

Circular Dichroism Measurements on Oriented Films Containing Dissymmetric Cobalt Complexes

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A method for obtaining assignments of hidden or strongly mixed transition bands by measuring circular dichroism of oriented films is described. The long wavelength electronic transitions of (+)tris(*d*-propylene-diamine)cobalt(III) tri(dodecylsulphate) and *trans*-bis(*l*-propylenediamine)-bis(dodecylamine)cobalt(III) chloride have been analyzed by this method. The results for the tris-diamine compound suggest an orientation degree of about 0.1 in the plane of the film, which was oriented perpendicular to the direction of the luminous flux, and show that the *d*→*d* transition components have the same magnitudes and separation as in the corresponding ethylenediamine complex. The assignments obtained for the *trans*-bis(diamine) complex gave an order for the transitions which was the reverse of that suggested²³ for *trans*-bis(*l*-propylenediamine)diamminecobalt(III) chloride.

For a little more than fifteen years the methods of *crystal field* (CF) *theory* and *ligand field* (LF) *theory* have been applied to the study of the spectra of transition metals. The fundamental idea behind CF theory is that the one electron *d* orbital set is split by an octahedral field to give the well known t_{2g} and e_g pair and that the electron transition can be regarded, in a one electron sense, as involving $t_{2g}-e_g$ excitation ($d^1: {}^2T_{2g} \rightarrow {}^2E_g$). With a lower symmetry and with more than one electron, however, the picture becomes more complex, and for certain transitions it is generally very difficult to make assignments of the experimentally observed absorption bands on purely theoretical grounds. One way to get further empirical information is to study the *polarized spectra* or the *circular dichroism* (CD).

The use of polarized spectra depends upon the fact that the direction of the transition dipole moment in the molecule is different for different electronically allowed transitions, provided that the molecule is not perfectly cubic. Thus the transitions may be distinguished and identified by examining a crystal of the complex with plane-polarized light. This can be done either in the pure crystal¹ or in optically dilute form in host crystals.² If one knows the symmetries of the electronic states in a ligand field of, e.g., O_h symmetry,

then with *group theory* one can predict: 1. the states generated by a new lower symmetry, 2. the allowed transitions between the new states, and 3. their symmetries.³ By comparing these theoretical relations with the experimental data from polarized spectra direct assignments of the observed absorption bands can often be made.

As circular dichroism of, for instance, a metal complex is related to a non-zero scalar product of the electric and magnetic moments of an electronic transition in the complex, this quantity may give information about the type of transition (*e.g.*, whether or not it is a magnetic dipole transition). From the changes of sign of CD when passing, *e.g.*, from lower to higher energy in the spectrum, the assignments of the transitions have been obtained in many cases.⁴⁻⁶

A new criterion for the absolute configuration of dihedral metal complexes has recently been suggested by Ballard, McCaffery and Mason⁷ which makes it possible to distinguish the $A_1 \rightarrow E_a$, $A_1 \rightarrow A_2$ components even in solution. Mason *et al.* measured the circular dichroism of a crystal, $2[(+)\text{Co}(\text{ethylenediamine})_3]\text{Cl}_3 \cdot \text{NaCl} \cdot 6\text{H}_2\text{O}$, of which the absolute configuration had been determined by an X-ray diffraction study.⁸ Circularly polarized light was propagated along the optic axis of the crystal (which coincides with the C_3 -axis), so that the radiation field could give rise only to transitions of E symmetry. The result established that the $A_1 \rightarrow E_a$ transition has a *positive* rotational strength and, by comparison with the solution circular dichroism, that it has the lower energy in the $(+)\text{[Co(en)}_3\text{]}^{3+}$ ion. Because the components have opposite rotational strength, they can be identified in the solution CD spectrum but as the trigonal splitting, $\nu_{E_a} - \nu_{A_1}$, is very low (-70 cm^{-1})^{9,7} the components cancel to within 5% and the absorption spectrum shows only *one* band. The excellent demonstration of Mason *et al.*⁷ clarifies not only the assignments of the transitions, but also the relation between the rotational strengths of the transitions in question, *viz.*, $R_{E_a} = -R_{A_1}$.

The purpose of the investigation reported here was to find a method to master a situation similar to that described above, by measuring CD in an oriented sample but with less perturbation than in the crystal site. The methods of orientation that we have taken into consideration (and in some cases tried) include: electric orientation¹⁰ (Kerr effect), orientation by association to larger orientated aggregates ("imbibition", Vermaas¹¹) and a method given by Jablonski,¹² which depends on the almost perfect orientation which is often obtained in a stretched film of certain host polymers containing small amounts of an optically anisotropic dye. Direct application of these methods did not give, however, any positive result.*

In connection with the phenomenon of *streaming double refraction*, calculations have been carried out for the hydrodynamics of long molecules in laminar flow. Different models have been used. Kuhn¹³ considered the particles in a solution to be either anisotropic and rigid, or isotropic and flexible. The rigid, anisodimensional particles can be assumed to have the shape of ellipsoids of

* A field of 4 kV/cm perpendicular to the light ray did not induce any measurable CD change [under the conditions: 1 mM $(+)\text{[Co(en)}_3\text{]}^{3+}$ or 1 mM *trans*- $\text{Co}(l\text{-pn})_2\text{Cl}_2^+$ in methanol; pathlength of light: 1.2 and 7.5 cm; Al-electrodes covered with polyethylene]. Films, made of polyvinyl-alcohol and the above-mentioned cobalt complexes, became opaque (in the visible and UV regions) even at very low concentrations of the inorganic salt.

revolution, cylinders, or thin laminae.¹⁴ Peterlin and Stuart introduced an *anisotropic field*¹⁵⁻¹⁷ and considered the particle motion in three dimensions. It is generally assumed that the concentrations are low so that during flow each constituent is orientated as if it alone were present in solution and there were no interaction forces. However, to obtain a proper picture of the effects in a concentrated solution (*e.g.*, in a stretched film), one must consider *intermolecular* forces and also deformation effects of the species in the solution. An orientation effect occurs in pure liquids and Newtonian solutions at high rates of shear. It is most marked, however, in *non-Newtonian* solutions containing asymmetrical molecules. A number of experiments have been performed in this laboratory with streaming solutions of Co(III) complexes substituted with ligands containing long alkane chains (C_n , $n = 8, 10, 12, 14$). Though very high velocity gradients ($G = 10^5 \text{ sec}^{-1}$) could be used no trustworthy effect could be detected in circular dichroism (flow perpendicular to the direction of the incident light) or optical rotation.* It was, however, found that certain of the compounds had a very high solubility and the increase of concentration was accompanied by a remarkable increase in viscosity. The solution could be "stretched" as a syrup film between two glass plates. The orientation effect of such a film was originally discovered from the strong double refraction observed with a polarizing microscope but could later be confirmed by polarized IR spectroscopy. The optic axis coincided with the direction of shear.

EXPERIMENTAL

The preparation of (+)tris(ethylenediamine)cobalt(III) chloride tartrate, (+)[Co(en)₃]Cl·C₄H₄O₆·5H₂O, has been described elsewhere.¹⁸ d-Propylenediamine (d-pn) was prepared by resolution of *dl*-propylenediamine (Eastman Organic C., practical quality) with tartaric acid according to Dwyer, Garvan and Shulman.¹⁹ l-Propylenediamine was prepared by repeated recrystallisation of the tartrate according to a method of Larsen.²⁰ (+)Tris(d-propylenediamine)cobalt(III) chloride tartrate, (+)[Co(d-pn)₃]Cl·C₄H₄O₆·3H₂O, was prepared according to Dwyer, Garvan and Shulman.¹⁹ (Found: C 30.4, H 7.87; N 16.3. Calc. for CoC₁₃H₄₀N₆O₉Cl: C 30.1; H 7.77; N 16.2). trans-Dichloro bis-(l-propylenediamine)cobalt(III) chloride, trans-[Co(l-pn)₂Cl₂]Cl, was prepared according to Wentworth and Piper.²¹ The CD ($M^{-1}cm^{-1}$) of the compound in methanol solution agreed with the literature^{21,22} to within 1 %.

(+)Tris(ethylenediamine)cobalt(III)tri(dodecylsulphate), (+)[Co(en)₃][CH₃·(CH₂)₁₁·SO₄]₃, was prepared by mixing aqueous solutions of (+)[Co(en)₃]Cl·C₄H₄O₆·5H₂O and CH₃(CH₂)₁₁OSO₃Na. The precipitate was filtered off, washed with hot water, and dried for 48 h at 60°. (Found: C 45.7; H 9.66; N 7.68; S 8. Calc. for CoC₄₂H₉₉N₆S₃O₁₂: C 48.7; H 9.64; N 8.18; S 9).

(+)Tris(d-propylenediamine)cobalt(III)tri(dodecylsulphate), (+)[Co(d-pn)₃][CH₃·(CH₂)₁₁·SO₄]₃, was prepared in a way analogous with the preparation of the ethylenediamine compound. (Found: Co 5.8; N 7.74; S 9. Calc. for CoC₄₂H₁₀₅N₆S₃O₁₂: Co 5.5; N 7.80; S 9).

(+)Tris(d-propylenediamine)cobalt(III)tri(tetradecylsulphate), (+)[Co(d-pn)₃][CH₃·(CH₂)₁₃·SO₄]₃, was prepared analogously. (Found: Co 5.5; C 50.5; H 10.2; N 7.47; S 8.1. Calc. for CoC₅₁H₁₁₇N₆S₃O₁₂: Co 5.1; C 53.2; H 10.1; N 7.24; S 8.3).

cis-Dichlorobis(l-propylenediamine)cobalt(III) chloride, cis-[Co(l-pn)₂Cl₂]Cl, was obtained by evaporation of a neutral aqueous solution of the *trans*-compound at 70°.

* For this purpose was used a servo polarimeter (Perkin Elmer 141) supplied with a He-Ne laser. The light was propagated through a capillary tube (diam. 0.06 cm, length 10 cm), *i.e.*, parallel with the laminar flow. That the flow was laminar followed from the fact that the measured rates of flow and pressure differences obeyed Poiseuille's equation.

It has not been possible to prepare *trans*-bis-(*l*-propylenediamine)bis(dodecylamine)-cobalt(III) chloride in pure state. On mixing solutions of *trans*-[Co(*l*-pn)₂Cl₂]Cl and dodecylamine (in methanol and in equivalent amounts) the absorption spectrum showed that the 610 nm peak of the *trans*-[Co(*l*-pn)₂Cl₂]⁺ ion disappears while simultaneously a new peak forms at about 540 nm, corresponding to *trans*-Co[(*l*-pn)₂(dodecylamine)Cl]²⁺. If this solution was evaporated almost to dryness at 70° the 540 nm peak is shifted to about 520 nm, which we have interpreted as indicating the formation of the *cis*-complex. The CD spectra show that the *trans*-compound has only one negative peak at about 510 nm while the *cis*-compound gives rise to a negative band at 550 nm and a positive smaller one at 470 nm. This spectrum was, as expected, also obtained with the compound prepared in the same manner but from the *cis*-[Co(*l*-pn)₂Cl₂]Cl₂. *Trans*-bis-(*l*-propylenediamine)bis-(dodecylamine)cobalt(III) chloride was now prepared principally by the method developed by O'Brien and coworkers²³ for obtaining the corresponding bis-diammine compound, by treating solid *trans*-[Co(*l*-pn)₂Cl₂]Cl with an excess of liquid dodecylamine at 30°. The excess of amine was evaporated *in vacuo*. Although simple paper chromatography tests (ethanol solution) did not indicate any colored impurities, the absorption spectrum (Fig. 4) showed a maximum at 480–490 nm, which could mean that the bis(dodecylamine) compound was contaminated with the *cis*- or *trans*-mono-amine complex. According to Mathieu²⁴ the corresponding absorption maxima of the *ammine* complex should be situated at 470 nm and 530 nm, respectively, and be of approximately equal magnitude). Another possibility might be the presence of small amounts of *cis*-[Co(*l*-pn)₂(dodecylamine)₂]Cl₂; the negative 520 nm CD band is stronger than the corresponding band of the diammine complex reported by Larsen and coworkers,²⁵ although the bands are situated at the same wavelengths. However, the *cis*-complex has been prepared, from *cis*-[Co(*l*-pn)₂Cl₂]Cl, and it shows a strong negative band at 510 nm ($\Delta\epsilon \approx -0.6$) and a positive smaller band at 430 nm ($\Delta\epsilon = 0.2$). Based on this qualitative investigation, the impurities of possible importance mentioned above can be neglected.

The circular dichroism and absorbance of dilute solutions as well as of concentrated ones (in films) of the above compounds have been measured with a Roussel-Jouan Dichrograph and a Hitachi EPS 3-T spectrophotometer. In addition, *polarized* absorption spectra of the films have been recorded in the wavelength range 340–700 nm, but no linear dichroism could be observed between the spectra obtained with the plane of polarization of the incident light parallel and perpendicular to the direction of shear.

In order to correlate the change in CD which occurs on passing from a random system to an oriented one with the *degree of orientation*, polarized IR spectra of the films between CsBr plates were recorded with a Perkin Elmer IR spectrophotometer Model 521 supplied with a gold wire-grid polarizer (No. 186–0187). A small linear dichroism at 720 cm⁻¹ was observed indicating an orientation of the CH₂-rocking transition dipole²⁵ perpendicular to the direction of shear. Due to the lack of suitable plates with transparency both in visible wavelength range and at 720 cm⁻¹ it was not possible to compare CD and IR of one film. Another circumstance, which is probably misleading when comparing CD and IR dichroism, may be the effect of orientation *in the plane* of the film (caused by radial shear from an unavoidable *pressing*). Such an effect should contribute to the CD polarization but cannot be expressed in terms of the linear IR dichroism (or double refraction). Therefore the *degree of orientation*, *f*, (defined as the hypothetical fraction of perfectly ordered molecules, when the remainder is perfectly random) obtained from linear dichroism measurements, *i.e.*, *via* a transition dipole, the orientation of which is known, cannot be used to resolve the change in CD (ΔCD) if the light is propagated perpendicular to the direction of shear. The average IR linear dichroism gives, however, the *minimum orientation in the plane*: A *dichroic ratio*, $R = \epsilon_{\perp} / \epsilon_{\parallel} = 1.062$, was recorded for the CH₂-rocking at 720 cm⁻¹ in a film of *trans*-[Co(*l*-pn)₂(dodecylamine)₂]Cl₂, which implies an *f*-value of at least 0.04 in the plane.* With (+)[Co(*d*-pn)₃](alkylsulphate), the CH₂-rocking at 720 cm⁻¹ was hidden and the spectrum difficult to analyze.

* $f = (\epsilon_{\perp} / \epsilon_{\parallel} - 1) / (\epsilon_{\perp} / \epsilon_{\parallel} + \frac{1}{2})$ when the transition dipole is positioned perpendicular to the direction of orientation, *i.e.*, has an *E* representation. This follows from the definition of *f*: If the transition dipole were parallel with the direction of orientation, *i.e.*, has an *A* representation $\epsilon_{\parallel} / \epsilon_{\perp} = [f + (1-f)/3] / [(1-f)/3]$, *i.e.*, $f = (\epsilon_{\parallel} / \epsilon_{\perp} - 1) / (\epsilon_{\parallel} / \epsilon_{\perp} + 2)$. With the transition dipole perpendicular to the direction of orientation one obtains instead: $\epsilon_{\perp} / \epsilon_{\parallel} = [f/2 + (1-f)/3] / [(1-f)/3]$.

In order to make certain that the observed CD effects are not due to *artefacts* caused by birefringence or depolarization *via* scattering, a number of tests have been performed:

1. We have observed that a strong *linear dichroism* (*e.g.*, generated by stretching a film of polyvinylalcohol containing some optically anisotropic and asymmetric dyestuff) can give rise to CD. It is, for instance, obvious that a sample with linear dichroism should exhibit *optical activity*: If the light is introduced with its plane of polarization at an angle to the *y*-axis which is *non-zero* and $\epsilon_x \neq 0$ but $\epsilon_y = 0$, the *x*-component of the "plane vibration" will be decreased by absorption while the *y*-component will not. The resulting plane of polarization will form an angle with the original plane. In the Jouan dichrograph the circular dichroism is evaluated from the ratio between two signals. As the evaluation is not rigorously restricted to the points of the signal which correspond to perfectly circular polarized light (but also, to some extent, depends on the elliptically polarized intermediates when passing from one direction of polarization to the other) an interaction with the original plane of polarization *e.g.*, from a sample exhibiting linear dichroism, might be expected to give rise to CD deflection. In such a case the orientation of the sample in relation to the direction of the original plane of polarization (*i.e.*, the axis of the elliptical polarization) should be important. Thus we found that linear dichroic samples showed very different CD when the transition dipole of the sample was orientated parallel with and perpendicular to the original direction of polarization of the light. An example of such an observation is given in Fig. 2, where an almost perfect reflection in the *zero-line* gives the relation between spectra recorded with the sample rotated 90° in the plane perpendicular to the direction of the incident light. Thus we suggest the following criterion. *If a sample (a film) exhibits variation in CD when rotated perpendicular to the direction of the incident light the result is unreliable.*

2. Velluz, Legrand and Grosjean²⁶ have calculated the error involved in CD measurements in which the light can encounter double refraction (*before* the polarizer or the sample — *after* is of no importance). They show that the error will be at a maximum when the optic axes of the double refraction are parallel with the induced axes of the ADP crystal of the dichrograph, *i.e.*, $\pm 45^\circ$ to the original plane of polarization. Double refraction and scattering (*depolarization*) have been checked for by measuring CD with and without a *test solution* with known CD placed after the film. *If the CD obtained did not consist of the sum of the CD of the film and of the test solution* (for all possible orientations of the film) *the light was considered depolarized and the measured CD of no value.* However, we found it possible to perform a meaningful measurement even on a sample with double refraction if, when rotating the sample a varying tilt of the zero line (observed in a region free from Cotton effects) was the only effect and the CD (Cotton effect) remained constant when corrected for the tilt. Of the CD spectra recorded on films (about 100) for the compounds reported here, however, less than half required this procedure.

From (+)Co(en)₃(alkylsulphate)₃ no film could be prepared because of an extremely low solubility (about 10 mM in methanol). From the other compounds films were prepared by dissolving the dry compound in methanol (or ethanol), evaporating the solution at 50° to a final concentration of about 1 M, and stretching it between glassplates. It was visually checked that the film was transparent and without bubbles (from cavitation) after the stretching. The CD and the absorbance of the film could be related to those quantities of the corresponding random solution by dissolving 1 cm² of the film in a volume corresponding to the same area in the cells, *e.g.*, with the pathlengths 0.1 cm and 1 cm (*i.e.* 0.1 ml and 1 ml). The thickness of the film was checked with a micrometer. (Example: thickness 0.0058 cm, conc. 0.86 M Co(*d-pn*)₃...) Approximately the same absorbance was obtained for the film and the solution. This was expected as no linear dichroism had been detected. It was checked that the observed effects were not due to any concentration dependence of the CD and that a thermal desorientation diminished the effects (10 % by 48 h aging at 40°). ($\Delta \epsilon_{A_2(\max)}/\Delta \epsilon_{E_d(\max)}$) was found to vary linearly with the concentration of (+)Co(*d-pn*)₃(dodecylsulphate)₃. It increased linearly from 0.36 to 0.40 between 0 and 0.6 M. An approximately linear dependence on temperature was also obtained: from 0.390 at 17.0° to 0.366 at 42.0°. A further "proof" that the effects observed were not artefacts was obtained: It was found that a stretched film of (+)Co(*d-pn*)₃tartrate chloride (in water) did not exhibit any CD change. The results are reproduced in Figs. 1–4 and in Table 1.

Table 1. Maximum effects (CD) in the stretched films. The direction of orientation perpendicular to the direction of the incident light.

Compound	Solvent	Absorption		CD change			Assignment
		λ_{\max} (nm)	ϵ_{\max} ($M^{-1}cm^{-1}$)	λ_{\max} (nm)	$\Delta\epsilon_{\max}$ ($M^{-1}cm^{-1}$)	film $\Delta\epsilon_{\max}$ ($M^{-1}cm^{-1}$)	
(+)[Co(en) ₃](dodecylsulphate) ₃	methanol	340	70	350	+0.24		${}^1A_1 \rightarrow {}^1E_b$ (1T_2) ${}^1A_1 \rightarrow {}^1A_2$ (1T_1) ${}^1A_1 \rightarrow {}^1E_a$ (1T_1)
		469	80	429	-0.24		
				492	+1.75		
(+)[Co(d-pn) ₃](dodecylsulphate) ₃	methanol, ethanol, or dodecanol	340	85	345	+0.26	+0.23	${}^1A_1 \rightarrow {}^1E_b$ (1T_2) ${}^1A_1 \rightarrow {}^1A_2$ (1T_1) ${}^1A_1 \rightarrow {}^1E_a$ (1T_1)
		469	92	440	-0.56	-1.48	
				493	+1.72	+0.86	
<i>trans</i> -[Co(<i>d-pn</i>) ₂ (dodecylamine) ₂] Cl ₃	methanol	480	70	350	-0.1	-0.2	$({}^1A \rightarrow {}^1A)$ (1T_2) ${}^1A \rightarrow {}^1A$ (1T_1) ${}^1A \rightarrow {}^2{}^1B$ (1T_1)
				460	+0.27	+0.70	
				510	+0.30	-0.03	

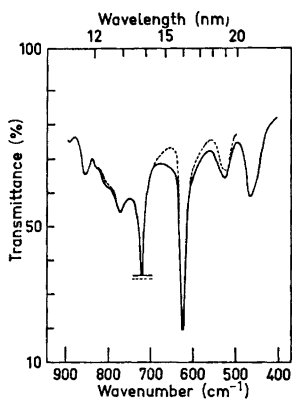


Fig. 1. IR dichroism of a film of *trans*-[Co(*l*-pn)₂(dodecylamine)₂]Cl₃. Light polarized perpendicular to (---) and parallel with (—) the direction of shear.

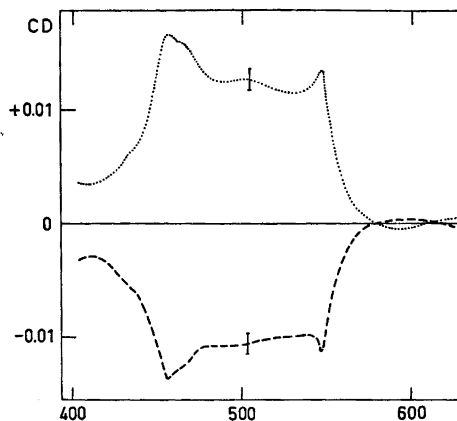


Fig. 2. Example of CD induced by strong anisotropy. CD spectra for two orientations, differing by 90°, of a stretched film of polyvinylalcohol containing 1,1'-diethyl-2,2'-cyanine iodide. The vertical bars indicate the noise level.

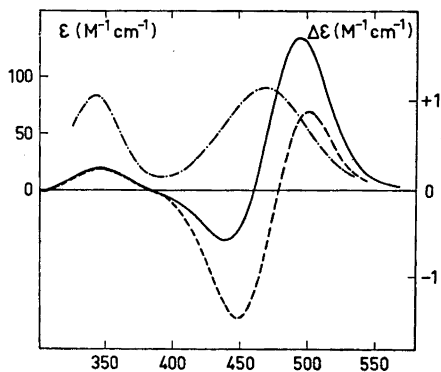


Fig. 3. Absorptivity (---) and circular dichroism, in solution, *i.e.*, random (—) and as a film, *i.e.*, orientation perpendicular to the light beam (---), of (+)[Co(*d*-pn)₃](dodecylsulphate)₃.

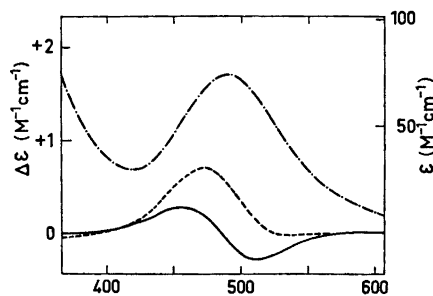


Fig. 4. Absorptivity (---) and circular dichroism of [Co(*l*-pn)₂(dodecylamine)₂]Cl₃, in solution, *i.e.*, random (—) and as a film, *i.e.*, orientation perpendicular to the light beam (---).

A number of experiments with complexes with long chain anions other than dodecylsulphate have been carried out. It was possible to repeat the polarized CD technique with films of (+)Co(*d*-pn)₃(CH₃(CH₂)_{*n*}SO₄)₃, with *n*=7,9, and 13 but with shorter tails the CD dichroism appeared to be smaller. We have also tried to use complexes with polystyrenesulphonate, nitrates of cellulose, and poly-L-glutamate as outer-sphere ligands. However, on mixing the corresponding aqueous solutions the neutral complex precipitated and it was not possible to find any suitable solvent for these precipitates.

RESULTS

Since we have not been able to obtain any value of the degree of orientation, f , corresponding to a given CD dichroism, it was not possible to calculate the E_a and A_2 components of the CD or, consequently, the trigonal splitting, $\nu_{A_1} - \nu_{E_a}$. Starting, however, from the assumption that the absolute magnitudes of R_{A_1} and R_{E_a} are the same in the (+)Co(en) $_3^{3+}$ and the (+)Co(*d*-pn) $_3^{3+}$ case (which seems reasonable^{27,28}) we have roughly estimated the magnitude of f .

If we regard the absorptivities ε_{E_a} and ε_{A_1} measured in a perfectly oriented sample with the plane of plane polarized light perpendicular to and parallel with, respectively, the C_3 axes of the tris-diamine complex ions in the film we shall find that the absorptivity of a *random* solution is given by

$$\varepsilon_r = (\varepsilon_{A_1} + 2 \varepsilon_{E_a})/3 \quad (1)$$

We further assume that if the total absorptivity at a certain wavelength, λ , is $\varepsilon(\lambda) = \sum_v \varepsilon_v(\lambda)$, where ε_v ($v=1, 2, \dots$) represents the contribution from a certain transition (v), the CD can be approximately expressed as $\Delta\varepsilon(\lambda) = \sum_v c_v \varepsilon_v(\lambda)$ with certain coefficients c_v . Thus the CD of, for instance, a film of (+)Co(*d*-pn) $_3$ (dodecylsulphate) $_3$, will be $\Delta\varepsilon_{f=1}(\lambda) = \frac{1}{2}(c_A \varepsilon_{A_1}(\lambda) + c_E \varepsilon_{E_a}(\lambda))$ and $\Delta\varepsilon_{f=0}(\lambda) = \frac{1}{3}(c_A \varepsilon_{A_1}(\lambda) + 2c_E \varepsilon_{E_a}(\lambda))$ with perfect and random orientation, respectively. If the transitions were sufficiently separated, $\Delta\varepsilon(\lambda_1)_{f=1} \equiv \Delta\varepsilon_{E_a, f=1} = \frac{3}{4} \Delta\varepsilon_{E_a, f=0} \equiv \frac{3}{4} \Delta\varepsilon(\lambda_1)_{f=0}$ and $\Delta\varepsilon(\lambda_2)_{f=1} \equiv \Delta\varepsilon_{A_1, f=1} = \frac{3}{2} \Delta\varepsilon_{A_1, f=0} \equiv \frac{3}{2} \Delta\varepsilon(\lambda_2)_{f=0}$ should be obtained with certain λ_1, λ_2 . Combining these expressions,

$$\Delta\varepsilon(\lambda)_{f=1} = \frac{3}{4} \Delta\varepsilon_{E_a}(\lambda)_{f=0} + \frac{3}{2} \Delta\varepsilon_{A_1}(\lambda)_{f=0} \quad (2)$$

and forming a linear combination, $\Delta\varepsilon_f = f \cdot \Delta\varepsilon_{f=1} + (1-f) \cdot \Delta\varepsilon_{f=0}$, one obtains

$$\Delta\varepsilon(\lambda)_f = f \left\{ \frac{1}{2} \Delta\varepsilon_{A_1}(\lambda)_{f=0} - \frac{1}{4} \Delta\varepsilon_{E_a}(\lambda)_{f=0} \right\} + \left\{ \Delta\varepsilon_{A_1}(\lambda)_{f=0} + \Delta\varepsilon_{E_a}(\lambda)_{f=0} \right\} \quad (3)$$

The last term is the CD of the random solution.

We have used an approximately Gaussian resolution of the E_a and A_2 components of (+)Co(en) $_3^{3+}$ (according to Bürer²⁹) with a $\nu_{A_1} - \nu_{E_a} = +100$ cm^{-1} . With an f of about 0.1 the theoretical CD spectrum fits the experimentally obtained dichroism given in Fig. 3. The corresponding f value for the E_b transition has also been estimated by using the $\Delta\varepsilon_{E_b, \text{cryst}} = +0.9$ (obtained with the light propagated along the C_3 -axis of a 2[(+)Co(en) $_3$ Cl $_3$], NaCl, 6H $_2$ O crystal^{6,30}). As the transition has E symmetry and is consequently perpendicular to the C_3 -axis, $\Delta\varepsilon_{E_b, f=0} = \frac{2}{3}(+0.9) = +0.6$ (cf. eqn. (1)). The $\Delta\varepsilon_{\text{max}}$ reported for a solution is +0.26,³⁰ which can be explained by a transition with opposite rotational strength, and A symmetry (e.g., a wing of the A_2 transition), and with $\Delta\varepsilon_{A_1, f=0} = -0.3$. With our observed CD value for the film, +0.23, and eqn. (3) we have: $0.23 = f \cdot (0.5(-0.3) - 0.25 \cdot 0.6) + 0.26$, i.e., $f = 0.1$. This value compares well with the earlier obtained value, considering the rather low precision of the measurement. In any case we have now determined f independently of the earlier estimates on the $E_a - A_2$ bands.

DISCUSSION

The CD spectra of the investigated compounds in methanol solution are given in Figs. 3–4. The CD spectrum of (+)Co(en)₃(dodecylsulphate)₃ (Table 1), which was also recorded, shows that the perturbing effect of the sulphate groups is in fact very low (compared, *e.g.*, with that of ethylenediaminetetraacetic acid^{31,37}). As the compound is insoluble in water and therefore probably not dissociated in methanol, it seems reasonable to seek the explanation of the CD effect of shear in the orientation of the fixed alkylsulphate groups.

The CD spectrum of the (+)Co(*d*-pn)₃(dodecylsulphate)₃ films shows that with light, whose direction of propagation is perpendicular to the film surface (and the direction of shear) the 440 nm transition is favoured and the band at 490 nm, and to some extent the 340 nm band too, are depressed. If the alkyl chains are orientated in the plane of the film and if the alkylsulphate ions are associated to Co(*d*-pn)₃³⁺ so that two or at least one is positioned along the C₃-axis,* then the latter should be preferentially orientated in the plane of the film. In this position transitions of *A*-symmetry will be favoured but those of *E*-symmetry depressed compared with a random orientation (eqn. (3)). If one regards the possible isomers which are obtained with the methyl groups in different positions (*cis*- or *trans*-) as approximately equally represented the effective symmetry of the “average” molecule beyond doubt remains D₃ (like Co(en)₃³⁺). Thus the sublevels from ¹T_{1g} consist of A₂ and E_(a) and from ¹T_{2g}, A₁ and E_(b). As the energetic order of T₁ and T₂ is T₁ < T₂ the assignments are obvious (Table 1).

In the case of *trans*-[Co(*l*-pn)₂(dodecylamine)₂]Cl₃ a problem arises in assigning an effective symmetry for the molecule, even though we now know the directions of approach of the alkyl chains. The energy levels of *trans*-[Co(en)₂X₂]ⁿ⁺ complexes, which possess D_{4h}-symmetry, have been identified from polarized crystal spectra.^{1,33} The order of the sublevels E_g and A_{2g} (in D_{4h}) from the ¹T_{1g} cubic level has been obtained using both an electrostatic model and approximated LCAO-MO models.³⁴ The result agrees well with the experimentally obtained order and has also been applied to the related *trans*-[Co(*l*-pn)₂Cl₂]⁺ complex by Larsen and coworkers.²² They point out that, as the order is expected to remain the same for all *trans*-[Co(*l*-pn)₂X₂]⁺ compounds with ligands X which are lower in the spectrochemical series than *l*-pn,³⁵ the order of the Cotton effect signs should remain independent of X in D_{4h} (provided that the absolute configuration of the complex is retained). Thus they suggested that the symmetry of *trans*-[Co(*l*-pn)₂(NH₃)₂]³⁺ is lower than D_{4h} (the ¹E_g-level is split), because with this compound they found the Cotton effects reversed. They considered therefore the effective symmetry to be D₂ and made the assignments: B₃ or B₂ (518 nm) and B₂ or B₃, partly B₁ (463 nm). The components from the T_{2g} level (357 nm) were not identified. We can only agree with Larsen *et al.* that the substitution of N for Cl in *trans*-[Co(*l*-pn)₂Cl₂]⁺ makes it necessary to consider the alkyl portion of the chelate and thus the effective symmetry is reduced to D_{2h} if the chelate ring puckering and the CH₃-groups are ignored – to D₂ if the ring puckering (but not the

* According to the concept of Mason³² this is the preferred direction for the approach of oxyanions to tris(diamine)cobalt(III) complexes.

CH₃ groups) is taken into consideration. If the effective symmetry is D_{4h} or D_{2h} , however, the allowed transitions should be transitions with vibronic coupling. In D_{4h} the only forbidden transition is the one between the ground state (A_{1g}) and A_{2g} along the z direction. The results from our polarized CD spectrum imply that the proper assignments (in D_{4h}) for the transitions are: $A_{1g} \rightarrow A_{2g}$ ($\perp z$, 510 nm), $A_{1g} - E_g$ (\parallel and $\perp z$, 460 nm), $A_{1g} \rightarrow B_{2g} + E_g$ (\parallel and $\perp z$, 350 nm). As the last mentioned transitions should not be polarized, the increased CD of the 350 nm band in the film is a little confusing. The small magnitude of the increase suggests that it may be due to a slight error in the calculation of the absolute CD of the film. Another plausible explanation is that the effect is caused by the influence of a polarized charge transfer band. — The assignment of the 510 nm band agrees with the original assignments of Larsen *et al.*²² (based on the assumption of retention of absolute configuration during the substitution of the preparation). For steric reasons it is not probable that the presence of the alkylamine should induce any configurational change (the CH₃ groups are already in equatorial positions). This assignment implies thus a higher position in the spectrochemical series for the *monodentate* amino nitrogen than for the *bidentate* one.

In D_2 the T_1 cubic level is split into the sublevels B_1 , B_2 , and B_3 . As the D_2 symmetry lacks a center of inversion, certain pure electronic transitions are allowed: $A_1 \rightarrow B_1$ ($\parallel z$), $A_1 \rightarrow B_2$ ($\parallel y$) and $A_1 \rightarrow B_3$ ($\parallel x$). The CD dichroism satisfies the assignments $A_1 \rightarrow B_1$ (460 nm), $A_1 \rightarrow B_2 + B_3$ (510 nm). This explanation does not agree, however, with the one given by Larsen *et al.*²² Because the B_1 level has A_{2g} (D_{4h}) parentage they propose that it should give rise to a negative CD. Further, the change of sign order of the Cotton effects is explained by a lower symmetry than D_{4h} (B_2 and B_3 in D_2 should give different signs).

Another interpretation, which is perhaps more adequate here since the methyl groups of the propylenediamine molecules must be taken into symmetry considerations now when there are nitrogen atoms also in the *trans*-positions, is to refer the molecule to the symmetry to which it indeed belongs, namely C_2 (the CH₃ groups are taken into account). In C_2 , T_{1g} is split into one A and two B levels. The $A \rightarrow A$ transition is allowed along the z -axis while the two $A \rightarrow B$ transitions are polarized in the xy -plane. This implies the assignments reported in Table 1. As the A level has A_{2g} tetragonal parentage it is suggested (on the basis of the CF-analysis of *trans*-[CoA₄X₂]⁺ by Yamatera³⁶) that the A band should have roughly the same energy as the T_{1g} band of Co(NH₃)₆³⁺ (470 nm). As the A band must be positioned somewhere between the recorded CD band assigned A and the absorbance maximum, *i.e.* between 460 nm and 480 nm, this suggestion obviously finds strong support. Our assignments provide a change of sign when passing from R_A (D_{4h}) to R_{B_1} (D_2) or R_A (C_2). This is principally not expected as A_2 is given by an only *one*-dimensional representation and, therefore, cannot give rise to levels with opposite rotational strengths.

Concluding remark. The purpose of this investigation has been, in the first place, to experimentally test the correctness of the Moffitt-Mason model of the electronic transitions in the (+)Co(en)₃³⁺ ion by means of a *semi*-oriented system. It soon appeared, however, that two main difficulties had to be overcome: the difficulty of producing any *orientation* in a dilute solution and the

difficulty of maintaining the transparency to the light in a concentrated one. We found it, however, possibly to induce mechanical orientation in a concentrated solution of the corresponding *d*-propylenediamine compound substituted with alkylsulphate (in the outer co-ordination sphere) and dissolved in a semipolar solvent (methanol or ethanol), the solution was excellently transparent. When it was exposed to shear it exhibited double refraction and the CD spectrum underwent a radical change, which could be explained by an orientation effected by the alkylsulphate groups, presuming these to be attached to the complex in the way predicted by Mason *et al.*³²

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REFERENCES

1. Yamada, S., Nukakara, A., Shimura, Y. and Tsuchida, R. *Bull. Chem. Soc. Japan* **28** (1955) 22, 222.
2. Piper, T. S. and Carlin, R. L. *J. Chem. Phys.* **35** (1961) 1809.
3. Cotton, A. F. *Chemical Applications of Group Theory*, Wiley, New York and London 1964.
4. McCaffery, A. J. and Mason, S. F. *Trans. Faraday Soc.* **59** (1963) 1.
5. Bürer, T. *Helv. Chim. Acta* **46** (1963) 2388.
6. Mason, S. F. *Quart. Rev.* **17** (1963) 20.
7. Ballard, R. E., McCaffery, A. J. and Mason, S. F. *Proc. Chem. Soc.* **1962** 331.
8. Nakatsu, K., Shiro, M., Saito, Y. and Kuroya, H. *Bull. Chem. Soc. Japan* **30** (1957) 158.
9. Yamada, S. and Tsuchida, R. *Bull. Chem. Soc. Japan* **33** (1960) 98.
10. Labhart, H. *Tetrahedron* **19** (1963) 223.
11. Vermaas, D. *Z. physik. Chem. (Leipzig)* **B 52** (1942) 131.
12. Jablonski, A. *Nature* **133** (1934) 140.
13. Kuhn, W. *Z. physik. Chem. (Leipzig)* **A 161** (1932) 1, 427.
14. Haller, W. *Kolloid-Z.* **61** (1932) 26.
15. Peterlin, A. *Z. Physik.* **111** (1938) 232.
16. Peterlin, A. and Stuart, H. A. *Z. Physik.* **112** (1939) 1, 129.
17. Peterlin, A. and Stuart, H. A. *Z. Physik.* **113** (1939) 663.
18. Broomhead, J. A., Dwyer, F. P. and Hogarth, J. W. *Inorg. Syn.* **6** (1960) 186.
19. Dwyer, F. P., Garwan, F. L. and Shulman, A. J. *Am. Chem. Soc.* **81** (1959) 290.
20. Larsen, E. *Private communication.*
21. Wentworth, R. A. D. and Piper, T. S. *Inorg. Chem.* **4** (1965) 202.
22. Hawkins, C., Larsen, E. and Olsen, I. *Acta Chem. Scand.* **19** (1965) 1915.
23. O'Brien, T. D., McRynolds, J. P. and Bailar, J. C. J. *Am. Chem. Soc.* **70** (1948) 749.
24. Mathieu, J. P. *Bull. Soc. Chim. France* **3** (1936) 477.
25. Weissberger, A. *Technique of organic chemistry* **9** (1960) 344.
26. Velluz, L., Legrand, M. and Grosjean, M. *Optical Circular Dichroism*, Academic, London 1964.
27. Corey, E. J. and Bailar, J. C. J. *Am. Chem. Soc.* **81** (1959) 2620.
28. Woldbye, F. and Snatzke, G. *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry*, Heyden 1968, p. 101.
29. Bürer, T. *Helv. Chim. Acta* **46** (1963) 242.
30. McCaffery, A. J. and Mason, S. F. *Mol. Phys.* **6** (1963) 359.
31. Nordén, B. *Acta Chem. Scand.* *In press.*
32. Mason, S. F. and Norman, B. J. *Proc. Chem. Soc.* **1964** 339.
33. Ballhausen, C. J. and Moffitt, W. J. *J. Inorg. Nucl. Chem.* **3** (1965) 178.

34. Schäffer, C. E. and Jörgensen, C. K. *Absorption spectra and chemical bonding in complexes*, Pergamon, Oxford 1962.
35. Orgel, L. E. *An Introduction to Transition Metal Chemistry*, 2nd Ed., Methuen, London 1966, p. 96.
36. Yamatera, H. *Bull. Chem. Soc. Japan* **31** (1958) 95.
37. Nordén, B. *Acta Chem. Scand.* **23** (1969) 2925.

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