## 392. *Magnetic-dipole-allowed Transitions in Optically Active Molecules.*

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It is possible to distinguish between spectral transitions from the same ground state to different excited levels on the basis of the rotational strength associated with the transition, where one of the transitions is magnetic-dipole-allowed.[1,2] Measurements of the circular dichroism of octahedral trisbidentate chelates are collected in Tables 1—3, with assignments of the bands made on this criterion. The frequencies of maximum absorption,

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[1] Moffitt, *J. Chem. Phys.*, 1956, **25**, 1189.

[2] Mason, *Proc. Chem. Soc.*, 1962, 137.

$\nu_{\text{abs}}$, are taken from a recent book [3] where possible, except for trisoxalatorhodate(III) [4] and the value for trispropylenediaminecobalt(III) which has been measured. $\nu_{\text{CD}}$ is the frequency of the maximum circular dichroism, mostly from a compilation by Mathieu.[5] We have taken a dissymmetry factor, $g' =$ maximum circular dichroism/maximum extinction coefficient, numerator and denominator referring to the same transition. This leads to a smaller value for $g'$ of trisoxalatocobaltate(III) than was given in ref. 6. We shall comment on the nature of the dissymmetry factor elsewhere. References in the Tables give the sources of circular dichroisms. The transitions observed for solutions are discussed here as if the complexes had $O_h$ symmetry, whereas, strictly, they have $D_3$ symmetry only.

TABLE 1.

Trisoxalato-complexes of metals with the $(t_{2g})^6$ configuration.

| | ${}^1A_{1g} \longrightarrow {}^1T_{1g}$ | | | ${}^1A_{1g} \longrightarrow {}^1T_{2g}$ | | | |
|---|---|---|---|---|---|---|---|
| Compound | $\nu_{\text{abs}}$ | $\nu_{\text{CD}}$ | $g'(\times 10^2)$ | $\nu_{\text{abs}}$ | $\nu_{\text{CD}}$ | $g'(\times 10^2)$ | Ref. |
| Co $\text{ox}_3$ | 16·5 | 16·1 | 1·4 | 23·8 | 23·8 | 0·1 | 6 |
| Rh $\text{ox}_3$ | 25·0 | 24·7 | 2·02? | (30) | — | — | *a* |
| Ir $\text{ox}_3$ | — | 22·0 | 1 | — | — | — | 5 |

(*a*) Badoz, Billardon, and Mathieu, *Compt. rend.*, 1960, **251**, 1477.

TABLE 2.

Trisdiamine complexes of metals with the $d^6$ configuration.

| | ${}^1A_{1g} \longrightarrow {}^1T_{1g}$ | | | ${}^1A_{1g} \longrightarrow {}^1T_{2g}$ | | | |
|---|---|---|---|---|---|---|---|
| | $\nu_{\text{abs}}$ | $\nu_{\text{CD}}$ | $g'(\times 10^2)$ | $\nu_{\text{abs}}$ | $\nu_{\text{CD}}$ | $g'$ | Ref. |
| Co $\text{en}_3$ | 21·4 | 20·4 | 2·0 | 29·5 | — | — | 6 |
| Co $\text{pn}_3$ | 21·4 | 20·4 | 2·1 | 29·5 | — | — | 6 |
| Rh $\text{en}_3$ | 33·2 | 32·3 | 1·5 | 39·6 | — | — | *b* |
| Ir $\text{en}_3$ | — | 31·7 | ? | — | — | — | *b* |

(*b*) Mathieu, *J. Chim. phys.*, 1936, **33**, 78.

These oxalato-compounds are mentioned by both Moffitt [1] and Mason.[2] It seems clear that the broad absorption described by Jørgensen [7] for the trisoxalatoiridate ion conceals a ligand-field band; reliable absorption data are lacking.

The triplet band observed by Jørgensen [7] for trisoxalatorhodate(III), at 19,200 cm.$^{-1}$, with $\varepsilon_{\text{max.}}$ 8, does not contribute to circular dichroism; if this band were magnetic-dipole-allowed, with the minimum possible $g$ value of 0·01, the circular dichroism (about 0·1) should be easily observed, as it is in trisethylenediamineiridium(III) (see below). If this band were in fact magnetic-dipole-allowed, it should give rise to a Cotton wave in the molecular rotatory dispersion of about 200° amplitude, centred at 18,000—19,000 cm.$^{-1}$. This has not been observed by ourselves or others. This suggests that the triplet arises from intensity " borrowed " from the ${}^1A_{1g} \longrightarrow {}^1T_{2g}$ transition. The existence of this triplet band could not be verified.

Piper and Carlin [8] studied the absorption of polarised light by crystalline trisoxalatocobaltate, and concluded that both transitions are electronically allowed, occurring by the electric-dipole mechanism, without excitation of asymmetric vibrational modes. If this were true, the $g'$ value should be much less than $10^{-2}$; in fact, it is $1 \cdot 4 \times 10^{-2}$. It is conceivable that the crystal of potassium trisoxalatocobaltate trihydrate does not contain three bidentate oxalate groups for each cobalt atom; the analogous compound of rhodium(III) apparently has a water molecule bound to the rhodium atom.[9] The ready

[3] Jørgensen, " Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962.

[4] Albinak, Bhatnagar, Kirschner, and Sonnessa, *Canad. J. Chem.*, 1961, **39**, 2360.

[5] Mathieu, in " Victor Henri Commemorative Volume," Desoer, Liège, 1947.

[6] Kuhn and Bein, *Z. anorg. Chem.*, 1934, **216**, 321.

[7] Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 500.

[8] Piper and Carlin, *J. Chem. Phys.*, 1961, **35**, 1809.

[9] Gutowsky, Porte, and Harris, *J. Chem. Phys.*, 1961, **34**, 67.

racemisation of the cobalt(III) compound in the solid state could also be explained by such a structure.

Jørgensen attributes a fairly weak band at 33,100 cm.$^{-1}$ for trisethylenediamine-iridium(III) to transitions to one of the triplet levels. However, the circular dichroism is obviously due to this band, which therefore is, at least, strongly vibrationally coupled with the $^1A_{1g} \longrightarrow {}^1T_{1g}$ band. A band owing its existence to " stealing " of intensity from the $^1A_{1g} \longrightarrow {}^1T_{2g}$ transition would not show such marked circular dichroism.

TABLE 3.
Trischelate complexes of chromium.

| | $^4A_{2g} \longrightarrow {}^4T_{2g}$ | | | $^4A_{2g} \longrightarrow {}^4T_{1g}$ | | | |
|---|---|---|---|---|---|---|---|
| | $\nu_{abs}$ | $\nu_{CD}$ | $g'(\times 10^2)$ | $\nu_{abs}$ | $\nu_{CD}$ | $g'$ | Ref. |
| Cr ox$_3$ .................. | 17·5 | 18·2 | 4·0 | 23·9 | — | — | 5 |
| Cr en$_3$ .................. | 21·85 | 21·8 | 2·6 | 28·5 | — | — | 5 |

The transitions of the trisoxalatochromate have again been called electric-dipole-allowed. The rotational strength is too high for this to be true, and a similar feature of the crystal structure to that found in the trisoxalatorhodate(III) system [9] might be expected. Chromioxalate also racemises in the solid state, undergoing a marked colour change. The reported crystal structure [10] was calculated through the improper space group, although the same does not apply to the ammonium salt.[11]

In general, measurements of optical rotatory dispersion of co-ordination compounds do not readily yield information about rotational strengths of transitions; however, in the case of the " chromium doublet " bands recently investigated by Kling and Woldbye [12] by means of rotatory dispersion, the strongest Cotton effects are symmetrical. By applying Kuhn's equation,[13] the following dissymmetry factors were calculated:

Trisethylenediaminechromium(III) ......... $\nu_{max.}$ 14,945 cm.$^{-1}$, $g_0 = 3{\cdot}8 \times 10^{-2}$
Tristrimethylenediaminechromium(III)...... $\nu_{max.}$ 14,900 cm.$^{-1}$, $g_0 = 2{\cdot}4 \times 10^{-2}$

These bands are thus magnetic-dipole-allowed.

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[10] Van Niekerk and Schoening, *Acta Cryst.*, 1952, **5**, 196.
[11] Van Niekerk and Schoening, *Acta Cryst.*, 1952, **5**, 499.
[12] Kling and Woldbye, *Acta Chem. Scand.*, 1961, **15**, 704.
[13] Kuhn, *Ann. Rev. Phys. Chem.*, 1958, **9**, 417.