

## Evidence for the Arrangement in the Outer Co-ordination Sphere of Dihedral Metal Complexes from Circular Dichroism Measurements on Oriented Films

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Recently the circular dichroism (CD) spectrum of  $[(+)\text{Co}(d\text{-pn})_3]^{3+}$  has been studied<sup>1</sup> under the conditions of a *semi*-oriented system with laurylsulphate ( $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-$ ) as counter-ion. The changes in intensity of the  $d-d$  transitions  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  and  ${}^1A_{1g} \rightarrow {}^1E_{a,g}$ , into which the transition  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  (in  $O_h$ ) breaks down in a dihedral complex ( $D_3$ ), indicated a preferential orientation of the  $C_3$  (three-fold) axes of the complex ions in a plane perpendicular to the direction of the incident luminous flux, coinciding with the plane containing the direction of stress (=orientation).<sup>1</sup> This was interpreted as showing (since the metal complex ion is approximately spherical in itself) that the outer sphere ligands (the alkylsulphate-anions) were not randomly disposed but arranged preferentially along the  $C_3$  axes.

The result was also in agreement with the concept introduced by Mason,<sup>2</sup> that anions with the possibility of hydrogen-bonding should approach along the  $C_3$  axis in  $[(+)\text{Co}(\text{en})_3]^{3+}$  and other *tris*-diamine complexes with *lel* conformation in the chelatic rings. In  $[\text{Co}(\text{en})_3]^{3+}$  *lel* is the most stable conformation and in  $[(+)\text{Co}(d\text{-pn})_3]^{3+}$  *lel* conformation is fixed by the chirality of *d*-pn. *lel*-Conformation is also found in  $[(-)\text{Co}(l\text{-pn})_3]^{3+}$  but in  $[(-)\text{Co}(d\text{-pn})_3]^{3+}$  and  $[(+)\text{Co}(l\text{-pn})_3]^{3+}$  *ob* conformation is preferred.<sup>3</sup> X-Ray studies have led to the conformational assignments.<sup>4-6</sup>

That the " $C_3$  axis position" was considered the most favourable in the *lel* cases is based upon the fact that there are two sets of three N-H bonds directed nearly parallel to the  $C_3$  axis (Fig. 2a). In  $(+)\text{Co}(d\text{-pn})_3^{3+}$  it was suggested that

\* (+) or *d*, (-) or *l* refers to the optical isomer having positive (*dextro*) and negative (*laevo*) optical rotation. en=ethylenediamine, pn=propylenediamine.

the methyl groups even impeded the formation of hydrogen bonds directed perpendicular to the  $C_3$  axis.<sup>2</sup> However, in  $(-)\text{Co}(d\text{-pn})_3^{3+}$ , the *ob* conformation of the propylenediamine molecules will imply that no two N-H bonds have a common orientation (Fig. 2b). According to Mason<sup>2</sup> the arrangement in the ion pair of  $(-)\text{Co}(d\text{-pn})_3^{3+}$  with, e.g., an oxyanion, should not be the same as in the corresponding complex with  $(+)\text{Co}(d\text{-pn})_3^{3+}$  or  $(+)\text{Co}(\text{en})_3^{3+}$ . This was proposed on the basis of the reported fact<sup>7</sup> that the effect on the rotational strengths of the above mentioned  $E_a$  and  $A_2$  components is not the same for those two complex ions when adding certain polarizable anions.<sup>2,7</sup>

The present communication reports the results of film experiments of the kind mentioned above, on the "*ob*" complexes  $[(+)\text{Co}(l\text{-pn})_3]$ (laurylsulphate)<sub>3</sub> and  $[(-)\text{Co}(d\text{-pn})_3]$ (laurylsulphate)<sub>3</sub>. The CD spectrum of  $[(+)\text{Co}(l\text{-pn})_3]^{3+}$  (and its complex with laurylsulphate, see Fig. 1) shows only one CD band corresponding to the  $A_{1g} \rightarrow T_{1g}$  transition, probably due to a zero trigonal splitting between the  $A_2$  and  $E_a$  (in  $D_3$ ) components. The apparent band is thus the residue of a positive  $E_a$  component (for correlation between rotational sign and configuration see, e.g., Ref. 12).

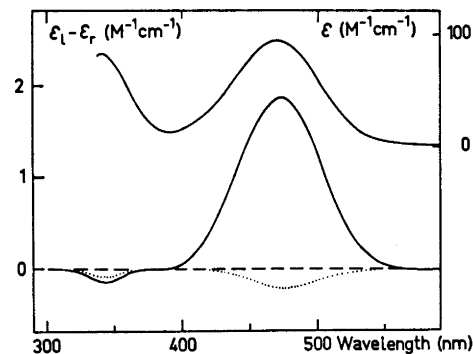


Fig. 1. Absorption spectrum (— above) and circular dichroism spectrum (--- below) of  $[(+)\text{Co}(l\text{-pn})_3]$  (laurylsulphate)<sub>3</sub> in ethanol and the circular dichroism spectrum of a film (thickness 0.090 mm) of this solution, which was stretched perpendicular to the direction of the incident light ray (...). In the random solution  $\Delta\epsilon(\text{max}, 470 \text{ nm}) = +1.80 \text{ M}^{-1}\text{cm}^{-1}$  and in the film  $\Delta\epsilon(\text{max}, 475 \text{ nm}) < 0$ .

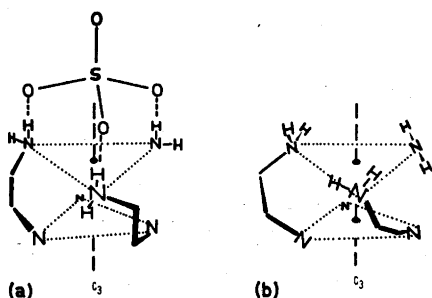


Fig. 2. The configuration of  $[\text{Co}(\text{l-el-diamine})_3]\text{SO}_4^+$  (a) and  $[\text{Co}(\text{ob-diamine})_3]^{3+}$  (b). For clarity one diamine molecule and the cobalt atom have been omitted.

In Fig. 1 a representative result is given of the CD of a film (of  $[(+)\text{Co}(\text{l-pn})_3](\text{laurylsulphate})_3$  in ethanol) which had been stretched perpendicular to the direction of the incident luminous flux. Apparently the  $E_a$  band has diminished and/or the  $A_2$  band been favoured resulting in even a change in sign. From our earlier experiments with oriented films of  $[(+)\text{Co}(\text{d-pn})_3](\text{laurylsulphate})_3$  (where the effect of orientation was also a decrease in  $E_a$  and an increase in  $A_2$ ) we can conclude that also in the present case *the oxyanion (laurylsulphate) is bonded to the dihedral complex along the  $C_3$  axis.*

Corresponding experiments with  $[(-)\text{Co}(\text{d-pn})_3](\text{laurylsulphate})_3$  show a decrease of the *negative*  $E_a$  band and in some cases even a positive band as the result of stretching.

Preliminary measurements on  $[(-)\text{Co}(\text{d-pn})_3]\text{Cl}_3$  indicate a behaviour of the CD in the presence of  $\text{SO}_4^{2-}$ ,  $\text{EDTA}^{4-}$ , or tartrate $^{3-}$  which was the reverse of that reported by Mason<sup>7</sup> with  $\text{PO}_4^{3-}$  and  $\text{S}_2\text{O}_3^{2-}$ ; at least at low concentrations of the anions the rotational strength (of the negative  $E_a + A_2$  band at 475 nm) was reduced. This suggests a different structure of the outer sphere complexes between  $(-)\text{Co}(\text{d-pn})_3^{3+}$  (or  $(+)\text{Co}(\text{l-pn})_3^{3+}$ ) and  $\text{SO}_4^{2-}$ ,  $\text{EDTA}^{4-}$ , tartrate $^{3-}$  compared with those with  $\text{PO}_4^{3-}$  and  $\text{S}_2\text{O}_3^{2-}$ . As these groups of anions are characterised by the inability and ability, respectively, of giving rise to *inter-ionic charge-transfer bands*<sup>7-9</sup> in the corresponding outer-sphere complexes with tris-diamine complex metal ions, this seems very interesting. The contribution to the outer-sphere bonding, given by the

charge-transfer may thus favour a different structure (in the *ob* case).

On the other hand it may appear somewhat contradictory that the complex, partly stabilised by charge transfer to the cobalt(III)-ion, should not have the outer-sphere ligand positioned on the  $C_3$  axis, as this approach must be the closest one. However, the changed conformation of the propylenediamine molecules may have caused a different partition of the antibonding orbitals (of a set of extended MO's on the complex ion) which are the most suited for overlapping with a lone-pair orbital of the anion, favouring another position of the anion.

Another possibility is, that the structure is fixed (anion on the  $C_3$  axis) but the presence of an inter-ionic charge transfer with  $E$  symmetry,<sup>3</sup> which can couple with other  $E$  transitions, causes a separate CD effect with (in the *ob* case) a sign opposite to that of the ordinary CD polarisation (see, e.g., Refs. 8, 10) at the association of an anion.

The fact that the inter-ionic C.T. circular dichroism band has the same sign as the  $E_a$  band in both the *ob* and *l-el* cases does not make either of the two explanations more probable than the other, as the rotational strength of this transition can change with different outer-sphere configurations as well as with changed angles of the overlapping orbitals (with changed diamine conformation). However, it is in agreement with and even expected in the last mentioned explanation where the additional CD effect can be supposed to have opposite signs with *ob* and *l-el* conformation.

Though we have shown that the sulphate ion is associated along the  $C_3$ -axis to both  $(+)\text{Co}(\text{d-pn})_3^{3+}$  and  $(+)\text{Co}(\text{l-pn})_3^{3+}$  the effect of the accessibility of suitable hydrogen atoms (cf. Fig. 2a with 2b) is obvious from reported stability constants for the corresponding  $\text{SO}_4^{2-}$  complexes; 70 and 43  $\text{M}^{-1}$ , respectively.<sup>14</sup> The large difference between these values (and a comparison with the stabilities of non-hydrogen-bonded complexes with  $(+)\text{Co}(\text{en})_3^{3+}$ ) suggests the criterion of linearity  $-\text{H}\cdots$  for effective hydrogen bonding (cf. Refs. 15, 16).

*Experimental.*  $(-)\text{Co}(\text{d-pn})_3\text{Cl}_3$  was prepared by a chromatographic method according to Dwyer, MacDermott and Sargeson.<sup>17</sup> The salt was converted to that of laurylsulphate $^-$  by precipitation with this anion in water (washing

the precipitate with plenty of water). (+)Co(*l*-pn)<sub>3</sub>(laurylsulphate)<sub>3</sub> was prepared following in principle the method for fractional crystallisation given by Dwyer, Garwan and Shulman,<sup>11</sup> but the purity was found to be even better than for the isomer prepared using chromatography if (-)Co(*l*-pn)<sub>3</sub>(laurylsulphate)<sub>3</sub> was removed by successive addition of sodium laurylsulphate. The solution remaining from the last precipitation thus gave a CD considerably higher than that reported by Mason<sup>7</sup> for the Sargeson sample.

The preparation of an oriented film has been described elsewhere.<sup>1</sup> The CD measurements were made as before.<sup>1,12</sup>

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## On the Preparation of 1,4-Diphenylcyclohexa-1,3-diene

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In connection with our studies of non-transoid conjugated exocyclic dienes<sup>1</sup> we also prepared the endocyclic diene 1,4-diphenylcyclohexa-1,3-diene, which had not then been described. In the meantime, Courlot and Le Goff-Hays<sup>2</sup> have reported its synthesis by essentially the same method that we used. They describe, however, a byproduct never observed by us, while on the other hand we found that the 1,4-diene<sup>3</sup> appears as an intermediate in our synthesis.

When the elimination of water from 1,4-diphenyl-cyclohexane-1,4-diol is carried out in benzene solution containing *p*-toluenesulphonic acid, and the water removed by azeotropic distillation, there is always formed a mixture of three products. NMR spectroscopy shows clearly that these are 1,4-diphenylcyclohexa-1,3-diene (singlets at 6.55 and 2.78 ppm), 1,4-diphenylcyclohexa-1,4-diene (multiplets at 6.30 and 3.31 ppm), and *p*-terphenyl (singlet at 7.68 ppm). When the reaction is allowed to proceed until the theoretical quantity of water is removed, the proportion of *p*-terphenyl formed is much larger than if the reaction is stopped at an early stage. Also, the ratio of conjugated to nonconjugated diene increases with time.

This easy dehydrogenation to *p*-terphenyl under acidic condition is in accord with the reported<sup>2</sup> formation of *p*-terphenyl by simply passing the 1,3-diene through alumina. A disproportionation can be excluded, since there is no indication of diphenylcyclohexene or diphenylcyclohexane in the NMR spectrum.

It proved impossible to separate the formed *p*-terphenyl from the diene mixture by crystallization, by chromatography, or by zone-melting. A product free from *p*-terphenyl can, however, be obtained if the complex from the reaction of cyclohexane-1,4-dione and phenyl lithium<sup>4</sup> is stirred directly with 50% aqueous sulfuric acid. A vigorous reaction takes