

# Optical Activity of Spin-forbidden $d$ -Electron Excited States of Tris(diamine)chromium(III) and -cobalt(III) Complexes with $D_3(C_3)$ and $C_2(C_1)$ Symmetry

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The circular dichroism spectra of the series of complexes  $[\text{Cr en}_{3-x}\text{tn}_x]^{3+}$  ( $x=0,1,2,3$ ) and the Co(III) analogous have been measured in aqueous solution over the range 500–1000 nm (en=1,2-ethanediamine and tn=1,3-propanediamine). The optical activity associated with the quartet-doublet Cr(III) transitions and with the single-triplet Co(III) transitions (some of which have already been reported by various authors) may be assigned within an effective  $D_3$  symmetry irrespective of the actual symmetry of the chromophore.

In contrast to the optically active spin-allowed  $d$ -electron transitions of Cr(III) and Co(III) complexes – for which an extensive literature exists<sup>1</sup> – the spin-forbidden transitions, though known<sup>2</sup> for a number of years, have been relatively little investigated.

In a paper from 1961 by Kling and Woldbye<sup>3</sup> it was shown that  $[\text{Cr en}_3]^{3+}$  exhibit a composite optical rotatory dispersion and absorption between 700 and 600 nm. Quite recently Mason and Peart<sup>4</sup> observed the crystal circular dichroism of  $2[\Lambda\text{-Co en}_3\text{Cl}_3] \cdot \text{NaCl} \cdot 6\text{H}_2\text{O}$  at low temperature and the corresponding solution CD-spectra of  $\Lambda\text{-}[\text{Co en}_3]^{3+}$ ,  $\Lambda\text{-}[\text{Co S-pn}_3]^{3+}$  and  $\Lambda\text{-}[\text{Co tn}_3]^{3+}$  in the spectral region 500–1000 nm. The optical activity associated with the spin-forbidden transition were accounted for by Mason and Peart through spin-orbit coupling between the  $^3T_1$  and  $^3T_2$  octahedral states and the corresponding  $^1T_1$  state and by means of a dynamic-coupling ligand-polarisation model published previously by Mason and Seal.<sup>5</sup>

A somewhat different approach to an understanding of the  $d$ -electron optical activity of chiral transition metal complexes will be given in the present paper. From a group-theoretical point of view, we consider and describe various  $d$ -electron configurations within the specific symmetry of the chromophore and determine in this way the manifold of the electronic states. It should, however, be noted that this description could be a little misleading in cases where the sub-shell configurations possess major contributions from Slater-Condon-Shortley parameters of interelectronic repulsion.<sup>6,7</sup>

A consideration analogous to the present, as far as splittings of  $d^n$ -terms within  $D_{3d}$  and  $D_{2h}$  symmetry are concerned, has been dealt with previously by Gilde and Bàn.<sup>8</sup>

## EXPERIMENTAL

The preparation of the compounds as well as the resolution and purification has been stated elsewhere.<sup>9,10</sup> The circular dichroism spectra in the spin-forbidden  $d-d$  transition region of the complexes were recorded on a Jobin-Yvon Dichrographe Mark III. Solutions were ca. 0.1 molar and path length 1 cm.

## RESULTS AND DISCUSSION

*Chromium(III)*. The near infrared CD-spectra of the four  $[\text{Cren}_{3-x}\text{tn}_x]^{3+}$  complexes are reproduced in Fig. 1. Based on knowledge of crystal structures and absolute configurations<sup>11</sup> the following point symmetries for the various cations are

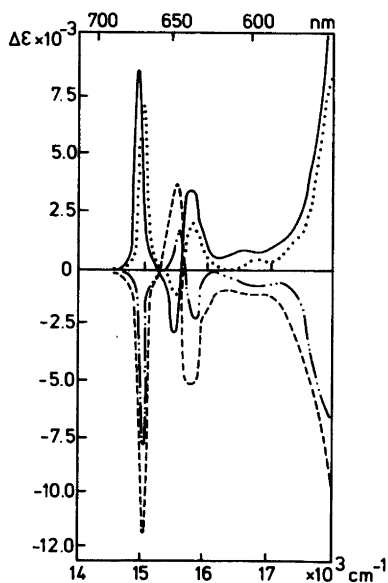
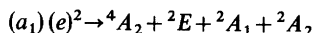


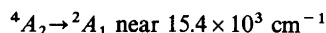
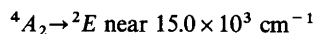
Fig. 1. The near infrared molar ( $M^{-1} \text{ cm}^{-1}$ ) circular dichroism spectra of  $\Delta$ -[Cr(en) $_3$ ] $^{3+}$  —,  $\Delta$ -[Cr(tn) $_3$ ] $^{3+}$  ---,  $\Lambda$ -[Cr(en) $_2$ tn] $^{3+}$  — —, and  $\Lambda$ -[Cr(en)tn $_2$ ] $^{3+}$  ··· in aqueous solution.

expected:  $D_3(\Delta(\lambda\lambda\lambda)-[\text{Cr(en)}_3]^{3+})$ ,  $C_3(\Delta(\lambda\lambda\lambda)-[\text{Cr(tn)}_3]^{3+})$  and  $C_2$  or lower ( $C_1$ ) for [Cr(en) $_2$ tn] $^{3+}$  and [Cr(en)tn $_2$ ] $^{3+}$  depending on diamine conformations.

For a Cr(III) complex with  $D_3$  symmetry the lowest electron configuration,  $(a_1)(e)^2$ , gives rise to the terms



The state of maximum multiplicity,  ${}^4A_2$ , is the ground state and thus among these quartet-doublet intercombinations we should expect two optically active transitions of different signs,  ${}^4A_2 \rightarrow {}^2E$  and  ${}^4A_2 \rightarrow {}^2A_1$ , and an inactive "symmetry-forbidden"  ${}^4A_2 \rightarrow {}^2A_2$  transition. With reference to Fig. 1 we make the tentative assignments:

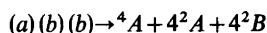


Further, in the CD spectrum we have one band near  $15.8 \times 10^3 \text{ cm}^{-1}$ . It would be tempting to assign this to the "forbidden"  ${}^4A_2 \rightarrow {}^2A_2$  transition

revealed through vibronic interaction or by spin-orbit coupling with the spin-allowed  ${}^4A_2 \rightarrow {}^4E$  transition near  $21.3 \times 10^3 \text{ cm}^{-1}$ . However, another possibility exists, i.e. configuration interaction between the lowest electron configuration  $(a_1)(e)^2$  and the two excited configurations  $(a_1)^2(e)$  and  $(e)^3$ , both of which produce a  ${}^2E$  term. Thus we could assign the  $15.8 \times 10^3 \text{ cm}^{-1}$  transition as  ${}^4A_2 \rightarrow {}^2E$ . This latter alternative is considered the most likely since the 15.0 and 15.8 ( $10^3 \text{ cm}^{-1}$ ) CD bands exhibit the same sign.

The chromophoric symmetry of [Cr(tn) $_3$ ] $^{3+}$  is either  $D_3$  (twisted boat form) or  $C_3$  (chair form). In the former case we would make the same assignments as those given above. With  $C_3$ -symmetry, however, the states resulting from the lowest electron configuration,  $(a)(e)^2$ , are  ${}^4A + {}^2E + 2{}^2A$  together with  ${}^2E$  states [from the excited configurations  $(a)^2(e)$  or  $(e)^3$ ]; thus the only difference in comparison with the  $D_3$  case is an additional optically active  ${}^2A$  state. Although an assignment based on  $C_3$  symmetry is possible, it may be seen from Fig. 1 that there is, except for intensity, a striking similarity between all the spectra, suggesting  $D_3$  or effective  $D_3$  symmetry.

Such an effective  $D_3$  chromophoric symmetry is less obvious considering the compounds [Cr(en) $_2$ tn] $^{3+}$  and [Cr(en)tn $_2$ ] $^{3+}$ , since the symmetry of either of these complexes cannot be higher than  $C_2$  and is probably lower, ( $C_1$ ). Assuming  $C_2$  symmetry with a lowest electron configuration,  $(a)(b)(b)$ , and taking configuration interaction into account, we get



The optically active transitions  ${}^4A \rightarrow {}^2A$  and  ${}^4A \rightarrow {}^2B$  have opposite signs and thus we should, for an effective  $C_2$  symmetry, considering furthermore the resolving power of the dichrograph, expect a rather uncharacteristic CD spectrum due to intensity cancellation within the narrow spectral range of the spin-forbidden absorption bands.<sup>2</sup> However, also in this case there is indication of a corresponding effective  $D_3$  chromophoric symmetry. The reason for this most probably is that the  $d$ -electrons in all instances are dominated by the  $N_6$  ligator group.

In the spectral range discussed, no further quartet-doublet transitions are expected, and additional doublet states from excited electron configurations

are most certainly hidden under spin-allowed transitions in the spectral range 600–400 nm recently studied by phase modulation spectroscopy on single crystals of the  $[\text{Cr en}_3]^{3+}$  chromophore.<sup>12,13</sup>

**Cobalt(III).** The near infrared CD spectra of  $[\text{Co en}_3]^{3+}$  and  $[\text{Co tn}_3]^{3+}$  obtained by Mason and Peart<sup>4</sup> are identical with CD spectra obtained by us. Furthermore, CD spectra of  $[\text{Co en}_2\text{tn}]^{3+}$  and  $[\text{Co en tn}_2]^{3+}$  in the same spectral range have, except for intensity, a striking similarity with the spectrum of  $[\text{Co en}_3]^{3+}$ . Therefore, in the following, we shall refer to the work of Mason<sup>4</sup> with regard to spectra. A comparison between the CD spectra of the spin-forbidden transitions within the Co(III) and the Cr(III) series reveals that the former appear rather broad, in contrast to the latter which exhibit sharp line bands. The reason for this difference in appearance is due to the fact that, with Co(III), we have transitions between different electron configurations, just as in the case of the spin-allowed transitions, while, with Cr(III), we have transitions within the ground state configuration (presumably interacting with two excited states in close proximity).

The lowest electron configurations for Co(III) tris-diamine complexes,  $(a_1)^2(e)^4(D_3)$ ,  $(a)^2(e)^4(C_3)$ , and  $(a)^2(b)^2(b)^2(C_2)$  or  $(b)^2(a)^2(b)^2$  or  $(b)^2(b)^2(a)^2$  will invariably give a singlet  $^1A_1$  or  $^1A$  ground state.

The excited electron configuration,  $(a_1)^2(e)^3(e)(D_3)$ , yields  $^3E + ^3A_2 + ^3A_1 + ^1E + ^1A_2 + ^1A_1$  with the triplet states placed on the low-energy side of the spin-allowed singlet-singlet transitions. The configuration,  $(a_1)(e)^4(e)(D_3)$ , yields  $^3E + ^1E$  as well, with the triplet placed on the low-energy side of the singlet. Other possible electron configurations such as  $(e)^3(e)^3$  or  $(a_1)(e)^3(e)^2$  are unlikely since they represent, configurationally, "two-electron" transitions. If we omit the subscript 1 and 2 on the terms  $A_1$  and  $A_2$  we then produce the case of  $C_3$  symmetry where all transitions to  $^3A$  and  $^1A$  are now optically active and of opposite signs in comparison with transitions to  $^3E$  and  $^1E$  states.

It now remains to look at the  $C_2$  case. As mentioned earlier, we expect a  $^1A$  ground state arising from the electron configuration of say,  $(b)^2(a)^2(b)^2$ . In the excited configuration we have, by virtue of configuration interaction between  $(b)^2(a)^2(b)(a)$  and  $(b)^2(a)(b)^2(a)$  and because of two upper  $d$ -orbitals ( $a$ ), the states  $2^3B + 2^3A + 2^1B + 2^1A$ . The electron configuration,  $(b)(a)^2(b)^2(a)$ , also with configuration interaction, yields  $2^3B + 2^1B$ .

Table 1. Tentative, spectral assignments for the  $\Lambda$ - $(\delta\delta\delta)$ - $[\text{Co en}_3]^{3+}$  chromophore of  $D_3$  symmetry.

Transition	Position $10^3 \times \text{cm}^{-1}$	Sign in CD	Type
$^1A_1 \rightarrow ^3E$	11.5	+	$d-d$
$^1A_1 \rightarrow ^3A_1$	?	inactive	$d-d$
$^1A_1 \rightarrow ^3A_2$	13.5	-	$d-d$
$^1A_1 \rightarrow ^3E$	16.5	+	$d-d$
$^1A_1 \rightarrow ^1E$	20.3	+	$d-d$
$^1A_1 \rightarrow ^1A_1$	?	inactive	$d-d$
$^1A_1 \rightarrow ^1A_2$	23.7	-	$d-d$
$^1A_1 \rightarrow ^1E$	28.5	+	$d-d$
$^1A_2 \rightarrow ^3A_1$	?	-	CT
$^1A_1 \rightarrow ^3A_1$	?	inactive	CT
$^1E \rightarrow ^3A_1$	?	+	CT
$^1A_2 \rightarrow ^1A_1$	48	-	CT
$^1A_1 \rightarrow ^1A_1$	?	inactive	CT
$^1E \rightarrow ^1A_1$	58	+	CT
$^1E \rightarrow ^1A_1$	58?	+	CT

The charge transfer (CT) bands are assumed to arise from a transfer of a "lone pair" electron on nitrogen (symmetry:  $a_1 + a_2 + 2e$ ) to a  $d_{z^2}$  or  $4s$  orbital both of  $a_1$  symmetry.

Any theory of optical activity of transition metal complexes (restricted here to  $d$ -electrons) must necessarily, in order to be complete, include not only the spin-forbidden transitions discussed above, but also it must include the spin-allowed transitions which, as mentioned in the introduction, is a well documented subject.

The present author has recently published full details on the elucidation of the optically active spin-allowed transitions of the Co(III) complexes here in question.<sup>14,15</sup> On the basis of this and other information we make the tentative spectral assignments given in Table 1 for  $\Lambda$ - $(\delta\delta\delta)$ - $[\text{Co en}_3]^{3+}$  of  $D_3$  symmetry.

Obviously, similar assignments may be given for the chromophores  $[\text{Co tn}_3]^{3+}$ ,  $[\text{Co en}_2\text{tn}]^{3+}$  and  $[\text{Co tn}_2\text{en}]^{3+}$  within  $D_3$  symmetry, since the number of spin-forbidden bands ( $3$ )<sup>4</sup> in all cases suggests this to be the effective symmetry of the chromophores. This is indeed a comforting observation since CD spectra of tris(diamine)cobalt(III) and -chromium (III) complexes generally have, as may *e.g.* be seen from the greater part of the references, been treated as if the chromophores exhibited trigonal ( $D_3$ ) symmetry.

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