Coordination Chemistry Reviews
Published by Elsevier Company, Amsterdam – Printed in The Netherlands

BONDING EFFECTS IN CIRCULARY DICHROIC COBALT (III) COMPLEXES

L.I. KATZIN*

Department of Chemistry, Tel-Aviv University and Department of Inorganic and Analytical Chemistry, The Hebrew University, Tel-Aviv (Israel)

and I. ELIEZER

Department of Chemistry, Tel-Aviv University, Tel-Aviv (Israel)

(Received May 7th, 1971)

CONTENTS

A. INTRODUCTION

Cotton[1] demonstrated that when an optically active ligand was attached to a transition metal ion, the characteristic absorptions of the metal ion became circularly dichroic. Werner's classic work[2] showed that even without dissymetric ligands, complexes of Co(III) could be produced which, when themselves dissymetric, exhibited optical activity. The complexes of the type tris(ethylene diamine)cobalt (III) have engaged particular attention, because of the relation of the optical isomerism to the two possibilities for orientation of the chelating chains, to give respectively right- or left-hand dihedral helices when viewed along the threefold axis[3]. The interest in this was obviously related to theories on optical activity such as that of Kuhn[4], which involved spiral motion of electrons.

In the absence of ligands showing absorption bands in the same region (e.g., iodide, the acetylacetonate group, etc.), the absorption spectra in the visible and near-ultraviolet of Co(III) complexes are remarkably similar. The principal feature is two partly resolved broad bands (with others being found at shorter wavelength). With the advent of the

---

* On leave from Argonne National Laboratory, Argonne, Illinois; support from U.S. Atomic Energy Commission gratefully acknowledged.

crystal field interpretation of ionic spectra, these two bands have been characterized as due to transitions (in O_h symmetry) from the ${}^1A_{1g}$ ground state of a spin-paired d^6 configuration to ${}^1T_{1g}$ and ${}^1T_{2g}$ upper states, respectively. Under reduced symmetry (of most interest to us, when one or more ligands are optically active, or the complex itself is dissymmetric), the T states split to two or three states of lower degeneracy, and circular dichroic spectra of some complexity may result. The absorption spectra may be little affected.

Similar phenomena have been observed with other d^6 ions that form kinetically inert complexes, and with d^3 systems like Cr(III), but further discussion will be limited to the Co(III) complexes. These embody the largest mass of data and variety of species, and analysis of them can lead to conclusions which may, as appropriate, be extended to other systems on which fewer independent data are available.

B. THE TRIS(ETHYLENEDIAMINE)COBALT(III) SYSTEM

The type-species for the conventional analysis is $(+)\text{-}[\mathrm{Co(en)_3}]^{3+}$. Being dextrorotatory in the region of the sodium D line, as indicated, it has been labelled[3] the *d* or *D* form. Crystal structure analysis[5] has shown the arrangement of the ethylenediamine units to correspond to the left-handed helix, and so it is designated[6] Λ by some authors. The first absorption band, $T_{1g}(O_h)$, should be split in the D_3 symmetry to A_2+E. No clear indication of such splitting is generally seen in the absorption spectrum, but the CD spectrum shows a major positive component, with its maximum at lower energy than the absorption maximum, and a minor negative dichroism near the high-energy limit of the absorption peak. This is generally interpreted [7-9] as a strong positive E component, with a weaker negative A_2 component that has its maximum at slightly higher energy. Concentrating attention on this peak in the absorption spectrum, the correlation has been strongly advocated[8,9] that a positive sign of the major CD component of the T_{1g} (O_h) band means A orientation of the chelate ring in all complexes. "Absolute configurations" have been assigned to a large number of Co(III) chelates essentially on this basis. (The same argument has, in fact, been extended to other d^6 systems [10-15].)

Because of interest in the question of "absolute configuration", attention has generally been centered on the first absorption band and its circular dichroism. The circular dichroism of the second band is often, though not universally, considerably weaker than that of the first band. An explanation for this in terms of the magnetic moment representation of the "parent" $T_{1g}(O_h)$ level given some time ago by Moffitt[7] is generally repeated. However, since in any relevant case the "parent" level is split to states of lower symmetry, it is the conformity of these to the selection rules which is significant. It is, for example, the E-representation nature of the daughter state which is determinative, not what its higher-degeneracy parent representation might have been.

In any event, in terms of the ligand field splitting of the upper states, $T_{1g}(O_h)$ and $T_{2g}(O_h)$ should give the same number of derived components and dimensionality of representations under similar lower symmetries. The differences to be expected reflect the selection rules for optical activity. These require that the direct product of the irreducible representations of the ground state and the excited state span the representation of the magnetic dipole vector operator in addition to that of the electric dipole operator which the absorption indicates. With the $^1A_{1g}$ ground state of the Co(III) complexes, the states into which $T_{1g}(O_h)$ splits all satisfy this requirement. $T_{2g}(O_h)$ may, in contrast, give some components which fail the test, e.g. as when an $^1A_1$ component is derived in D_3 symmetry. Because there is no a priori symmetry reason why the splitting effects of a lower-symmetry field on the $T_{1g}(O_h)$ and $T_{2g}(O_h)$ should otherwise differ, discrepancies between the findings in the two peaks call for interpretation.

The ion (+)-$[Co(en)_3]^{3+}$ in the solid state shows symmetry D_3, as anticipated, with configuration Λ-*kkk* (ref. 5). The first-band circular dichroism in aqueous solution has been described above; the second band has a small symmetric positive CD which lies completely below the energy of the band maximum, and in the upper energy half of the band there is no circular dichroism reported[9]. By the shorthand to be adopted in this paper, this will be designated a [L,–S] [+,0] CD pattern*. In D_3, the splittings are $E+A_2$ and $E+A_1$ respectively, for the two peaks. $A_1 \rightarrow E$ should be optically active, $A_1 \rightarrow A_1$ should not. All components of the first peak, as mentioned above, should be active. There would appear, therefore, to be a perfect match between theory and observation, as to number and energy order of components between the two peaks, and the symmetry relations.

The ion (+)-$[Co(+pn)_3]^{3+}$ has the same arrangement[16] of the ethylenediamine skeleton as does (+)-$[Coen_3]^{3+}$, but the methyl groups reduce the symmetry to C_3, so *both* bands should show *two* optically active components. The circular dichroism, however, seems[11,14,17] to be virtually identical to that of the tris(ethylenediamine) compound of D_3 symmetry. Some tris-diamines which contain both pn and en, or +pn and –pn, seem to have very similar dichroisms [13,14,17], though the actual symmetries are C_2 and C_1, which would require three components in each band.

Consider now another complex with D_3 symmetry like that of $[Coen_3]^{3+}$, namely, $(-)_{546}$-$[Co(ox)_3]^{3-}$. The CD pattern[18] is [L,–S] [+,–,+], with three clear components in the second peak, which would be appropriate to C_2 or C_1 symmetry, but not D_3. The amino acid complexes with the analogous structure and symmetry (C_3) as the tris(propylenediamine) complex, which are designated as *facial*, *cis*, or β-$[Co(aa)_3]$ by the various authors, also show the [L,–S] [+,–,+] CD formula or its sign inverse in many cases (alanine, aspartic acid, leucine, proline). The tris-glycine compound shows [L(–S)] [+,–], which

---

* The two brackets will be used to represent first and second peaks, respectively. [L,–S] means large positive CD, small negative CD, in the order of increasing energy. The L,S designations will be restricted to the first peak. Some asymmetric bands of single sign, with shapes significantly different from that of the corresponding absorption band, imply the existence of a smaller component which is completely masked because of the small splitting from and low intensity relative to the larger one; they may be indicated by [L(–S)], [(S)–L], etc. A component the implication for whose existence is more questionable will be given with a question mark, as [L(–S?)].

In the second peak, where CD component intensities are generally comparable to each other and components are clearly resolved, only the signs of components will be indicated in the order in which they appear, e.g. [+,–]. A symmetrical positive CD the full width of the second band will be indicated as [*n*+] inasmuch as the number of components cannot be definitely ascertained. If one component is of a size distinctively greater than the other(s) in the band, it will appear with a double sign in parentheses, e.g., [(++),–] or [+,–,(++)], etc. When intensity differences are indefinite in the first band, the [+–] designations will also be used, with [+] or [–] being used when no clear indication for a second component is seen.

is compatible with the C_3 symmetry, but the spectrum is different from the appearance of the tris(propylenediamine) complex pattern.

Without going into more detail at this point, there seems adequate reason to re-examine the currently popular approach to the CD of these complexes, and the "absolute configurations" deduced from them without crystallographic or other confirmation. One may go further and attempt an analysis of the implications in the procedures used, but this will be deferred to a later point and another context.

The spectroscopic parameters which come into consideration are (a) derived components; (b) order of levels; (c) signs and intensities of CD components. Contributing to these are not only the obvious structural symmetries of the environment, but a number of more subtle factors which have generally been disregarded in the concentration on the field symmetry and the dihedral orientation of chelate rings, and which may be lumped under the rubric "bonding effects". These may easily be imagined to play a role in determining ordering of levels, signs of dichroic components and their intensities, and perhaps even in determining effective field symmetries. In the following, an attempt will be made to sort from the literature (summarized in Table 1) clues to the operation of some of these bonding effects.

C. THE *cis*-[Coen$_2$AB] SYSTEMS

The class of *cis*-[Coen$_2$AB] compounds carries considerable potential for useful study. When neither A nor B is optically active, dichroism must come from the arrangement of the en ligands, which must in turn match the arrangements in one of the two isomers of $[Coen_3]^{3+}$. When A = B, or when AB is a symmetric chelate group other than en, the symmetry is C_2; otherwise it is C_1. With A = B, (+)-$[Coen_2(NH_3)_2]^{3+}$ is [L,–S] [*n*+], and the CD looks very much like that of many of the tris-diamines. The same relationships in the first peak, but varied second-peak patterns, are found for $(NH_3)(CN)$, with [–L,S] [–,–]; $(CN)(NO_2)$, [L,–S] [+,+]; $(CN)(H_2O)$, [L,–S] [–,+]; and $(NO_2)_2$, also [L,–S] [–,+]. The apparent level ordering in the first peak is reversed in $(haloacetate)_2$, [–S,L] [*n*–]; $(N_3)_2$, [–S,L] [*n*–]; and $(Cl)_2$, [–S,L] [+,–]. The following group, in which the distinction between S and L becomes difficult, may be considered an intermediate phase: (CN)(OH), with [+,–] [(++), +]; (CN)(Br), [+,–] [+,–,+?]; and (CN)(I), with [+,–] [–,+,?]. Possibly most provocative is the group with L and S of the same sign, viz. $(CN)_2$ with [L,S] [+,–,0?]; $(NH_3)(Cl)$, [–L,–S] [(––),–]; $(NH_3)(Br)$, [–L,–S] [(––),–]; and $(NH_3)(H_2O)$, [–L,–S] [(––),–]. $(NH_3)(CNS)$, which looks like [–] [–,0?], could be a member of the same group, in which the two components are not resolved. Chemical analogy suggests this, but this is not a unique formulation of the CD trace.

In addition to these variations in the peak patterns, all of these complexes should, from symmetry considerations, have three components in each band, whereas, with a few second-band exceptions, reliable indications of only two components can be seen. No obvious harmony can be seen between, for example, signs of the second-band components and particular ligands, but there are some clear hints of chemical relationships. Thus, if the first-peak variations for the $(NH_3)(X)$ group are put in an increasing order of effect (call it sign of S), one could write the X groups in the series NH_3, CN, H_2O, Cl, Br, while the (CN)(X) series, aligned crudely for another effect (relative intensity, or degree of split of

TABLE 1

Circular dichroism spectra of Cobalt(III) complexes

Complex	CD formula	Ref.
$(+)$-$[Co(en)_3]^{3+}$	[L,–S] [+,0]	1–3
$(+)$-$[Co(+pn)_3]^{3+}$	[L–S] [+,0?]	2, 3
$(-)$-$[Co(pn)_3]^{3+}$	[(S?)–L] [+,0]	2, 4, 5
$(+)$-$[Co(-pn)_3]^{3+}$	[L] [–,–]	3, 4
[a]$(+)$-$[Co(+pn)_2(en)]^{3+}$	[L,–S] [*n*–]	3, 4, 6
$(+)$-$[Co(-pn)_2(en)]^{3+}$	[L] [+,+] or [+,+,0?]	3, 4, 6
[a]$(+)$-$[Co(+pn)_2(-pn)]^{3+}$	[L,–S] [*n*+(?)]	3, 6
[a]$(+)$-$[Co(+pn)(en)_2]^{3+}$	[L,–S] [*n*+] or [+,0?]	3, 4, 6
$(+)$-$[Co(-pn)(en)_2]^{3+}$	[L(?)] [+,+] or [+,+,0?]	3, 6
$(-)_D$-$[Co(bgH)_3]^{3+}$	[–,+] [*n*–]	7
$(+)$-*cis*-$[Co(en)_2(NH_3)_2]^{3+}$	[L,–S] [*n*+]	8, 9
$(+)$-*cis*-$[Co(en)_2Cl_2]^{+}$	[–S,L] [+,–]	9
*cis**-$[Co(en)(NH_3)_2{}^*Cl_2{}^*]^{+}$	[–S,L] [(––),+]	10
*cis**-$[Co(-pn)(NH_3)_2{}^*Cl_2{}^*]^{+}$	[–S,L] [(––),+]	10
$(-)$-*cis*-$[Co(en)_2(N_3)_2]^{+}$	[–S,L] [*n*–]	9
cis-$[Co(en)_2(halac)_2]^{+}$	[–S,L] [*n*–]	11
$(+)$-*cis*-$[Co(en)_2(NO_2)_2]^{+}$	[L,–S] [–,+]	9
$(+)$-*cis*-$[Co(en)_2(CN)_2]^{+}$	[L,S] [+,–,0(?)]	9
$(-)_D$-$[Co(en)_2(NH_3)Cl]^{2+}$	[–L,–S] [(––),–]	12
$(-)_D$-$[Co(en)_2(NH_3)Br]^{2+}$	[–L,–S] [(––),–]	12
$(-)_D$-$[Co(en)_2(NH_3)(H_2O)]^{3+}$	[–L,–S] [(––),–]	12
$(-)_D$-$[Co(en)_2(NH_3)(CNS)]^{2+}$	[–L] [–,0(?)]	12
cis-$[Co(en)_2(NH_3)(CN)]^{2+}$	[–L,S] [–,–]	13
cis-$[Co(en)_2(CN)(NO_2)]^{+}$	[L,–S] [+,+]	13
cis-$[Co(en)_2(CN)(OH)]^{+}$	[+,–] [(++),+]	13
cis-$[Co(en)_2(CN)(H_2O)]^{2+}$	[L,–S] [–,+]	13
cis-$[Co(en)_2(CN)I]^{+}$	[+,–] [–,+,–(?)]	13
cis-$[Co(en)_2(CN)Br]^{+}$	[+,–] [+,–,+(?)]	13
cis-$[Co(en)_2(CO_3)]^{+}$	[L(–S?)] [+,–,+]	9
cis-$[Co(en)(NH_3)_2(CO_3)]^{+}$	[L(–S)] [+,–,+]	10
$(-)$-*cis*-$[Co(en)_2(ox)]^{+}$	[–L(S)] [–,+?,–]	3
$(+)$-*cis*-$[Co(-pn)_2(ox)]^{+}$	[L(–S?)] [+,–,+]	9
$(-)$-*cis*-$[Co(-pn)_2(ox)]^{+}$	[–L(S?)] [–,–]	9
$(-)_D$-*cis*-$[Co(en)_2(phen)]^{3+}$	[–] [+]	14
$(-)$-*cis*-$[Co(en)_2(sal)]^{+}$	[–,+,L] [*n*–?]	15
$(-)$-*cis*-$[Co(en)_2(salH)]^{2+}$	[–L] [*n*–?]	15
$(+)_D$-*cis*-$[Co(en)_2(gly)]^{2+}$	[L(–S)] [+,+]	16, 17
$(+)_{546}$-*cis*-$[Co(en)_2(pic)]^{2+}$	[L(–S)] [+,+]	17
$(+)$-*cis*-$[Co(en)_2(sar)]^{2+}$	[L(–S?)] [–,+]	18
$(+)_D$-*cis*-$[Co(en)_2(L\text{-}meth)]^{2+}$	[L,–S] [+,–,+]	17

TABLE 1 - CONTINUED

Complex	CD formula	Ref.
$(-)_{\mathrm{D}}$-*cis*-$[\mathrm{Co(en)_2(L\text{-}meth)}]^{2+}$	[–L(S)] [–,–]	17
$(+)_{\mathrm{D}}$-*cis*-$[\mathrm{Co(en)_2(L\text{-}threo)}]^{2+}$	[L,–S] [+,+]	17
$(-)_{\mathrm{D}}$-*cis*-$[\mathrm{Co(en)_2(L\text{-}threo)}]^{2+}$	[–L(S)] [–,–]	17
$(-)_{546}$-$[\mathrm{Co(en)_2(D\text{-}leuc)}]^{2+}$	[–L,S] [–(+)–]	16
$(-)_{\mathrm{D}}$-$[\mathrm{Co(en)_2(L\text{-}pro)}]^{2+}$	[–L(S)] [–,–]	17
$(+)_{546}$-$(\mathrm{Co(en)_2(L\text{-}Øala)}]^{2+}$	[L,–S] [+(–)+]	16
$(-)_{546}$-$[\mathrm{Co(en)_2(L\text{-}Øala)}]^{2+}$	[–L(S)] [+,+]	16
β-$[\mathrm{Co(gly)_3}]$	[L(–S)] [+,–]	19
α-$[\mathrm{Co(gly)_3}]$	[L(–S)] [(?)*n*–]	19
β-$[\mathrm{Co(L\text{-}ala)_3}]$	[L,–S] [+,–,+]	19, 20
β′-$[\mathrm{Co(L\text{-}ala)_3}]$	[–L,(S)] [–,+,–]	19,20
β′-$[\mathrm{Co(D\text{-}ala)_3}]$	[L(–S)] [+,–,+]	19
α-$[\mathrm{Co(L\text{-}ala)_3}]$	[L,–S] [*n*–]	19–21
α′-$[\mathrm{Co(L\text{-}ala)_3}]$	[–L] [*n*+]	19–21
β-$[\mathrm{Co(L\text{-}leuc)_3}]$	[+,–] [+,–,+]	20
β′-$[\mathrm{Co(L\text{-}leuc)_3}]$	[–L] [–,(++),–]	20
α-$[\mathrm{Co(L\text{-}leuc)_3}]$	[L,–S] [*n*–]	20
α′-$[\mathrm{Co(L\text{-}leuc)_3}]$	[–L] [*n*+]	20
β-$[\mathrm{Co(L\text{-}val)_3}]$	[L,–S] [+,–]	22
β′-$[\mathrm{Co(L\text{-}val)_3}]$	[–L] [–,+]	22
α-$[\mathrm{Co(L\text{-}val)_3}]$	[–,–] [*n*+]	22
α′-$[\mathrm{Co(L\text{-}val)_3}]$	[–,(++),–] [*n*–]	22
β-$[\mathrm{Co(L\text{-}prol)_3}]$	[L,–S] [+,+]	20
	[+,(++),–] [+,+]	23
β′-$[\mathrm{Co(L\text{-}prol)_3)}]$	[–L,S] [–,+,–]	20
α′-$[\mathrm{Co(L\text{-}prol)_3}]$	[–L,–S] [*n*+]	20
β-$[\mathrm{Co(L\text{-}hydroxylprol)_3}]$	[+,(++), –S] [+,+]	23
β-$[\mathrm{Co(L\text{-}asp)_3}]^{3-}$	[L,–S] [+,–,+]	24
β′-$[\mathrm{Co(L\text{-}asp)_3}]^{3-}$	[(S)–L] [–,–,–]	24
α-$[\mathrm{Co(L\text{-}asp)_3}]^{3-}$	[L(–S)] [*n*+]	24
α′-$[\mathrm{Co(L\text{-}asp)_3}]^{3-}$	[–L] [*n*–]	24
α-$[\mathrm{Co(L\text{-}glut)_3}]^{3-}$	[–,+,(––)] [–,–]	21
β-$[\mathrm{Co(L\text{-}glut)_3}]^{3-}$	[L,–S] [*n*–]	21
$(+)_{546}$-*trans (N)*-$[\mathrm{Co(gly)_2(ox)}]^{-}$	[–S,–L] [*n*+]	25
$(+)_{546}$-*trans (N)*-$[\mathrm{Co(L\text{-}ala)_2(ox)}]^{-}$	[–S,–L] [*n*+]	25
$(-)_{546}$-*trans (N)*-$[\mathrm{Co(L\text{-}ala)_2(ox)}]^{-}$	[S,L] [*n*–]	25
$(-)$-$[\mathrm{Co(ox)_3}]^{3-}$	[L,–S] [+,–,+]	26
$(-)_{546}$-$[\mathrm{Co(ox)_2(en)}]^{-}$	[L,S] [+,–,+]	3, 26
$(+)_{546}$-$[\mathrm{Co(ox)_2(en)}]^{-}$	[–L,–S] [–,+,–]	27
$(+)$-$[\mathrm{Co(ox)_2(-pn)}]^{-}$	[L,S] [+,–,+,]	3
$(-)_{546}$-$[\mathrm{Co(mal)_2(en)}]^{-}$	[+,–,+] [+,–,(++)]	27

TABLE 1 – CONTINUED

Complex	CD formula	Ref.
$(-)_{546}$-$[\mathrm{Co(ox)_2(gly)}]^{2-}$	[?+] [+,−,+]	26
$(-)_{546}$-$[\mathrm{Co(ox)_2(aca)}]^{2-}$	[?+] [*n*−] ?[b]	26
$(-)_{546}$-$[\mathrm{Co(ox)(aca)_2}]^{-}$	[?+] [*n*−] ?[b]	26
(−)-cis-$[\mathrm{Co(aa)_2)(NO_2)_2}]^{-}$	[−L(S?)] [+,(−−),..?]	28
$[\mathrm{Co(NH_3)_4(L\text{-}ala)}]^{2+}$	[−,+,(−−)] [*n*−]	29
$[\mathrm{Co(NH_3)_4(D\text{-}ala)}]^{2+}$	[+,−,(++)] [*n*+]	29
	[−S,L] [*n*+]	30
$[\mathrm{Co(NH_3)_4(L\text{-}leuc)}]^{2+}$	[S,−L] [*n*−]	30
$[\mathrm{Co(NH_3)_4(D\text{-}\phi ala)}]^{2+}$	[+,−,(++)] [*n*+]	16
$[\mathrm{Co(NH_3)_4(L\text{-}\phi ala)}]^{2+}$	[−,+,−] [*n*−]	16
$[\mathrm{Co(NH_3)_4(L\text{-}hist)}]^{2+}$	[S,−L] [*n*+]	30
$[\mathrm{Co(NH_3)_4(sarc)}]^{2+}$	[−S,L] [*n*−]	18, 31
cis-$[\mathrm{Co(NH_3)_4(L\text{-}alaH)_2}]^{3+}$	[S,−L] [*n*+]	29, 32
$[\mathrm{Co(NH_3)_5(L\text{-}alaH)}]^{3+}$	very weak[+,−]	29
cis-$[\mathrm{Co(NH_3)_4(H_2O)(L\text{-}alaH)}]^{3+}$	[+,−] [+]	32
cis-$[\mathrm{Co(NH_3)_4(glyH)(L\text{-}alaH)}]^{3+}$	[−,+,(++)] [−]	29
cis-$[\mathrm{Co(NH_3)_4(glyH(L\text{-}alaH)}]^{3+}$	[−,+,(++)] [−]	29
	[L,−S] [*n*+]	32
cis-$[\mathrm{Co(NH_3)_4(\beta\text{-}alaH)(L\text{-}alaH)}]^{3+}$	[L(−S?)] [*n*+]	32
cis-$[\mathrm{Co(NH_3)_4(sarH)(L\text{-}alaH)}]^{3+}$	[L(−S?)] [*n*+]	32
cis-$[\mathrm{Co(NH_3)_4(L\text{-}prolH)_2}]^{3+}$	[L,−S] [*n*+]	32
$[\mathrm{Co(NH_3)_5(L\text{-}\phi alaH)}]^{3+}$	very weak [−]	29
(+)-*trans*-$[\mathrm{Co(l\text{-}pn)_2NH_3)_2}]^{3+}$	[−S,L] [−,0]	3, 33
$[\mathrm{Co(l\text{-}pn)(NH_3)_4}]^{3+}$	[−S,L] [−,0]	33
trans-$[\mathrm{Co(l\text{-}chn)_2(NH_3)_2}]^{3+}$	[−S,L] [−,+,0?]	34
trans-$[\mathrm{Co(l\text{-}pn)_2Cl_2}]^{+}$	[(−S?)L] [*n*−]	33, 36
	or [(−S?)L] [(−−),−]	3, 35
trans-$[\mathrm{Co(l\text{-}pn)(NH_3)_2Cl_2}]^{+}$	[(−S?)L] [*n*−]	33
trans-$[\mathrm{Co(l\text{-}pn)(NH_3)_2{}^{*}Cl_2}]^{+}$	[−L,S] [+,−]	10
trans-$[\mathrm{Co(l\text{-}pn)_2Br_2}]^{+}$	[(−S)L] [*n*−]	33, 36
*trans**-$[\mathrm{Co(l\text{-}pn)(NH_3)_2Br_2{}^{*}}]^{+}$	[(−S)L] [0?]	33
trans-$[\mathrm{Co(l\text{-}pn)_2(NCS)_2}]^{+}$	[L,−S] [−..]	33
trans-$[\mathrm{Co(l\text{-}pn)_2(NO_2)_2}]^{+}$	[−L,S] [−..]	35
trans-$[\mathrm{Co(l\text{-}pn)(NH_3)_2{}^{*}(SO_3)_2}]^{-}$	[L(−S)] [−−−−]	33
trans-$[\mathrm{Co(l\text{-}chn)_2Cl_2}]^{+}$	[(−S?)L] [*n*−]	33, 34
trans-$[\mathrm{Co(l\text{-}chn)_2F_2}]^{+}$	[(−S)L] [*n*−]	34
trans-$[\mathrm{Co(l\text{-}chn)_2Br_2}]^{+}$	[(−S)L] [*n*−?]	34
trans-$[\mathrm{Co(l\text{-}chn)_2(NH_3)Cl}]^{2+}$	[L,−S] [*n*+] or [−,(++)]?	34
trans-$[\mathrm{Co(l\text{-}chn)_2(NO_2)_2}]^{+}$	[−L,S] [*n*+]?	34
trans-$[\mathrm{Co(N_1\text{-}CH_3pn)_2Cl_2}]^{+}$	[L(−S)] [*n*−]	37

TABLE 1 – CONTINUED

Complex	CD formula	Ref.
$(-)_D$-*trans, trans*-$[\mathrm{Co(CH_3en)_2Cl_2}]^+$	[L(+S?)] [+,(−−)]	37
trans-$[\mathrm{Co(\text{-}N.CH_3en)_2Cl_2}]^+$	[−?,+] [*n*−]	12
trans-$[\mathrm{Co(\text{-}N.CH_3en)_2(NO_2)_2}]^+$	[−L,S] [−,+]	12
$(-)_{546}$-$[\mathrm{Co(EDTA)}]^-$	[L,−S] [+,+]	27, 38
$(+)_{546}$-$[\mathrm{Co(EDTA)Cl}]^{2-}$	[S,−L] [+,(−−)]	39
$(-)_{546}$-$[\mathrm{Co(EDTA)Cl}]^{2-}$	[−S,L] [−,(++)]	40
$(+)_{546}$-$[\mathrm{Co(EDTA)Br}]^{2-}$	[(+S?)−L] [+,(−−)]	39
$(-)_{546}$-$[\mathrm{Co(EDTA)(NO_2)}]^{2-}$	[+,−,−] [+,(−−)]	39
$(+)_{546}$-$[\mathrm{Co(EDTA)(NO_2)}]^{2-}$	[−,+,+,] [−,(++)]	40
$(-)_{546}$-$[\mathrm{Co(YOH)Br}]^-$	[+] [−,(++)]	40
$(+)_{546}$-$[\mathrm{Co(YOH)NO_2)}]^-$	[−,+(+)] [−,(++)]	40
$(-)_{546}$-$[\mathrm{Co(MEDTA)Cl}]^-$	[+] [−,(++)]	40
cis-$[\mathrm{Co(IDA)_2}]^-$	[+,−] [(+)(+)]	38
$(-)_{546}$-$[\mathrm{Co(1,3PDTA)}]^-$	[+,−] [(+)(+)]	38
$(-)_{546}$-$(\mathrm{Co(EDTP)}]^-$	[S,−L] [+,(++)]	38
(+)-*trans*-$[\mathrm{Co(EDDA)(CO_3)}]^-$	[L,−S] [*n*+]	41
(also oxalate, malonate, ethylenediamine and L-alaninate)		
trans-$[\mathrm{Co(EDDA)(DMen)}]^+$	[L,−S] [*n*+]	42
trans-$[\mathrm{Co(EDDA)(Men)}]^+$	[L,−S] [*n*+]	42
trans-$[\mathrm{Co(DMEDDA)(en)}]^+$	[+(+?)] [+,(?),(−−)]	42
trans-$[\mathrm{Co(DEEDDA)(en)}]^+$	[L,S] [+,−]	42
trans(N)-$[\mathrm{Co(ata)(L\text{-}ala)}]^-$	[−,+,(−−)] [*n*+]	43, 44
(also serine, valine, proline)		
cis(N)-$[\mathrm{Co(ata)(L\text{-}ala)}]^-$	[−,+] [*n*−]	43
(also serine and valine)		
trans(N)-$[\mathrm{Co(L\text{-}alada)(gly)}]^-$	[L,−S(−?)] [*n*+]	44
trans(N)-$[\mathrm{Co(L\text{-}alada)(L\text{-}ala)}]^-$	[−,+,(−−)] [*n*+]	44
trans(N)-$[\mathrm{Co(D\text{-}alada)(L\text{-}ala)}]^-$	[(−−),+,(−−−)] [*n*+]	44
trans, cis, cis-$[\mathrm{Co(L\text{-}NH_2CH_2\text{-}NH_2CH\text{-}COOH)_2}]^2$	L−1: [+,−,+] [*n*+]	45
	L−2: [L,−S] [−,+]	
	L−3: [−,+] [+,0]	
$(+)_{546}$-*cis,cis,cis*-$[\mathrm{Co(D,L\text{-}diaminopropiato)}]^+$	[−L,S] [*n*+]	45

[a] (+)-Co(+pn)... *and* (−)-Co(−pn)...
[b] Interfering absorption bands.

Symbols used: en = ethylenediamine; pn = propylenediamine; bgH = biguanide; halac = haloacetate; gly = glycine; ala = alanine; leuc = leucine; val = valine; prol = proline. asp = aspartate; ox = oxalate; phen = phenanthroline; sal = salicylate; pic = picrolonate; sar = sarcosinate; meth = methionine; threo = threonine; Øala = phenylalanine; glut = glutamate; mal = malonate; aca = acetylacetone; aa = amino acid; hist = histidine; chn = 1,2-cyclohexyl diamine; EDTA = ethylenediamine tetraacetic acid; YOH = *N*-hydroxyethylethylenediaminetriacetate; MEDTA = *N*-methyl(ethylenediamine)-*N,N'N'*-triacetic acid; 1,3-PDTA = 1,3-propanediamine-*N,N,N',N'*,-tetraacetic acid; IDA = iminodiacetate; EDTP = ethylenediamine-*N,N,N'N'*-tetrapropionic acid; EDDA = ethylene diamine-*N,N'*-diacetic acid; DMEDDA = *N,N'*-

diamine-*N,N,N'N'*-tetrapropionic acid; EDDA = ethylenediamine-*N,N'*-diacetic acid; DMEDDA = *N,N'*-

REFERENCES FOR TABLE 1

1. A.J. McCaffery and S.F. Mason, *Mol. Phys.*, 6 (1963) 359.
2. A.J. McCaffery, S.F. Mason and B.J. Norman, *Chem. Commun.*, (1965) 49.
3. A.J. McCaffery, S.F. Mason, B.J. Norman and A.M. Sargeson, *J. Chem. Soc. A*, (1968) 1304.
4. B.E. Douglas, *Inorg. Chem.*, 4 (1965) 1813.
5. J.R. Golloghy and C.J. Hawkins, *Chem. Commun.* (1968) 689.
6. A.M. Sargeson, in R.L. Carlin (Ed.), *Transition Element Chemistry*, Vol. 3, New York, 1966, pp. 301 ff.
7. K. Michelson, *Acta. Chem. Scand.*, 19 (1965) 1175.
8. A.M. Sargeson and G.H. Searle, *Inorg. Chem.*, 4 (1965) 45.
9. A.J. McCaffery, S.F. Mason and B.J. Norman, *J. Chem. Soc.*, (1965) 5094.
10. C.J. Hawkins, J.A. Niethe and C.L. Wong, *Chem. Commun.* (1968) 427.
11. R.A. Haines and E.B. Kipp, *Can. J. Chem.*, 47 (1969) 949.
12. B.J. Norman, *Inorg. Chim. Acta*, 1 (1967) 177.
13. K. Ohkawa, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Japan*, 40 (1967) 2830.
14. J. Hidaka and B.E. Douglas, *Inorg. Chem.*, 3 (1964) 1180.
15. K. Garbett and R.D. Gillard, *J. Chem. Soc., A*, (1968) 979.
16. C.T. Liu and B.E. Douglas, *Inorg. Chem.*, 3 (1964) 1356.
17. S.K. Hall and B.E. Douglas, *Inorg. Chem.*, 8 (1969) 372.
18. D.A. Buckingham, S.F. Mason, A.M. Sargeson and K.R. Turnbull, *Inorg. Chem.*, 5 (1966) 1649.
19. B.E. Douglas and S. Yamada, *Inorg. Chem.*, 4 (1965) 1561.
20. R.G. Denning and T.S. Piper, *Inorg. Chem.*, 5 (1966) 1056.
21. E. Larsen and S.F. Mason, *J. Chem. Soc., A*, (1966) 313.
22. M. Shibata, H. Nishikawa and Y. Nishida, *Bull. Chem. Soc. Japan*, 39 (1966) 2310.
23. T. Yasui, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Japan*, 38 (1965) 2025.
24. M. Shibata, H. Nishikawa and K. Hosaka, *Bull. Chem. Soc. Japan*, 40 (1967) 236.
25. J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Japan*, 40 (1967) 2312.
26. F.P. Dwyer, I.K. Reid and A.M. Sargeson, *Australian J. Chem.*, 18 (1965) 1919.
27. B.E. Douglas, R.A. Haines and J.G. Brushmiller, *Inorg. Chem.*, 2 (1963) 1194.
28. R.G. Denning, M.B. Celap and D.J. Radanovic, *Inorg. Chim. Acta.*, 2 (1968) 58.
29. J. Fujita, T. Yasui and Y. Shimura, *Bull. Chem. Soc. Japan*, 38 (1965) 654.
30. J.H. Dunlop and R.D. Gillard, *J. Chem. Soc.*, (1964) 2822.
31. S. Larsen, K.J. Watson, A.M. Sargeson and K.R. Turnbull, *Chem. Commun.*,, (1968) 847.
32. T. Yasui, J. Fujita and Y. Shimura, *Bull. Chem. Soc. Japan*, 42 (1969) 2081.
33. C.J. Hawkins, E. Larsen and I. Olsen, *Acta Chem. Scand.*, 19 (1965) 1915.
34. R.S. Treptow, *Inorg. Chem.*, 5 (1966) 1593.
35. R.A.D. Wentworth and T.S. Piper, *Inorg. Chem.*, 4 (1965) 202.
36. I. Haruko, J. Fujita and K. Saito, *Bull. Chem. Soc. Japan*, 42 (1969) 1286.
37. M. Saburi, Y. Tsujito and S. Yoshikawa, *Inorg. Nucl. Chem Letters*, 5 (1969) 203.
38. C.W. Van Saun and B.E. Douglas, *Inorg. Chem.*, 8 (1969) 1145.
39. R.A. Haines and B.E. Douglas, *Inorg. Chem.*, 4 (1965) 452.
40. C.W. Van Saun and B.E. Douglas, *Inorg. Chem.*, 7 (1968) 1393.
41. C.W. Van Saun and B.E. Douglas, *Inorg. Chem.*, 8 (1969) 115.
42. J.I. Legg and B.E. Douglas, *Inorg. Chem.*, 7 (1968) 1452.
43. N. Koine, N. Sakota, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Japan*, 42 (1969) 1583.
44. N. Koine, N. Sakota, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Japan*, 42 (1969) 1799.
45. W.A. Freeman and C.F. Liu, *Inorg. Chem.*, 7 (1968) 764.

L and S) would give I, Br, OH, H_2O, NO_2, NH_3, with some degree of correlation in the ordering in the two series.

One could tentatively bring some of these points together in the following way: the presence, in general, of only two components in the second-band CD for the $[Coen_2AB]$ complexes could be ascribed to a pseudo-C_3 symmetry, based upon the *cis* position of the two ethylenediamine ligands, positioned as they would have been in $[Coen_3]^{3+}$. They would, in general, lack the dihedral symmetry of the D_3 model. The question of the sign of individual CD components would have to be linked to some characteristic of the ligands. The influence of ligands on the apparent level ordering, in the absence of significant symmetry difference, is another item which makes clear the chemical influences.

We are essentially suggesting that the factors of electron distribution in the bonds to the metal ion itself are actually the significant ones, and that the dihedral and helical effect visualized from solid three-dimensional models of ligand metal ion systems (with the implications therein as to effects of the fields of bonds which connect the nuclei in the chelating chain, rather than the bonds to the metal ion) is misleading. Thus, the close resemblance of the $[Coen_3]^{3+}$ CD pattern to that of (+)-$[Co(+pn)_3]^{3+}$ and the various $[Coen_{3-a}(pn)_a]^{3+}$ as well as to $[Coen_2(NH_3)_2]^{3+}$ should be largely ascribable to binding amino nitrogen, while poorly related to the symmetry which ranges from D_3 through C_3 and C_2 to C_1.

D. THE OXALATO COBALT(III) SYSTEMS

Clearer indication of the operation of these factors is seen if one goes to the tris-oxalate, $[Co(ox)_3]^{3-}$, D_3 in symmetry like the $[Coen_3]^{3+}$ complex. The CD pattern is [L,–S] [+,–,+], and by the terms of our hypothesis the difference results from the binding of carboxyl groups in a chelate rather than amino groups. The three CD components would be appropriate to C_2 or C_1 symmetry, rather than the actual D_3 form. One possible *interpretation of this is that when carboxyl is bound in this complex, the symmetry of the* excited state is lower than that of the ground state (e.g., C_2 rather than D_3), whereas when amino groups are bound, the symmetry of the excited state is not less than that of the ground state.

Substitution of one carboxyl by an amino group, as in $(-)_{546}$-$[Co(ox)_2gly]^{2-}$, does not diminish the effect, as the CD pattern is [?,+] [+,–,+]. Even (+)-$[Co(ox)_2en]^-$ and $[Co(ox)_2(-pn)]^-$ both show the CD pattern, [L,S] [+,–,+], with the two dicarboxylic chelating ligands determining the effective symmetry. The phenomenon is not limited to oxalate, since $(-)_{546}$-$[Co(mal)_2en]^-$ has a [+,–,+] [+,–,+] pattern.

As has already been remarked, the β-tris-amino acid complexes with alanine, leucine, aspartic acid, and probably proline, show a [L,–S] [+,–,+] pattern, though the CD of the tris-glycine compound, as reported, is [L(–S)] [+,–] and the CD of the valine complex is [L,–S] [+,–]. This composition, with three carboxyls and three amino groups, therefore seems to be close enough to a changing point to be sensitive to additional weak factors. The α-tris-amino acid complexes, in which one of the groups has been turned around so that the three nitrogens (or the carboxyls) are equatorially arranged, rather than at the corners of one of the trigonal faces, are apparently variable, in that α-$[Co(gly)_3]$ seems to be [L(–S)] [*n*–], the alanine compound, [L,–S] [*n*–], the asparagine compound, [L(–S)] [*n*+], while the tris-valine and tris-proline both are [–L,–S] [*n*+], and the glutamate apparently

[–,+,(––)] [–,–] . The three-component splitting prominent in the second band of the β forms seems definitely lost, though there are suggestions of it in some first bands, and there is considerable variety in correlations between the bands.

With two amino acid groups arranged so that their carboxyl groups are *cis*, and their amino groups *trans*, as in (+)$_{546}$-*trans*-(N)-[Co(gly)$_2$ox]$^-$, the CD formula is [–S,–L] [*n*+] , and that of the corresponding L-alanine compound is the same. Thus, four carboxyls arranged equatorially fail to give the same sort of effect as three carboxyls arranged facially or *cis* to each other. Interestingly, the [L(–S?)] [+,–,+] pattern is given by (+)-*cis*-[Co(–pn)$_2$(ox)]$^+$ and (probably) (+)-[Coen$_2$(ox)]$^+$. Not only does (+)-[Coen$_2$(CO$_3$)]$^+$ show the [L(–S?)] [+,–,+] , but even *cis*-[Coen(NH$_3$)$_2$(CO$_3$)] is [L(–S)] [+,–,+] , though one of the en groups has, in effect, undergone scission. Finally, there is the clear indication that many, if not all, of the [Co(NH$_3$)$_4$ (amino acid)]$^{2+}$ complexes show three components in the first band, as [–,+(––)] [*n*–] for the L-amino acids. In this case the asymmetry structurally depends on the amino acid itself, but in the context of the influence of chemical bonding the source of the asymmetry may be irrelevant.

E. THE *trans*-BIS(DIAMINO)COBALT(III) SYSTEMS

Optical activity of *trans*-bisdiamines depends on optical activity of the diamine, as above, and here we see an interesting continuation of the relations: *Trans*-[Co(1-pn)$_2$(NH$_3$)$_2$]$^{3+}$ and *trans*-[Co(1-chn)$_2$(NH$_3$)$_2$]$^{3+}$ show the related formulae for the CD: [–S,L] [–,0?] and [–S,L] [–,+,0?] . In [Co(1-pn)(NH$_3$)$_4$]$^{3+}$ with only one active group, the CD is still [–S,L] [–,0] . For the *trans*-[Co(1-diam)$_2$X$_2$]$^+$, where diam = pn or chn and X = F, Cl, Br, respectively, the uniform CD response describable as [(–S?)L] [*n*–] is seen, the first-peak CD being rather symmetrical but possibly displaced to higher energy from the absorption peak. Again, scission of a diamine chain, as in *trans*-[Co(1-pn)(NH$_3$)$_2$Cl$_2$*]★ and *trans*-[Co(1-pn)(NH$_3$)$_2$*Br$_2$*] , does not change the CD pattern, whereas *trans*-[Co(-pn)(NH$_3$)$_2$Cl$_2$]$^+$ shows [–L,S] [+,–] . Replacement of the halide in *trans*-[Co(1-pn)$_2$(NCS)$_2$]$^+$ gives [L,–S] [–?] and *trans*-[Co(1-chn)$_2$(NO$_2$)$_2$]$^+$ seems to be [–L,S] [+] . *Trans*-[Co(1-pn)(NH$_3$)$_2$*(SO$_3$)$_2$]$^-$ with [L(–S)] for the first peak differs in sign from its chloro analog, while *trans*-[Co(1-chn)$_2$(NH$_3$)Cl]$^{2+}$ with [L,–S] [+] (or [–,(++)]?) differs from either the bis-ammine or the bis-chloride.

F. SUMMARY AND CONCLUSIONS

Summarizing, we have demonstrated from gross experimental evidence that the qualitative details of the CD patterns that characterize the first two absorption peaks of dissymmetric Co(III) complexes are dependent on the chemical nature of the groups bound, as well as their distribution over the coordination positions. This is true for "physical" or "symmetry" features such as the number of components exhibited in a given peak, as well as for the sign of a given dichroism component. We have cited cases in which replacement of one set of monodentate ligands by another, without change of molecular symmetry group, results in interchange of energy ordering of the apparent L and S components

---

★ Ligands which are *trans* are followed by *.

in the CD of the first absorption peak. Cases can be pointed to in which the two components in fact have the same sign following such a change, rather than the general opposition in sign.

The signs of components in the CD for the second absorption peak may be altered, with alteration of the chemical nature of the ligand. The chemical influences may make the apparent components into which the $T_{2g}(O_h)$ transition is split conform in some cases to expectation for symmetries higher than the actual, and, in others, to lower symmetries. The reaction of the CD to chemical differences, as distinct from purely configurational ones, is not unique to Co(III). Thus, in 1:1 chelate complexes of Ni(II) with L-alanine, and with L-lactic acid, respectively, the difference between amino nitrogen and hydroxylic oxygen results in a difference in sign of CD components [19]. With Co(II), whose spectrum is simpler, the difference is more striking[20]

A reasonable extension of the logic of these correlations leads to criticism of the practice, for Co(III) and related complexes, of assigning the "absolute configuration" of a dissymmetric complex from the sign of the major CD component in the first peak. This, as was pointed out above, is based, in the first instance, on considering the apparent alignment of internuclear σ bonds in the ligand ring to be the determinative factor. Other than that the distribution of the nuclei should somehow determine a vectorial field, it has never been clear how this was supposed to operate. The chemical relations in the data, which we have pointed out, would seem to cast suspicion even on this axiom.

In addition, it is generally assumed that the major CD component in the first band matches the E-representation component derived from the $T_{1g}(O_h)$, and the lesser component corresponds to the A-representation member. A compelling basis for this identification seems lacking. Moreover, as we have pointed out, there are cases where the sign of this component is different between complexes in which monodentate ligands have been changed without altering the chelating ligands which determine the "absolute configuration". There is the further technical point of certain carboxylic acid chelates in which the first peak CD shows the pattern [–,+,(——)], for example. The implication is that the first two components result from the splitting of an E state into two one-dimensional components, which largely cancel each other, leaving the original A_2 component as the most intense. Such a pattern could easily be mistaken for [S,–L] in our standard designation, and any conclusion as to "absolute configuration", whether correct or wrong, comes from false premises as to the data. Even with correct interpretation of the CD, one does not know the sign for the parent E state, nor whether the assumed correlation may be extended to situations in which this is split. This has a bearing on the systems with C_2 and C_1 symmetries, where three components would be expected and only two show. The major one may be an unresolved pair of the same sign; did both members come from the parent E state, or is one the A_2 component of the parent state?

These several considerations seem sufficient to cast a large shadow on the common procedure, and the conclusions drawn from it, unless they are supported by crystallographic structure determinations. There are pitifully few examples in this category. In the meantime, it would seem worthwhile to plan for further investigations bearing elucidation of the chemical relations in mind. There also seems room for real study of the factors which determine the sign of CD components in the spectra of these complexes, and further for defining the bonding relations which determine the apparently differing symmetries of excited states for different transitions in the same spectrum.

REFERENCES

1. A. Cotton, *Ann. Chem. Phys.*, 8 (1896) 347.
2. A. Werner, *Chem. Ber.*, 44 (1911) 1887; *Bull. Soc. Chim.*, 11 (1912) 1.
3. A. Werner, *Chem. Ber.*, 45 (1912) 122.
4. W. Kuhn, *Z. Physik. Chem.*, B4 (1929) 14; W. Kuhn and E. Braun, *Z. Physik. Chem.*, B8 (1930) 281.
5. K. Nakatsu, M. Shiro, Y. Saito and H. Kuroya, *Bull. Chem. Soc. Japan*, 30 (1957) 158.
6. T.S. Piper, *J. Amer. Chem. Soc.*, 83 (1961) 3908.
7. W. Moffit, *J. Chem. Phys.*, 25 (1956) 1189.
8. S.F. Mason, *Quart. Rev.*, 17 (1963) 26.
9. A.J. McCaffery and S.F. Mason, *Mol. Phys.*, 6 (1963) 359.
10. E.J. Corey and J.C. Bailar, Jr., *J. Amer. Chem. Soc.*, 81 (1959) 2620.
11. A.J. McCaffery, S.F. Mason and B.J. Norman, *Chem. Commun.*, (1965) 49.
12. A.M. Sargeson and G.H. Searle, *Inorg. Chem.*, 4 (1965) 45.
13. A.M. Sargeson, in R.L. Carlin (Ed.), *Transition Element Chemistry*, Vol. 3, Dekker, New York, 1966, pp. 301ff.
14. A.J. McCaffery, S.F. Mason, B.J. Norman and A.M. Sargeson, *J. Chem. Soc., A*, (1968) 1304.
15. J.P. Mathieu, *Ann. Phys. Paris*, 19 (1944) 335.
16. Y. Saito, H. Iwasaki and H. Ota, *Bull. Chem. Soc. Japan*, 36 (1963) 1543.
17. B.E. Douglas, *Inorg. Chem.*, 4 (1965) 1813.
18. F.P. Dwyer, I.K. Reid and A.M. Sargeson, *Australian J. Chem.*, 18 (1965) 1919.
19. L.I. Katzin and E. Gulyas, *J. Amer. Chem. Soc.*, 91 (1969) 6490.
20. L.I. Katzin, unpublished.