can induce circular dichroism in the $d-d$ transitions of an octahedral "robust" transition metal complex. The CD effect observed in $[\text{Co}(\text{NH}_3)_6](+)\text{tartrate}^+$ has the same sign (negative) as the main Cotton effect reported for $[\text{Co}(\text{NH}_3)_4(+)\text{tartrate}]^+$,²⁰ but is about ten times weaker (*cf.* also Ref. 30). Measurements on concentrated solutions show only one CD band. It is situated at the wavelength of the absorption maximum, which may characterise this type of effect (B).

In the corresponding complex with $\text{Co}(\text{en})_3^{3+}$, the CD due to the outer sphere ligand is stronger and has been regarded as being composed of partly the effect just spoken of (B) at the wavelength of the absorption maximum (469 nm) and partly an effect of the type observed at the association of an inactive anion¹¹ (at about 450 nm and with the same sign as the CD of the free metal complex). The CD effect has thus its maximum between the maxima of these two effects (459 nm), and is negative with $(+)\text{tartrate}^{2-}$ and positive with $(-)\text{tartrate}$.

The reported CD effects have so far appeared to be single Cotton effects, contrary to those of chelatic inner sphere complexes ($\text{Co}(\text{NH}_3)_6(+)\text{tartrate}^+$),^{20,30} but with more sensitive methods other effects may be revealed. Thus, if, *e.g.* in $\text{Co}(\text{NH}_3)_6(+)\text{tartrate}^+$, an eleven-membered chelate ring³¹ is imagined (by hydrogen bonding to two adjacent ammonia molecules), the effect should be a reduced CD of the type observed in $\text{Co}(\text{NH}_3)_4 l\text{-pn}^{3+}$ (see Ref. 15), *i.e.* arising from components which the transition $A_{1g} \rightarrow T_{1g}$ splits up into when the symmetry is reduced (from O_h to, *e.g.*, C_2).

A symmetry discussion of the above mentioned kind might also be applied to explain or at least make a rule for the general CD polarisation of a dissymmetric metal ion at outer sphere complex formation with an ordinary anion. (The approach of an anion along the C_3 -axis¹¹ may thus lower the effective symmetry, *e.g.* to C_3 , implying a splitting of the E_g component into components ($A + B_1$) possibly with different signs.)

The study of effects on circular dichroism of optically active transition metal complexes at the association of ligands in the outer sphere has been considered interesting not only from a spectroscopic point of view but also from a chemical one. The nature of such complexes (some are very strong^{12,37}) in aqueous solution can give information of a type of bonding* that may be involved elsewhere, e.g. in the complex dynamics of biological metabolism.

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* A recent study^{34,35} on semi-oriented systems of (+)Co(*d*-pn)₃³⁺ and (+)Co(*l*-pn)₃³⁺ containing alkylsulphate (—CH₂—OSO₃[−]) in the outer sphere gives evidence for a strong complex with the sulphate positioned along the "C₂-axis" in both cases. In the *d*-pn complex the conformations of the chelate rings (*lel*) give opportunity for hydrogen-bonding to the sulphate oxygens, but in the *l*-pn complex the conformations (*ob*) are disadvantageous for such an approach.

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