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 suggested 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}→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., O₄₈ 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. 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.

A new criterion for the absolute configuration of dihedral metal complexes has recently been suggested by Ballard, McCaffery and Mason which makes it possible to distinguish the \( A_1 \rightarrow E' \), \( A_1 \rightarrow A_2 \) components even in solution. Mason et al. measured the circular dichroism of a crystal, \( 2[(+\text{Co(ethylene-diamine)}_3 \text{Cl}_3 \cdot \text{NaCl} \cdot 6 \text{H}_2 \text{O}) \), of which the absolute configuration had been determined by an X-ray diffraction study. Circularly polarized light was propagated along the optic axis of the crystal (which coincides with the \( C_4 \)-axis), so that the radiation field could give rise only to transitions of \( E \) symmetry. The result established that the \( A_1 \rightarrow E' \) transition has a positive rotational strength and, by comparison with the solution circular dichroism, that it has the lower energy in the \((+\text{Co(en)})_3^{3+}\) ion. Because the components have opposite rotational strength, they can be identified in the solution CD spectrum but as the trigonal splitting, \( \nu_{E_2} - \nu_{A_1} \), is very low (−70 cm\(^{-1}\))^6 the components cancel to within 5% and the absorption spectrum shows only one band. The excellent demonstration of Mason et al. clarifies not only the assignments of the transitions, but also the relation between the rotational strengths of the transitions in question, \( \nu_{A_1} \), \( R_{E_2} = -R_{A_1} \).

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 orientation (Kerr effect), orientation by association to larger oriented aggregates ("imbibition", Vermaas) and a method given by Jablonski, 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. Kuhn 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

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* A field of 4 kV/cm perpendicular to the light ray did not induce any measurable CD change (under the conditions: 1 mM \((+\text{Co(en)})_3^{3+}\) or 1 mM \(\text{trans-Co(l-pn)}_3\text{Cl}^+\) in methanol; pathlength of light: 1.2 and 7.5 cm; Al-electrodes covered with polyethylene). Films, made of polyvinylalcohol 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.\textsuperscript{14} Peterlin and Stuart introduced an anisotropic field\textsuperscript{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\textsubscript{n}, n = 8, 10, 12, 14). Though very high velocity gradients (G = 10\textsuperscript{5} sec\textsuperscript{-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.\textsuperscript{*} 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, \((+)[Co(en)\textsubscript{3}]Cl,C\textsubscript{6}H\textsubscript{5}O\textsubscript{5}\textsubscript{H}O\), has been described elsewhere.\textsuperscript{18} d-Propylenediamine (d-pn) was prepared by resolution of dl-propylenediamine (Eastman Organic C\textsubscript{\textregistered}, practical quality) with tartaric acid according to Dwyer, Garvan and Shulman.\textsuperscript{19}\(+\)Propylenediamine was prepared by repeated recrystallisation of the tartrate according to a method of Larsen.\textsuperscript{20} \((+)-(+)\)-Tris(d-propylenediamine)cobalt(III) chloride tartrate, \((+)[Co(d-pn)\textsubscript{3}]Cl\), was prepared according to Dwyer, Garvan and Shulman.\textsuperscript{19} Calc. for Co\textsubscript{13}H\textsubscript{45}N\textsubscript{2}O\textsubscript{14}: C 30.1; H 7.77; N 16.2. \textsuperscript{21} trans-Dichloro bis-(1-propylenediamine)cobalt(III) chloride, \(-\)Co(l-pn)\textsubscript{3}Cl\textsubscript{2}, was prepared according to Wentworth and Piper.\textsuperscript{21} The CD (M "cm"\textsuperscript{-1}) of the compound in methanol solution agreed with the literature\textsuperscript{21,22} to within 1\%.

\((+)-(+)\)-Tris(ethylenediamine)cobalt(III)tri(dodecylsulphate), \((+)[Co(en)\textsubscript{3}]Cl\textsubscript{2}(CH\textsubscript{2})\textsubscript{11}SO\textsubscript{4}Na\textsubscript{2}\textsuperscript{2}, was prepared by mixing aqueous solutions of \((+)[Co(en)\textsubscript{3}]Cl\textsubscript{2}C\textsubscript{6}H\textsubscript{5}O\textsubscript{5}\textsubscript{H}O\textsubscript{2}\textsubscript{H}\textsubscript{2}O\textsubscript{2} and CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{11}OSO\textsubscript{4}Na. The precipitate was filtered off, washed with hot water, and dried for 48 h at 60\textsuperscript{o}. (Found: C 45.7; H 9.66; N 7.68; S 8. Calc. for Co\textsubscript{13}H\textsubscript{45}N\textsubscript{2}S\textsubscript{1}O\textsubscript{14}: C 45.7; H 9.64; N 8.18; S 9).

\((+)-(+)\)-Tris(d-propylenediamine)cobalt(III)tri(dodecylsulphate), \((+)[Co(d-pn)\textsubscript{3}]Cl\textsubscript{2}(CH\textsubscript{2})\textsubscript{11}SO\textsubscript{4}\textsubscript{Na}\textsubscript{2}\textsuperscript{2}, was prepared in a way analogous with the preparation of the ethylenediamine compound. (Found: C 5.8; N 7.74; S 9. Calc. for Co\textsubscript{13}H\textsubscript{45}N\textsubscript{2}S\textsubscript{1}O\textsubscript{14}: C 5.5; N 7.80; S 9).

\((+)-(+)\)-Tris(d-propylenediamine)cobalt(III)tri(tetradecylsulphate), \((+)[Co(d-pn)\textsubscript{3}]Cl\textsubscript{2}(CH\textsubscript{2})\textsubscript{13}SO\textsubscript{4}\textsubscript{Na}\textsubscript{2}\textsuperscript{2}, was prepared analogously. (Found: C 5.5; C 50.5; H 10.2; N 7.47; S 8.1. Calc. for Co\textsubscript{13}H\textsubscript{47}N\textsubscript{2}S\textsubscript{1}O\textsubscript{14}: C 5.1; C 53.2; H 10.1; N 7.24; S 8.3).

cis-Dichlorobis(1-propylenediamine)cobalt(III) chloride, cis-[Co(l-pn)\textsubscript{3}]Cl\textsubscript{2}, was obtained by evaporation of a neutral aqueous solution of the trans-compound at 70\textsuperscript{o}.

\textsuperscript{*} 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 Poiseuill's equation.

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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)₂Cl₄]Cl and dodecylamine (in methanol and in equivalent amounts) the absorption spectrum showed that the 610 nm peak of the trans-[Co(l-pn)₂Cl₄]⁺ ion disappears while simultaneously a new peak forms at about 540 nm, corresponding to trans-Co(l-pn)₄(dodecylamine)Cl⁺.

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)₂Cl₄]Cl. Trans-bis-(l-propylenediamine)bis-(dodecylamine)cobalt(III) chloride was now prepared principally by the method developed by O'Brien and coworkers for obtaining the corresponding bis-diamine compound, by treating solid trans-[Co(l-pn)₂Cl₄]Cl with an excess of liquid dodecylamine at 20°. 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 Mathieu 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)₄(dodecylamine)]Cl₂; the negative 520 nm CD band is stronger than the corresponding band of the diamine complex reported by Larsen and coworkers although the bands are situated at the same wavelengths. However, the cis-complex has been prepared, from cis-[Co(l-pn)₂Cl₄]Cl, and it shows a strong negative band at 510 nm (Δε = −0.6) and a positive smaller band at 430 nm (Δε = 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-Σ spectrophotometer. In addition, polarized absorption spectra of the films have been recorded in the wavelength range 540—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 CH₃-rocking transition dipole 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, where 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 = ε₁/ε₀ = 1.062, was recorded for the CH₃-rocking at 720 cm⁻¹ in a film of trans-[Co(l-pn)₂(dodecylamine)]Cl₂, which implies an f-value of at least 0.04 in the plane.* With \((\pm)[Co(d-pn)₂](alkylsulphate)\), the CH₃-rocking at 720 cm⁻¹ was hidden and the spectrum difficult to analyze.

\*f = (ε₁/ε₀⁻1)/(ε₁/ε₀ + 1) 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 \(ε₁/ε₀ \equiv f + (1-f)/3\), i.e., \(f = (ε₁/ε₀⁻1)/(ε₁/ε₀ + 1)\). With the transition dipole perpendicular to the direction of orientation one obtains instead: \(ε₁/ε₀ \equiv f + (1-f)/3\).
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 \( \varepsilon_{\perp} \neq 0 \) but \( \varepsilon_{\parallel} = 0 \), 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 Grosjean 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., ± 45° 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 \((+)^{15} \text{Co(en)}_{3} \text{(alkylsulphate)}_{3}\) no film could be prepared because of an extremely low solubility (about 100 mg 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 \( \text{Co(d-pn)}_{3} \ldots \) 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 deorientation diminished the effects (10% by 48 h aging at 40°). \( \alpha E_{d}(\text{max})/E_{d}(\text{max}) \) was found to vary linearly with the concentration of \((+)	ext{Co(d-pn)}_{3}(\text{dodecylsulphate})_{3}\) 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 \((+)\text{Co(d-pn)}_{3}\text{tartrate chloride} \) 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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th><strong>Absorption</strong></th>
<th><strong>CD change</strong></th>
<th><strong>Assignment</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\varepsilon_{\text{max}}$ (M$^{-1}$cm$^{-1}$)</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
</tr>
<tr>
<td>$(\pm)[\text{Co(en)}_3]\text{(dodecylsulphate)}_2$</td>
<td>methanol</td>
<td>340</td>
<td>70</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td></td>
<td>469</td>
<td>80</td>
<td>429</td>
</tr>
<tr>
<td></td>
<td></td>
<td>492</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\pm)[\text{Co}(d\text{-pn})_3]\text{(dodecylsulphate)}_2$</td>
<td>methanol, ethanol, or dodecanol</td>
<td>340</td>
<td>85</td>
<td>345</td>
</tr>
<tr>
<td></td>
<td></td>
<td>469</td>
<td>92</td>
<td>440</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>493</td>
</tr>
<tr>
<td>trans-$[\text{Co}(l\text{-pn})_2(\text{dodecylamine})_2]$</td>
<td>methanol</td>
<td>480</td>
<td>70</td>
<td>350</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td></td>
<td></td>
<td></td>
<td>460</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>510</td>
</tr>
</tbody>
</table>
Fig. 1. IR dichroism of a film of trans-
[Co(t-pn)$_4$(dodecylamine)$_2$]Cl$_2$. 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)$_2$](dodecylsulphate)$_2$.

Fig. 4. Absorptivity (---) and circular dichroism of [Co(t-pn)$_4$(dodecylamine)$_2$]Cl$_2$, 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)$_2$(CH$_3$(CH$_2$)$_n$SO$_4$)$_2$, with $n=7,8$, 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 \( E_\alpha \) and \( A_2 \) components of the CD or, consequently, the trigonal splitting, \( \nu_{A_\alpha} - \nu_{E_\alpha} \). Starting, however, from the assumption that the absolute magnitudes of \( R_{A_\alpha} \) and \( R_{E_\alpha} \) are the same in the \((+){\text{Co(en)}_3}^{3+}\) and the \((+){\text{Co(d-pn)}}_3^{3+}\) case (which seems reasonable \(^{27,28}\)) we have roughly estimated the magnitude of \( f \).

If we regard the absorptivities \( \varepsilon_{E_\alpha} \) and \( \varepsilon_A \), 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

\[
\varepsilon_i = (\varepsilon_{A_\alpha} + 2\varepsilon_{E_\alpha})/3
\]

(1)

We further assume that if the total absorptivity at a certain wavelength, \( \lambda \), is \( \varepsilon_i = \sum \varepsilon_\nu(\lambda) \), where \( \varepsilon_\nu \) \((\nu=1, 2, \ldots)\) represents the contribution from a certain transition \( \nu \), the CD can be approximately expressed as \( \Delta \varepsilon(\lambda) = \sum \varepsilon_\nu \varepsilon_\nu(\lambda) \) with certain coefficients \( \varepsilon_\nu \). Thus the CD of, for instance, a film of \((+){\text{Co(d-pn)}}_3^{3+}(\text{dodecylsulphate})_3 \), will be \( \Delta \varepsilon_{1-1}(\lambda) = \frac{1}{2}(\varepsilon_{A_\alpha} + \varepsilon_{E_\alpha}(\lambda) + 2\varepsilon_A\varepsilon_{E_\alpha}(\lambda)) \) and \( \Delta \varepsilon_{1-0}(\lambda) = \frac{1}{2}(\varepsilon_{A_\alpha} + \varepsilon_{E_\alpha}(\lambda) + 2\varepsilon_A\varepsilon_{E_\alpha}(\lambda)) \) with perfect and random orientation, respectively. If the transitions were sufficiently separated, \( \Delta \varepsilon(\nu) = \Delta \varepsilon_{E_\alpha}(\nu) + \Delta \varepsilon_{A_\alpha}(\nu) = \frac{1}{2} \Delta \varepsilon_{E_\alpha}(\nu) + \frac{1}{2} \Delta \varepsilon_{A_\alpha}(\nu) \) should be obtained with certain \( \lambda_1, \lambda_2 \). Combining these expressions,

\[
\Delta \varepsilon(\lambda)_{f=1} = \frac{3}{2} \Delta \varepsilon_{E_\alpha}(\lambda)_{f=0} + \frac{3}{2} \Delta \varepsilon_{A_\alpha}(\lambda)_{f=0}
\]

(2)

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

\[
\Delta \varepsilon(\lambda)_{f=1} = f \cdot \Delta \varepsilon_{A_\alpha}(\lambda)_{f=0} - \frac{1}{2} \Delta \varepsilon_{E_\alpha}(\lambda)_{f=0} + \Delta \varepsilon_{A_\alpha}(\lambda)_{f=0} + \Delta \varepsilon_{E_\alpha}(\lambda)_{f=0}
\]

(3)

The last term is the CD of the random solution.

We have used an approximately Gaussian resolution of the \( E_\alpha \) and \( A_2 \) components of \((+){\text{Co(en)}}_3^{3+}\) (according to Büger \(^{29}\)) with a \( \nu_{A_\alpha} - \nu_{E_\alpha} = +100 \) 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 \( E_\alpha \) transition has also been estimated by using the \( \Delta \varepsilon_{E_\alpha}\text{cryst} = +0.9 \) (obtained with the light propagated along the \( C_3 \)-axis of a \( 2[(+){\text{Co(en)}}_3\text{Cl}_3],\text{NaCl},\text{H}_2\text{O} \) crystal \(^{29}\)). As the transition has \( E \) symmetry and is consequently perpendicular to the \( C_3 \)-axis, \( \Delta \varepsilon_{E_\alpha(f=0)} = \frac{3}{2}(+0.9) = +0.6 \) (cf. eqn. (1)). The \( \Delta \varepsilon_{E_\alpha} \) 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 \( \Delta \varepsilon_{A_\alpha(f=0)} = -0.3 \). With our observed CD value for the film, +0.23, and eqn. (3) we have: 0.23 = \( f \cdot (0.5(-0.3) - 0.25(-0.6)) + 0.26 \), 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 \( E_\alpha - A_2 \) bands.

DISCUSSION

The CD spectra of the investigated compounds in methanol solution are given in Figs. 3-4. The CD spectrum of \((+\mathrm{Co(en)_3(dodecysulphate)})_3\) (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). 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 \((+\mathrm{Co(d-pn)_3(dodecysulphate)})_3\) 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 alkysulphate ions are associated to \(\mathrm{Co(d-pn)_3}^{3+}\) so that two or at least one is positioned along the \(C_3\)-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 \(D_3\) (like \(\mathrm{Co(en)_3}^{3+}\)). Thus the sublevels from \(1T_{1g}\) consist of \(A_2\) and \(E_{(a)}\) and from \(1T_{2g}\), \(A_1\) and \(E_{(b)}\). As the energetic order of \(T_1\) and \(T_2\) is \(T_1<T_2\) the assignments are obvious (Table 1).

In the case of \(\mathrm{trans-[Co(l-pn)_3(dodecylamine)]_3Cl}_3\) 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 \(\mathrm{trans-[Co(en)_2X_2]}^{3+}\) complexes, which possess \(D_{4h}\)-symmetry, have been identified from polarized crystal spectra. 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. The result agrees well with the experimentally obtained order and has also been applied to the related \(\mathrm{trans-[Co(l-pn)_3Cl}_3]}^{3+}\) complex by Larsen and coworkers. They point out that, as the order is expected to remain the same for all \(\mathrm{trans-[Co(l-pn)_2X_2]}^{3+}\) compounds with ligands \(X\) which are lower in the spectrochemical series than \(l-pn\), 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 \(\mathrm{trans-[Co(l-pn)_2(NH_3)]_3]}^{3+}\) 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 \(D_3\) and made the assignments: \(B_2\) or \(B_1\) (518 nm) and \(B_2\) or \(B_3\), partly \(B_1\) (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 \(\mathrm{trans-[Co(l-pn)_3Cl}_3]}^{3+}\) 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 \(\mathrm{CH}_3\)-groups are ignored — to \(D_2\) if the ring puckering (but not the

* According to the concept of Mason 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 D₄ₕ or D₂ₙ, however, the allowed transitions should be transitions with vibronic coupling. In D₂ₙ the only forbidden transition is the one between the ground state (A₁ₛ) and A₂₉ along the z direction. The results from our polarized CD spectrum imply that the proper assignments (in D₄ₕ) for the transitions are: A₁ₛ → A₂ₙ (⊥ z, 510 nm), A₁ₛ → E₂ₙ (|| and ⊥ z, 460 nm), A₁ₛ → B₂ₙ + E₂ₙ (|| and ⊥ 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 D₂ the T₁ cubic level is split into the sublevels B₁, B₂, and B₃. As the D₂ symmetry lacks a center of inversion, certain pure electronic transitions are allowed: A₁ → B₁ (||z), A₁ → B₂ (||y) and A₁ → B₃ (||x). The CD dichroism satisfies the assignments A₁ → B₁ (460 nm), A₁ → B₂ + B₃ (510 nm). This explanation does not agree, however, with the one given by Larsen et al.²² Because the B₁ level has A₂ₙ (D₄ₕ) 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 D₄ₕ (B₂ and B₃ in D₂ 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 C₃ (the CH₃ groups are taken into account). In C₃, T₁₉ is split into one A and two B levels. The A → A transition is allowd along the z-axis while the two A → B transitions are polarized in the xy-plane. This implies the assignments reported in Table 1. As the A level has A₂ₙ tetragonal parentage it is suggested (on the basis of the CF-analysis of trans-[CoA₄X₄]⁺⁺ by Yamamura²⁵) that the A band should have roughly the same energy as the T₁₉ 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 R₄ₕ (D₄ₕ) to R₄ₚ (D₃) or R₄ (C₃). This is principally not expected as A₂ₙ 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 affected by the alkylsulphate groups, presuming these to be attached to the complex in the way predicted by Mason et al.\textsuperscript{32}

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