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Some Applications of the Optical Activity of Coordination Compounds

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The review covers the principal directions in which electronic absorption spectra, rotational dispersion curves, and circular dichroism are at present used in determining the absolute configurations of complex compounds and their structure. A list of 225 references is included.

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I. INTRODUCTION

During recent years the study of the dispersion of optical rotation and the circular dichroism of dissymmetric coordination compounds has become widely recognised as a method for solving spectroscopic and stereochemical problems. The discovery of definite relations between optical activity and various structural features of complex compounds, a more discriminating approach to the observed spectral characteristics (optical rotatory curves and circular dichroism spectra [1,2]), the enhanced sensitivity and extended spectral range of modern spectropolarimeters and dichrographs—all this has created a basis for the successful application of the optical rotatory dispersion and the circular dichroism of coordination compounds in solving various problems both in the chemistry of complex compounds and in organic chemistry.

The present review surveys some of the main directions in which the use of optical rotatory dispersion and circular dichroism has proved especially fruitful—the interpretation of electronic absorption spectra because of the better resolution of bands into individual transitions and further opportunities for their assignment, the determination of the absolute configurations of complex compounds from configurational effects (information which can be obtained by no other method except X-ray diffraction), determination of the absolute configurations of organic compounds from the sign of the rotatory power of $d-d$ transitions of metals in their complexes with the test substances, and the study of complicated natural macromolecules containing a coordinated metal ion.

The abbreviated symbols for ligands, often used in the text, are listed here for the convenience of the reader.

aaH	amino-acid
aba	*o*-aminobenzaldehyde
acacH	pentane-2,4-dione (acetylacetone)
ala	alanine
ala_2en	*NN'*-dialanylethylenediamine
alaglygly	alanylglycylglycine
allothr	allothreonine
asp	aspartic acid
atcH	acetylcamphor
big	biguanidine
bipy	2,2'-bipyridyl
bn	butane-2,3-diamine
2,3-bnpic	*NN'*-bis-(2-methylpyridyl)butane-2,3-diamine
chxn	cyclohexane-*trans*-1,2-diamine
cptn	cyclopentane-1,2-diamine
diam	diamine
dien	diethylenetriamine
1,10-diMetrien	2,5,8,11-tetra-azadodecane
2,9-diMetrien	2,9-dimethyl-1,4,7,10-tetra-azadecane
3,8-diMetrien	3,8-dimethyl-1,4,7,10-tetra-azadecane
5,6-diMetrien	5,6-dimethyl-1,4,7,10-tetra-azadecane
ece	*trans-NN'*-bis-(2-aminoethyl)butane-2,3-diamine [see 5,6-diMetrien]
edda	ethylenediaminediacetic acid
edta	ethylenediaminetetra-acetic acid
edts	ethylenediaminedisuccinic acid
eee	3,6-dithiaoctane-1,8-diamine
$ee(salH)_2$	1,8-bis-salicylideneamino-3,6-dithiaoctane
en	ethylenediamine
epe	4-methyl-3,6-dithiaoctane-1,8-diamine
$epe(salH)_2$	4-methyl-1,8-bis-salicylideneamino-3,6-dithiaoctane
glut	glutamic acid
gly	glycine
glyalagly	glycylalanylglycine
gly_2chxn	*NN'*-diglycylcyclohexane-*trans*-1,2-diamine
glyglyala	glycylglycylalanine
gly_2pn	*NN'*-diglycylpropylenediamine
hmcar	hydroxymethylenecarvone
hmch	hydroxymethylenecamphor
ibn	isobutane-1,2-diamine
leu	leucine
$\alpha\alpha$-Me_2gly	$\alpha\alpha$-dimethylglycine
N-Mepn	*N*-methylpropylenediamine
7-MesalH	*o*-hydroxyacetophenone
meth	methionine
5-Metrien	5-methyl-1,4,7,10-tetra-azadecane
mpkH	2-acetylpyrrole
ox	oxalic acid
pcaH	pyrrole-2-carboxaldehyde
pdta	propylenediaminetetra-acetic acid
penten	pentaethylenehexamine
pep	1,8-dimethyl-3,6-dithiaoctane-1,8-diamine
$pep(salH)_2$	1,8-dimethyl-1,8-bis-salicylideneamino-3,6-dithiaoctane
o-phen	1,10-phenanthroline
phenen	phenylethylenediamine
pn	propylenediamine
prol	proline
ptnta	pentane-2,4-diaminetetra-acetic acid
sal_2pn	*NN'*-disalicylidenepropylenediamine
ser	serine
stien	stilbenediamine
tart	tartaric acid
tdta	trimethylenediaminetetra-acetic acid
2,3,2-tet	1,4,8,11-tetra-azaundecane
$tet(salH)_2$	[1,11-disalicylidene-1,4,8,11-tetra-azaundecane (?)]
threo	threonine
tn	trimethylenediamine
trien	triethylenetetramine
val	valine

II. ELECTRONIC SPECTROSCOPY AND SPECTROPOLARIMETRY

Spectropolarimetry and ordinary electronic spectroscopy are complementary and undoubtedly mutually useful methods of solving structural and spectroscopic problems. Both consist essentially in recording electron transitions occurring in a symmetrical or an unsymmetrical environment. Their main advantage is the appearance of a new parameter—the sign of the optical rotation—in addition to the usual characteristics of an absorption band (extinction coefficient ϵ, frequency ν of maximum, and band half-width $\delta_{1/2}$). The complicated sigmoid character of individual inverse curves of optical rotatory dispersion corresponding to an individual transition often complicates interpretation of the curves observed when several such inverse curves are superposed.

Two bands of opposite sign can be distinguished in the circular dichroism spectra even if their separation does not exceed 100 cm^{-1}. In such a situation the absorption spectrum will give only a single overall band, which the usual methods—graphical and mathematical—are generally almost completely unable to resolve [3]. The use of circular dichroism spectra should be especially helpful in such cases, since the sum of the rotatory powers of bands obtained from almost degenerate transitions in related complexes of higher symmetry is zero [4].

Furthermore, certain differences in the selection rules for optically active and inactive absorption bands provide extremely valuable information for the assignment of bands in the absorption spectrum on the basis of an analysis of the intensities of the corresponding dichroic components. The rotatory power of an electronic transition is defined as the real part of the pseudoscalar product of the electrical and magnetic moments of the transition. The presence of the former is due to the transfer of charge (dipole moment), and of the latter to its rotation (magnetic dipole moment). And since by definition the transition is optically active only when the two moments act collinearly, this corresponds to a helical displacement of charge. Movement along a right-hand helix is associated with positive circular dichroism, and along a left-hand helix with negative circular dichroism [5].

As a consequence of this, transitions whose electrical and magnetic moments are mutually perpendicular cannot be optically active. Transitions that are magnetic-dipole-forbidden give a Cotton effect of insignificant amplitude [6]. On the other hand, d–d transitions of slight or moderate intensity (in the absorption spectrum) in dissymmetric metal complexes show strong dichroism, provided that these electronic transitions are magnetic-dipole-allowed in the given microsymmetry group [7]. Hence the character of the transition in an optically active molecule can be deduced from the value of the g-factor†, which usually exceeds 0.01 for magnetic-dipole-allowed transitions, and is smaller than this value for electric-dipole-allowed transitions [8]. For example, the anisotropy factors for the two transitions of Cr^{3+} in O_h symmetry, $^4T_{2g} \leftarrow {}^4A_{2g}$ and $^4T_{1g} \leftarrow {}^4A_{2g}$, are respectively 0.013 and 0.0008, in conformity with their magnetic-dipole-allowed and -forbidden character [9].

Another criterion which may be useful for assigning bands in the absorption spectrum to definite electron transitions is the specific effect of polarisable anions (phosphate, selenite, and certain others) on the circular dichroism spectra of complex cations. In the case of trisdiamine complexes (symmetry D_3), for example, the effect is evident in an increase in intensity of the A_2 dichroic component at the expense of a decrease in the E_g component, while the absorption spectrum in the region of the $^1T_{1g}$ band remains almost unchanged [10].

Thus important information on the number and nature of the components of an absorption band covering several closely located transitions can be obtained by determining and analysing the optical rotatory dispersion curves and especially the circular dichroism spectra.

On the other hand, progress in the electronic spectroscopy of certain metals, especially those free from d^3 spin (Cr^{3+}) and those with d^6 spin pairing (Co^{3+}, Rh^{3+}, Pt^{4+}), has enabled several empirical relations to be derived between the type of a transition and the sign of its rotatory power. These have subsequently been widely used for investigating the configuration of complexes, the conformation of the chelate ring in them, the configuration of asymmetric carbon atoms in a ligand, and several other stereochemical features of coordination compounds.

It has been established, for example, that all trichelate complexes of Co^{3+} having the absolute configuration $S(C_3)R(C_2)$ are characterised by a $^1E_a \leftarrow {}^1A_1$ transition of positive rotatory power [11]. This relation has since proved useful both for determining the absolute configuration of related complexes from the sign of the circular dichroism of this transition and for assigning a band to a definite transition on the basis of the sign of its circular dichroism with a known absolute configuration [12]. Qualitative similarity of the circular dichroism spectra in a certain spectral region for two complexes having the same absolute configuration can often be a basis for accepting that the energy levels of the d-orbitals of the complexing metals are arranged in the same sequence. Such comparison has been made [13] for the tri-α-alaninates of Co^{3+} and Rh^{3+}.

This type of interrelationship between electronic spectroscopy and spectropolarimetry makes a parallel study of all three types of spectra—absorption spectra, rotatory dispersion, and circular dichroism—especially fruitful. We shall examine several examples of spectroscopic results obtained by the use of optical rotatory dispersion and circular dichroism for various types of complexes of several transition metals.

1. Metals with d^3 and d^6 Electronic Configurations

Trisbidentate complexes $[M(AA)_3]^{n+}$

When six ammonia molecules in the coordination sphere of Co^{3+} are replaced by three ethylenediamine molecules, the d-levels of the metal are split in D_3 symmetry with the appearance of two dichroic components of opposite signs in the region of absorption band I of Co^{3+} ($^1A_{1g} \rightarrow {}^1T_{1g}$, a magnetic-dipole-allowed transition), corresponding to ^1E and $^1A_2$ transitions. Of the two components into which band II is split ($^1A_{1g} \rightarrow {}^1T_{2g}$), corresponding to ^1E and $^1A_1$ states, only the first transition is optically active. This resolution is insufficiently large to affect the absorption spectrum, which consists of two bands as before [14].

† The g-factor—or anisotropy factor—is defined as follows:

$$g = \frac{\epsilon_l - \epsilon_r}{\varepsilon},$$

where ϵ_l and ϵ_r represent absorption of the left-hand and the right-hand circularly polarised rays.

The corresponding trichelate complexes of Co^{3+} and Cr^{3+} with biguanidine (an optically inactive ligand, which on coordination forms planar rings containing the metal) are distinguished from the diamine chelates by a considerably greater intensity of the $d-d$ bands in the absorption and circular dichroism spectra, but the qualitative pattern of splitting is preserved in the latter spectrum. The chromium(III) complexes exhibit ^4E and $^4A_2$ components in the long-wavelength range, and only a ^4E component in the short-wavelength range [15].

The unsymmetrical character of amino-acids leads, on their coordination with metals, to the formation of two geometrical isomers of complexes of type $[M(AB)_3]$—1,2,3 (β) and 1,2,6 (α)—which differ in symmetry and can be identified spectroscopically. In fact the β-isomer is characterised by one Cotton effect in the region of absorption band II of Co^{3+}, whereas the less symmetrical α-isomer has three Cotton effects in the same region [11].

trans-Bisbidentate complexes $[MX_2(AA)_2]$

In these complexes the octahedral triplet states $^1T_{1g}$ and $^1T_{2g}$ are split into $^1A_{2g} + {}^1E_a$ and $^1B_2 + {}^1E_b$ components respectively [16]. The fact that band I is magnetic-dipole-allowed is responsible for the high rotatory power (of opposite signs) of the first two transitions in the complexes with diamines, in contrast to band II, where smaller circular dichroism is observed only for the E_b component [8]. Splitting of this type is exhibited also by the spectra of such complexes in polarised light [17].

The circular dichroism spectra of optically active bis- and tris-β-diketone complexes also consist of two components of opposite sign [18] in the region of band I (the dominant peak at a higher energy) and a broad maximum within the octahedral absorption band II of Co^{3+}.

Splitting of band I of Co^{3+} in the circular dichroism spectrum into two components is observed, also with *trans*-(*N*)-bis-amino-acid complexes having a *trans*-$[MO_4N_2]$ chelate unit, in conformity with the same microsymmetry (D_{4h}). However, splitting of this band into three components, corresponding to the true C_{2v} symmetry of such complexes, could be observed only in the circular dichroism curves of the vicinal effect for the ions $[MX_2(AB)_2]$, e.g. with AB = *L*-ala. [19]

cis-Bisbidentate complexes *cis*-$[MX_2(AA)_2]$

When AA = diam, four dichroic components are now observed in the region of the two $d-d$ bands in the absorption spectrum. Each absorption band corresponds to two dichroic maxima if X_2 represents unidentate ligands; when the latter are replaced by a single bidentate [and conjugated] ligand, one and three maxima in the circular dichroism spectrum are associated respectively with the long-wavelength and with the short-wavelength unpolarised absorption bands [20].

Similar complexes having configurational asymmetry with AA = acac [$X_2 = (NH_3)_2$ or en] exhibit a smaller separation in the circular dichroism spectrum—two components of opposite sign $A_1 \rightarrow B_1$ and $A_1 \rightarrow B_2 + A_2$ (dominant at higher energies) near absorption band I of CO^{3+} and a third component in the region of absorption band II. We note for comparison that $d-d$ transitions are represented in the absorption spectrum by one maximum in band I, while band II is represented by a shoulder on a neighbouring, more intense charge-transfer band [18].

Monobidentate complexes

The microsymmetry of these complexes, e.g. $[Co(L\text{-aa})(NH_3)_4]$, is D_{4h}. Resolution of the experimental optical rotatory dispersion curves into inverse curves corresponding to individual optically active transitions [8] showed the presence of two Cotton effects for band I and one in the region of band II. The g-factor of 0.002 for this last transition is consistent with an electric-dipole-forbidden transition [21]. Splitting of the octahedral $^1T_{1g}$ level into three singlet ^1A levels, corresponding to the actual symmetry C_1, could be observed in the circular dichroism spectrum of the monochelate complex with aa = leu (all components magnetic-dipole-allowed and therefore optically active). [22]

[Complexes with unidentate amino-acids]

In conformity with theory the circular dichroism spectra of such complexes as $[Co(L\text{-aaH})_2en_2]^{3+}$ and $[Co(L\text{-aa})(NH_3)_5]^{2+}$, which have D_{4h} and C_{2v} symmetry, show the resolution of Co^{3+} absorption band I into two components of opposite sign [22]. Under certain conditions the degeneracy of the E_g transition is also removed when the circular dichroism spectra of complexes of the latter type are determined, the two resolved components having opposite signs [23].

[Multidentate complexes]

It has never proved possible to observe splitting of the octahedral $^1T_{1g}$ level in the absorption spectra of the Co^{3+} complex with the multidentate ligand propylenediaminetetra-acetic acid, although theory predicts three components in the region of band I for the symmetry C_{2v} characteristic of this complex. The circular dichroism spectra exhibit two resolved components in conformity with the formal symmetry D_{4h} of this chelate unit $[MX_4Y_2]$. [3]

2. Metals with a d^7 Electronic Configuration

Interesting results have been obtained in the study of the absorption spectra and circular dichroism in the visible and near infrared of several square planar complexes of cobalt(II) with quadridentate Schiff bases of general formula (7-X-sal)$_2$(−)-pn, having the chelate unit $[MN_2O_2]$ and symmetry C_{2v}. Three of the ten spin-allowed $d-d$ bands of the metal should occur in the infrared, but they are represented by a single band in the absorption spectrum owing to the nearness of the $d_{xz,yz}$ and d_{z^2} orbitals. Determination of the circular dichroism spectra in the near infrared enabled all three components associated with the $(d_{xz} \pm d_{yz}), d_{z^2} \rightarrow d_{xy}$ transition to be observed [24]. In the visible range $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions could be identified only from the circular dichroism spectra, since interpretation of the absorption spectrum in this range is greatly impeded by the superposition of intense charge-transfer bands. The assignment of the bands led to the following proposed [24] scheme for the arrangement of a-orbitals in the cobalt(II) complexes investigated

$$d_{z^2} < \frac{1}{\sqrt{2}}(d_{xz} - d_{yz}) < \frac{1}{\sqrt{2}}(d_{xz} + d_{yz}) < d_{xy} < d_{x^2-y^2}.$$

3. Metals with a d^8 Electronic Configuration

(*a*) Octahedral coordination

In an octahedral field Ni^{2+} has three spin-allowed $d-d$ transitions. Measurement of the circular dichroism spectrum of the $[Ni(l\text{-chxn})_3]^{2+}$ ion in the range 300–1200 nm showed optical activity in all three bands, which, in view of their strong, moderate, and weak rotatory power, were assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions [25]. The first transition in the similar complex ion $[Ni(l\text{-pn})_3]^{2+}$ has $g = 0.23$, whereas for the other two transitions $g < 0.01$.[26] The complete absence of optical activity in the $d-d$ transitions in the nickel(II) complex of tribenzo[*bfj*]-1,5,9-triazacycloduodecine—a macrocyclic Schiff base—with appreciable rotatory power of the charge-transfer bands is rather unexpected [27].

(*b*) Square planar coordination

The nearness of the three possible $d-d$ transitions of square planar complexes of d^8 metals and their strong overlapping with charge-transfer bands create considerable difficulties in the interpretation of their absorption spectra. A further complication is the dependence of the energy levels of the d-orbital on the degree of tetragonal distortion of the chelate unit and on the strength of π-bonding of the metal with the ligand. This has resulted in several different arrangements of d-levels for square planar complexes of D_{4h} symmetry (Fig. 1).[28] Of the four possible $d-d$ transitions in scheme (III) (Fig. 1)—$d_{xy} \rightarrow d_{x^2-y^2}(A_{2g})$, $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}(E_g)$, and $d_{z^2} \rightarrow d_{x^2-y^2}(B_{1g})$—only the first two have magnetic moments, and in the A_{2g} transition the electrical and magnetic moments are mutually perpendicular. Hence only the transition to the E_g state should be optically active.

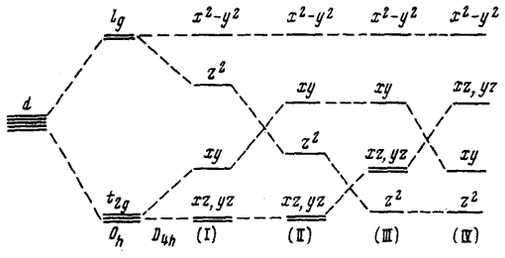


Figure 1. Possible types of splitting of the α-levels in square planar complexes of symmetry D_{4h}.

Scheme (III) is evidently supported [6,28] by the presence of two positive dichroic components in the $d-d$ region with several complexes of types $[M(diam)_2]^{2+}$ and $[MCl_2diam]$, where diam = l-pn, l-chxn and M = Pd^{2+}, Pt^{2+}, Au^{3+}. However, a study of the circular dichroism of the $[Ni(l\text{-pn})_3]^{2+}$ ion, which exists in certain solvents as a yellow (planar, diamagnetic) form, showed the existence of three dichroic $d-d$ bands, two of which had $g \geqslant 0.01$, which was interpreted as supporting scheme (IV).[26] A similar result was obtained from a study of the optical rotatory dispersion and the circular dichroism of dichelate complexes of Ni^{2+} and Pd^{2+} with amides of amino-acids, which also exhibited considerably greater splitting of the band in the circular dichroism spectra than in the absorption spectra [29]. The 1 : 1 and 1 : 2 complexes of Ni^{2+} with the amino-acids themselves have also been examined spectropolarimetrically [30].

The circular dichroism spectra of square planar complexes of Ni^{2+} and Pd^{2+} [31,32] with deprotonated tri- and tetra-peptides each contain two maxima in the $d-d$ range, which have been assigned, on the basis of their position and intensity, to $A_{1g} \rightarrow A_{2g}$ and $A_{1g} \rightarrow E_g$ transitions, in conformity with scheme (II) (Fig.1).

The pattern changes substantially on passing to complexes of nickel(II) with cysteine and its ester. The latter complex has three components in the absorption and circular dichroism spectra, the middle one of which is split into peaks of opposite sign in the complex of the cysteinate ion. Since only E_g among the three possible $d-d$ transitions is degenerate, this type of splitting of the bands indicates the sequence $A_{2g} < E_g < B_{1g}$ for the three transitions: i.e. the order of the a levels in complexes having the chelate unit $[MN_2S_2]$ differs significantly from their sequence in systems with an $[MN_4]$ chelate unit [31].

Complexes of nickel(II) with quadridentate Schiff bases [33,34], such as (sal)$_2$(−)-pn and its analogues produced by varying both the diamine component [RR(−)-chxn] and the aldehyde component (7-Mesal, acac, aba, pca, mpk), [35] exhibit an especially marked contrast between the circular dichroism and absorption spectra. The former displays up to three components in a range where the absorption spectrum contains only a shoulder on an intense charge-transfer band. As was to be expected, the increase in symmetry on passing to complexes with an $[MN_4]$ chelate unit, e.g. with (aba)$_2$(−)-pn as ligand, leaves only one transition in the circular dichroism spectrum, which does not appear at all in the absorption spectrum [35].

A new method of interpreting the absorption spectra of optically inactive complex compounds, based on a study of the circular dichroism induced in the $d-d$ transitions of the metal by optically active solvents, should prove extremely useful. Thus measurement of the circular dichroism spectra of the ions $[PtCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ in d(−)-butane-2,3-diol and d(−)-propane-1,2-diol respectively has confirmed scheme (I) for the arrangement of the d-levels of these metals [7,36].

4. Metals with d^1 and d^9 Electronic Configurations

Depending on the symmetry of the environment, Cu^{2+} ions may give up to four transitions in the $d-d$ range, whereas the absorption spectrum usually contains one or at best two individual bands. Even in the spectra of single crystals of $[Cu(L\text{-aa})_2]$ in polarised light only two transitions could be observed—$^2A \rightarrow {}^2A$ and $^2A \rightarrow {}^2B$.[37]

The circular dichroism spectra of 1 : 2 complexes of Cu^{2+} with amino-acids revealed all four components of magnetic-dipole-allowed $d-d$ transitions, in conformity with the predictions of theory for C_{2h} symmetry (*trans*-$[MN_2O_2]$ chelate unit). The signs of these dichroic bands for amino-acids of the L-configuration are +, +, −, − in the hypsochromic direction [38]. Complexes with D- and L-alanine, L-serine, L-valine, L-threonine, L-allo-threonine, L-proline, etc. have been investigated [39]. The circular dichroism spectra of 1 : 2 complexes of Cu^{2+} with

(+)-pseudoephedrine and (+)-2-aminopropanol each contain two dichroic components of opposite sign in each of the two bands in the absorption spectrum [40].

The circular dichroism spectra of complexes containing a *cis*-$[MN_2O_2]$ chelate unit—including chelates of Cu^{2+} with quadridentate Schiff bases from optically active diamines, e.g. R(−)-pn and RR(−)-chxn—contain three bands (symmetry of complexes C_2) all representing electric and magnetic-dipole-allowed transitions, and hence quite intense. These bands were assigned to $d_{z^2} \rightarrow d_{xy}$, $d_{x^2-y^2} \rightarrow d_{xy}$, and $d_{xz} \rightarrow d_{xy}$ transitions on the basis of a study of the effect of solvents coordinated along the z-axis of the complex on the circular dichroism spectra (the effect is largest with the $d_{z^2} \rightarrow d_{xy}$ transition) and an analysis of the relative sensitivity of these bands to the increasing degree of tetragonal distortion of the chelate unit when the azomethine hydrogen of the ligand is replaced by alkyl (the effect is greatest for the $d_{x^2-y^2} \rightarrow d_{xy}$ transition owing to the breakdown of π-bonding). The assignment of the bands led to the following proposed [41] sequence of the Cu^{2+} orbitals

$$d_{xy} \gg d_{x^2-y^2} > d_{z^2} > d_{xz}.$$

Observation of the individual components in the $d-d$ region has also permitted a more definite arrangement of all the ligands investigated [Schiff bases of various aldehydes with (−)-pn] with increase in the field that they produce [41].

Thus in these cases the circular dichroism spectra have proved extraordinarily useful not only as a method of observing individual $d-d$ transitions but also for studying the slightest distortions of planar complexes, information on which cannot be obtained in any other way [41].

The molecular orbital model predicts for oxovanadium-(IV) complexes the scheme of levels $^2B_2 < {}^2E < {}^2B_1 < {}^2A_1$, where the ^2E state may be resolved if the symmetry diminishes. The circular dichroism spectra of vanadyl-(IV) *d*-tartrato- and *l*-lactato-complexes show that this splitting into two components of opposite sign is sufficiently large only in the 1 : 2 complexes. In the region of one broad band in the absorption spectrum the circular dichroism spectrum reveals three electronic transitions, two of which ($^2B_2 \rightarrow {}^2E$ and $^2B_2 \rightarrow {}^2B_1$) are magnetic-dipole-allowed, while $^2B_2 \rightarrow {}^2A_1$ is not so allowed [42].

5. Metals with d^0 and d^{10} Electronic Configurations

The optical activity of complexes of zinc and isoelectronic metals is concentrated in the ultraviolet and is due only to internal transitions in the ligand and perhaps to a charge-transfer band. In zinc complexes of amino-acids, for example, an $n \rightarrow \pi^*$ transition of the acyl portion of the ligand is the first at long wavelengths [43]. However, valuable information on the structure of a complex can be extracted from the optical activity even of intraligand transitions. Thus the splitting of the $\pi \rightarrow \pi^*$ transition of the azomethine chromophore in the complex $[Zn(sal)_2(-)$-pn] into two components of opposite sign in the circular dichroism spectrum has been attributed, in conformity with the postulates of exciton theory, to a tetrahedral structure of the complex compound [33,34].

6. Metals with an f^n Electronic Configuration

The spectral behaviour of rare-earth metal complexes is especially complicated. The absorption spectra of lanthanide(III) ions in the visible and ultraviolet ranges are due to transitions of electrons from the ground j-level to the following j-levels in the f^n configuration ($n = 2-12$). Splitting of the j-levels of the free ion into the Stark components, which is usually too small to appear in the absorption spectra, is observed excellently in the circular dichroism spectra. The contrast between the resolving power of these two types of spectra is especially marked here. For example, the absorption spectrum of the 1 : 1 praseodymium(III)–tartrate complex contains three bands in the range 430–510 nm, whereas 21 components are observed in the same wavelength range of the circular dichroism spectrum [45]. Spectra of the latter type contain several sharp extrema near each band in the former with all the spectropolarimetrically investigated complexes of amino-acids with neodymium(III) [46] and praseodymium-(III), [47] hydroxy-acids with praseodymium(III), [45] and *l*-propylenediaminetetra-acetic acid with praseodymium-(III), neodymium(III), samarium(III), dysprosium(III), and erbium(III). [4]

The absorption spectra of rare-earth metal ions usually vary little with the chemical environment, in comparison with 3*d*-transition metal complexes. The only exceptions are a few transitions, which have been termed hypersensitive [48]. Study of the circular dichroism spectra of optically active rare-earth metal complexes has significantly expanded the number of such hypersensitive bands, which have been called c.d.-sensitive, in contrast to most other components of the circular dichroism spectrum, whose intensity is proportional to that of the corresponding band in the absorption spectrum. These latter dichroic maxima usually have g-factors of $10^{-5}-10^{-6}$, whereas this quantity increases tenfold for the c.d.-hypersensitive bands, to the order of $10^{-4}-10^{-3}$. [49]

The increase in the number of bands responsive to a change in the structure of the complex, on passing from the absorption to the circular dichroism spectrum, undoubtedly enhances the value of applying spectropolarimetry to structural investigations. For example, the conversion of unidentate ligands (amino-acids, gluconic and galactonic acids) in the coordination sphere of the europium(III) ion into chelated ligands, with increase in the pH, produces a considerable increase in intensity and reversal of sign in the dichroic band corresponding to the $^5D_1$ transition, while the absorption spectrum remains almost unchanged. The substantial differences both in intensity and in the character of the splitting of circular dichroism spectra may be due to finer structural differences in related ligands, such as e.g. alanine and serine, gluconic and galactonic acids [48].

The above values for anisotropy factors demonstrate the far smaller rotatory power of $f-f$ than of $d-d$ transitions. The weakening of the asymmetrising effect is probably due to the effective screening of f-electrons in the deeper atomic orbitals. The superposition of such weak Cotton effects due to $f-f$ transitions on the more intense Cotton effects centred in the short-wavelength region leads merely to a smooth resultant curve when the dispersion of optical rotation is measured, as has been observed e.g. with the lanthanide complexes of (−)-propylenediaminetetra-acetic acid. Because of such sharply diminished resolution of individual bands in the dispersion of optical rotation, this method is evidently far less useful for spectroscopic purposes. An interesting regularity in this case is the smooth increase in the molecular rotation at any point on such smoothed curves as a function of the ionic radius of the metal—from −275° to +210° for $[M]_D^{20}$ on passing from Yb^{3+} to La^{3+}. [50]

Thus the application of circular dichroism spectra to the investigation of rare-earth metal complexes is especially useful because of their higher resolving power compared with the absorption spectra and the presence of c.d.-hypersensitive (to fine structural features) bands.

III. DETERMINATION OF THE ABSOLUTE CONFIGURATION OF COORDINATION COMPOUNDS

It is important to determine the absolute configuration of optically active complex compounds not only for the sake of pure knowledge but also for spectroscopic purposes. As already remarked, bands observed in the absorption spectrum can be assigned to definite transitions on the basis of the sign and magnitude of the rotatory power of the latter, provided that the chirality of the environment of the metal ion is known.

Existing indirect methods for determining the absolute configuration of dissymmetric metal complexes usually involve measuring the circular dichroism and the optical rotatory dispersion and are of three types—(*a*) non-empirical methods based on the postulates of exciton theory, (*b*) semi-empirical methods, which include all kinds of octant rules, and (*c*) empirical methods, in which certain properties of the test substance (mostly the character of the dispersion of optical rotation or the circular dichroism in a certain range) are compared with those of a standard compound whose absolute configuration is known from X-ray examination.

As in organic chemistry, X-ray examination is undoubtedly the most direct and convincing. The sharp increase in the number of X-ray structural studies on optically active coordination compounds during recent years provides a firm foundation for further correlations among related compounds by means of the dispersion of optical rotation and circular dichroism [51].

1. Nomenclature

A quite varied notation has been used for absolute configurations in the literature. Opposite (left and right) chiralities in tri- and *cis*-di-chelate compounds are denoted as *D* and *L*, *M* and *P*,[52] Λ and Δ, $S(C_3)R(C_2)$ and $R(C_3)S(C_2)$, and are represented by the stereochemistry respectively of a left-handed and right-handed three-bladed propeller on clockwise rotation about the C_3 axis, and of right-handed and left-handed on rotation about the C_2 axis. The symbols Δ and Λ are used also to denote the absolute configurations of tetrahedral complexes of bivalent metals [34].

Preliminary proposals have recently been published for the nomenclature of conformations and configurations of octahedral six-coordinate complexes of various types, based on the representation of helical systems by two non-orthogonal skew lines [53].

2. Non-empirical Methods

The absolute configuration of a complex compound can be determined by quantum-mechanical calculation of the signs of the circular dichroism to be expected in the region of internal transitions of the ligands [54], especially those having their own system of π-bonds, such as 1,10-phenanthroline and 2,2′-bipyridyl [54]. This line of attack is especially important for complexes of metals having a d^0- or d^{10}-electron shell, to which the usual correlations based on the signs of the rotatory powers of *d*–*d* transitions are inapplicable [55].

The first successes in this field [56,57] have since been greatly extended by Bosnich [58,59] and several other workers [60–62]. The use of the exciton theory of optical activity to determine the absolute configuration of a complex ultimately requires knowledge merely of the direction of polarisation of a certain electron transition in the ligand and the approximate geometry of the complex. The method is based on analysis of the type of exciton splitting of one of the ligand transitions (most frequently $\pi \rightarrow \pi^*$) in the circular dichroism spectrum into two equal and opposite components. With a Λ absolute configuration about the central metal atom in tetragonal complexes, for example, the negative component of such a doublet should occur at a higher energy, but conversely with the Δ configuration [33]. In fact, with copper(II) complexes of quadridentate Schiff bases from RR(−)-chxn, which preserves stereospecifically the Δ configuration at the central metal ion, positive and negative resolved components of the azomethine $\pi \rightarrow \pi^*$ transition are observed at higher and lower energies respectively [41].

There are certain indispensable conditions for the exciton splitting of a transition: firstly, two or more chelate rings having π-electron systems must be present; secondly, the two chromophores of two ligand molecules in the complex must be non-coplanar (thus analysis of the optical activity of complex compounds in the ultraviolet yields the most valuable information on the smallest departures from planarity in the chelate unit); and thirdly, the transition should have approximately the same energy and intensity whether the ligand is free or coordinated [18]. A further condition for the successful application of this method is absence of overlapping between the components of the exciton splitting and adjacent bands, e.g. a charge-transfer band.

The predictions of the exciton theory have been confirmed by chemical methods [63] in a series of complexes related to $[Co\,phen_3]^{3+}$ and $[Co\,bipy_3]^{3+}$. Determination of the absolute configurations of complexes by means of the criteria of the exciton theory is undoubtedly a promising method [64,65].

3. Octant Rules

Various octant rules are widely applied in organic chemistry to determine the absolute configurations of cyclic carbonyl compounds from the sign of the Cotton effect for the $n \rightarrow \pi^*$ transition in the carbonyl group [66].

In coordination chemistry the situation is greatly complicated by the practical impossibility of finding any isolated non-degenerate transition common to all complexes of various metals with different types of ligands. Nevertheless, such regular relations between the signs of the Cotton effect and of the octant (and hence the configuration) have been established for *d*–*d* transitions chosen in a certain fashion.

The sign of each octant is given by the product of its coordinates; the octant sign of the complex is obtained by adding those of its component chelate rings, where the sign of each atom should correspond to that of the octant in which it is situated. The main rules for arranging complexes in a right-hand coordinate system were worked out by Hawkins and Larsen [67], who showed their applicability not only to diamine chelates but also to other complexes containing bi- and multi-dentate ligands [68,69]. This

last is especially important, because establishing the absolute configurations of complexes containing multidentate ligands by comparing their circular dichroism and optical rotatory dispersion with those of complexes of bidentate ligands does not always yield the correct results [70].

The following general empirical octant rule has been suggested for cobalt(III) complexes from an analysis of well known published data: if a cobalt(III) complex of symmetry D_3, D_2, C_2^a, and C_2^b‡ has a ^1E, $^1B_1$, ^1A, or ^1B transition respectively with a negative Cotton effect, it possesses an absolute configuration corresponding to a negative octant sign [71]. Similar rules can probably be deduced for complexes of other metals.

This general octant rule was found to apply also to several square planar complexes of copper(II) with such ligands as gly$_2$(−)-pn, gly$_2$(−)-chxn, and (+)-ala$_2$en. [72] On passing to complexes of copper(II), nickel(II), and palladium(II) with deprotonated tri- and tetra-peptides, however, their optical activity can no longer be explained in terms of a simple octant rule, since substituents attached to an α-carbon atom are situated in octants of opposite sign with the same absolute configurations of the amino-acid residues. A so called double octant or hexadecadic rule was therefore suggested, according to which the complex is placed in a coordinate system with sixteen sectors alternating in sign. The example in Fig. 2 shows that all methyl groups of the three L-alanine fragments are located in negative octants, which correlates well with the negative total Cotton effect of the $d-d$ transitions of this complex [73].

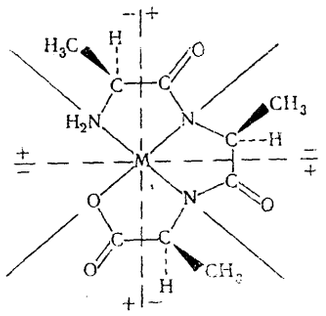


Figure 2. Distribution of charges in square planar complexes according to the octant rule.

Both the identity of sign of the dichroic bands for a series of tripeptides in which the position of an optically active amino-acid residue varies (e.g. alaglygly, glyalagly, glyglyala) and the additivity of the contributions made by asymmetric carbon atoms in different positions in an oligopeptide ligand in its 1 : 1 complex with nickel(II) [31] and palladium(II) [32] are excellently explained on the basis of the hexadecadic rule. Certain departures from additivity in the presence of an amino-acid residue with a bulky side-chain in the N-terminal position are explained by the appearance of a conformational contribution, opposite in sign to the vicinal contribution [31].

The octant rules for the $n \rightarrow \pi^*$ transition of the carbonyl chromophore, worked out by Moffitt for organic compounds, have been used equally successfully in coordination chemistry [74]. Thus a study of copper(II) complexes with L-cysteine and L-histidine showed that the Cotton effect of the $n \rightarrow \pi^*$ transition (~220 nm), which is positive in the copper(II) complex with the methyl ester of cysteine, becomes strongly negative in the complex with the free amino-acid. The opposite octant signs of the two complexes result from a change in conformation: chelation involving the carboxyl stabilises a conformation which is impossible for the ester [75,76].

Thus the employment of octant rules in interpreting optical rotatory dispersion and circular dichroism yields valuable information both on the absolute configuration of a complex and on its conformational features.

4. Empirical Methods

Several empirical methods can be distinguished depending on the way in which the relatedness of configurations of two complexes is established.

(*a*) Spectroscopic methods

The absolute configurations of two related dissymmetric molecules can be said to be identical if the Cotton effects have the same sign in the same spectral range. Thus the occurrence of a positive Cotton effect at 470 nm in the series of complexes—D(+)-[Co en$_3$]$^{3+}$, (+)-[Co(+)-pn$_3$]$^{3+}$, (−)-[Co(+)-chxn$_3$]$^{3+}$, (+)-[Co(−)-tn$_3$]$^{3+}$, (+)-[Co(*meso*-2,3-bn)$_3$]$^{3+}$, (+)-[Co(−)-cptn$_3$]$^{3+}$, and (+)-[Co en$_2$.ibn]$^{3+}$—enabled the same, D-configuration to be assigned to all of them on the basis of the L-configuration established for the first member by X-ray diffraction [77].

However, such configurational correlations without preliminary assignment of the bands give sufficiently correct results only with closely related compounds. The possibilities of the method are considerably extended by using the rotatory powers of individual transitions to relate the configurations. An empirical rule for trigonal metal complexes (symmetry D_3) connects their configuration with the sign of the rotatory power of the E_a transition ($^4E \leftarrow {}^4A$ for Cr^{3+} and $^1E \leftarrow {}^1A$ for Co^{3+}): the rotatory power (R) of the E_a transition is positive for complexes having the $M(C_3)(D,\Lambda)$ configuration and negative for complexes having the enantiomeric $P(C_3)(L,\Delta)$ configuration [78]. The second component A_2 of band I has negative and positive Cotton effects for the $M(C_3)$ and $P(C_3)$ configurations respectively [79]. The range of application of this rule is probably quite wide: it covers the most diverse cationic, anionic, and inner-complex compounds with bi- and multi-dentate ligands, e.g. [Co diam$_3$]$^{3+}$, [9] [Co aa en$_2$]$^{2+}$, [80,81] [Co edda(L)] (where [(L) =] L-gly, L-ala, en, l-pn), [82] [Co ox$_n$acac$_{3-n}$]$^{m-}$ (where n = 1, 2, 3), [83] [Co(+)-pdta]$^{3-}$, and [Co aa$_3$]. [52]

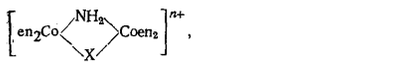
In the trisamino-acid complexes the $^1A \rightarrow {}^1E$ transition in the β-isomers and the dominant peak in the region of band I of Co^{3+} for the α-isomers have positive rotatory power if the complex has the D-configuration; [13,52,84] the latter has been confirmed by the determination by X-ray diffraction of the absolute configuration of α(+)-[CoL-ala$_3$]. [85] This rule was used in assigning the D-configuration to the 1,2,3-isomer of (+)-[Co(+)-hmch$_3$], having a

‡ The notation C_2^a and C_2^b denotes complexes of symmetry C_2 with (*a*) configurational and (*b*) conformational asymmetry.

related geometry, on the basis of the positive rotatory power of the E-transition [34].

Similar regularities constituted the grounds on which the $\Lambda(C_3)$ configuration was ascribed to a series of rhodium(III) complexes, such as $(+)_D$-[Rh aa$_3$] [86] and the mixed $(-)_D$-[RhL-aa en$_2$]$^{2+}$, where aa = ala, val, leu, ser, threo, meth [87].

The absolute configurations of dinuclear complexes, e.g.



are established on the basis of the analogy of their circular dichroism spectra and optical rotatory dispersion curves with those of corresponding mononuclear complexes [88,89].

An exception to the general rule is $(-)_D$-[Cr big$_3$] with a $\Lambda(C_3)$ configuration according to X-ray diffraction [90] and a negative E_a component in the circular dichroism spectrum [15]. On the other hand, further investigations have shown that the above relations are entirely correct only when sufficiently analogous complexes are compared. Thus the absolute configuration $(-)_D$-[Co tn$_3$]$^{3+}$ determined by X-ray examination [91] was enantiomeric to that previously assigned on the basis of rules for complexes containing five-membered chelate rings [77]. Moreover, the two cations $(-)_D$-[Co tn$_3$]$^{3+}$ and $(-)_D$-*cis*-[Co(NCS)$_2$tn$_2$]$^+$, which have the same absolute configuration (Λ) according to X-ray results [91,92], have enantiomeric circular dichroism spectra, probably owing to a change in the sequence of the E_a and A_2 components into which the absorption band I of Co^{3+} is resolved [93].

Considerable risk is entailed [95] in the spectroscopic assignment of absolute configurations to complexes of multidentate ligands on the basis of the analogy of their optical rotatory dispersion and circular dichroism with those of analogous complexes of bidentate ligands of known configuration [94]. Thus X-ray determination showed the absolute configuration of the ion $(+)_D$-[Co penten]$^{3+}$ to be enantiomeric to that predicted earlier from the circular dichroism spectra [97].

Here we have the additional difficulties of bringing the chirality of the arrangement of the rings in a multidentate ligand into unambiguous correspondence with the simple Δ and Λ configurations. Thus even in the coordination of a terdentate ligand (2,3-diaminopropionic acid) into a 1 : 2 complex, for example, the helicity of the arrangement of the ethylenediamine chelate rings corresponds to a Λ configuration, while the α- and β-amino-acid chelate rings are arranged about the metal in a Δ-configuration [98].

In such cases the most unequivocal results are undoubtedly obtained by X-ray examination of typical representatives of the classes of complexes. Determination of the absolute configuration of the cobalt(III) complex of L-3,8-diMetrien suggested [69] the following empirical relation between the sign of the circular dichroism and the chirality of the complex for linear quadridentate ligands: a complex having a negative Cotton effect in the region of the band corresponding to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition in Co^{3+} has a Δ-configuration [69].

However, errors can be avoided even within the limits of spectral methods by "ring pairing", which consists essentially in constructing every possible combination of two non-bonded chelate rings, and determining for every pair the chirality with respect to the C_2 axis. The dominant chirality determines the designation of the configuration [99].

In some cases it is useful, in determining the absolute configuration of the complex, to examine the effect of outer-sphere coordination of readily polarisable anions—such as selenite, sulphate, phosphate—on the dispersion of optical rotation and the circular dichroism. If the complex has a D-configuration, the effect is to increase the intensity of the A_2 component in the circular dichroism spectrum with a parallel decrease in the height of the E peak, probably owing to formation of an ion-pair [97,100].

It is evidently possible to use not only spin-allowed but also certain spin-forbidden $d-d$ transitions to determine the absolute configuration of a complex. The absolute configurations of trichelate complexes of chromium(III) with the most diverse ligands—en, tn, *o*-phen, ox, tart, etc.—correlate well with the sign of the rotatory power of the low-frequency component in the circular dichroism spectrum that corresponds to a ^2E_a transition: if its rotatory power is positive, the absolute configuration of the complex ion is $\Delta(C_2)$. [101]

Nuclear magnetic resonance spectroscopy has recently found increasing use for confirming results obtained by analysing the dispersion of optical rotation and the circular dichroism of complexes of diastereomeric type, i.e. with two sources of asymmetry [102-104]. For example, comparison of the n.m.r. spectra of the two isomers (+)- and (−)-[Co ox$_2$(−)-pn]$^-$ revealed that the chemical shifts of methyl protons in (−)-pn were larger in the Δ- than in the Λ-configuration [105].

Study of the stereochemistry of substituted metallocenes [106-112] is also based on comparing the signs of the circular dichroism of certain $d-d$ transitions, but this class of sandwich compound constitutes too specialised a field of coordination chemistry to be discussed in greater detail here.

(*b*) Non-spectral methods

Chemical conversion of a complex compound into another of known absolute configuration is a quite rigorous method for correlating configurations provided that the reaction does not involve rupture of any M−L bond. Until recently the use of chemical correlations in coordination chemistry was only incidental, since in most reactions of complex compounds this condition—and hence the preservation of the configuration during the changes—cannot be guaranteed [113].

The oxidation of (+)-[Ru phen$_3$]$^{2+}$ with potassium permanganate followed by reduction of the resulting 3,3′-dicarboxy-2,2′-bipyridyl in the coordination sphere to (+)-[Ru bipy$_3$]$^{2+}$ served as basis for assigning optical configurations to a long series of complexes of general type [M bipy$_n$phen$_{3-n}$]$^{m+}$, where $n = 1-3$, and M = Ru^{2+}, Fe^{2+}, Ru^{3+}, Os^{2+}, Os^{3+}, Co^{3+}, and Ni^{2+}. [114] A similar attempt to convert [Co phen$_3$]$^{3+}$ into the bipyridyl complex halted at the stage of complexes of cobalt(III) with 5-nitro-1,10-phenanthroline and 1,10-phenanthroline-5,6-quinone, which is also of some value [63].

Reduction of the [Ru en$_3$]$^{3+}$ ion to [Ru en$_3$]$^{2+}$, during which the optical activity was maintained, enabled the rules for the assignment of configurations obtained with d^6 metals to be extended to dissymmetric trigonal complexes of d^5 metals [115].

Two further reactions in which the asymmetric centre is unaffected are the oxidation of the cysteine complex of cobalt(III) to the cysteinesulphinate complex [116] and the conversion of L-[Co gly en$_2$]$^{2+}$ into L-[Co ser en$_2$]$^{2+}$ by Knoevenagel's reaction [117].

The chemical assignment of configurations by oxidising a dinuclear tartrato-complex to a monomeric oxalato-complex is not only of intrinsic interest but also a basis for further correlations in a series of bridged dinuclear complexes by their spectroscopic comparison with mononuclear complexes [118,119].

The general configurations of a series of complexes of general type $[CoXYen_2]^{n+}$ [where XY = $(CN^-)_2$, $(NCS^-)_2$, $(NCS^-)(NH_3)$, and $(NH_3)_2$] has been established, on the basis of the known absolute configuration of the first member, from their interconversions under conditions that exclude racemisation [120].

The change from [Co edta]$^-$ to $[Co\,en_3]^{3+}$ involves the rupture of M–L bonds. Nevertheless, it occurs with partial retention of optical activity, the sign of which can be used in a certain range to establish the configuration of complexes of multidentate ligands [121].

Another useful criterion in determining absolute configurations is provided by the stereospecific requirements of an optically active ligand. In many cases only one isomer can be formed without special strain, and its configuration can be determined by constructing models based on the known absolute configuration of the ligand [5,122,123]. Sometimes the absolute configuration can be deduced from the preferential formation of one isomer rather than another [124]. The configuration of a complex with an optically inactive ligand can be established by comparing its optical rotatory dispersion and circular dichroism with those of an analogous complex of an optically active ligand, provided that the latter is formed stereoselectively. This is based on the insignificance of the vicinal contribution compared with the configurational contribution. An example is the establishment of identical configurations for the ions $(+)_D$-*trans*-$[CoCl_2trien]^+$ and $(+)_D$-*trans*-$[Co(SS)Cl_2(3,8\text{-diMetrien})]^+$, which have similar circular dichroism spectra [125]. However, such correlations, based on stereoselectivity, should evidently be confined to $d-d$ transitions, since in the region of a charge-transfer band the vicinal contribution becomes sufficient to affect not only the magnitude but also the sign of the rotatory power [124].

A solubility rule may also be useful in establishing the configuration of an optically active complex. It states that complexes of similar configurations have similar solubilities [126].

However, X-ray structural analysis undoubtedly provides the last word in solving the problem of the absolute configuration of a complex compound, as well as the soundest foundation for further correlations in a series of closely related compounds. The number of publications in this field has grown rapidly during recent years, the classic papers on trisethylenediamine [127–129] and tris-*l*-propylenediamine [130,131] complexes of cobalt(III) and of ethylenediamine with chromium(III) [132,133] having been supplemented by investigations on complexes of other metals, e.g. $[Cu\,l\text{-}pn_3]^{2+}$ [134] and $[PtCl_2en_2]^{2+}$, [135] and complexes with new ligands, e.g. *trans*-$[Cr\,atc_3]$. [136] Several reviews on this subject give a more detailed account of the state of the problem [51,85,137].

IV. NATURALLY OCCURRING OPTICALLY ACTIVE COMPLEX COMPOUNDS AND THEIR MODELS

This Section reviews the application of the optical rotatory dispersion and the circular dichroism of coordination compounds to structural studies on certain optically active natural macromolecular complexes and also complexes of metals with optically active natural macromolecules (polypeptides, nucleic acids).

Study of the optical rotatory dispersion of natural materials must take into account, besides the contributions from the asymmetric centres of amino-acids and from the helical secondary structure (where present), the role of the metal atom, which, on becoming an asymmetric centre, may make a large contribution to the total optical rotatory dispersion of the molecule. Establishment of the structure and the optical rotatory power of natural complexes of this type is made more important by the fact that metal atoms are usually biologically active portions of the molecule.

Complexes of metals with di- and tri-peptides can be regarded as model compounds. They are also of intrinsic interest as chelates with multidentate ligands.

Complexes of Di- and Tri-peptides

The optical rotatory dispersion curves for copper(II) complexes with dipeptides are in general similar to those of the corresponding amino-acid complexes, the shape of the curve being determined by several factors [138]. As was to be expected, the absolute configuration of the amino-acid residue contained in the dipeptide is the decisive factor in complexes without configurational asymmetry: the curves for mixtures of the Cu^{2+} ion with gly-*L*-ala and gly-*L*-ala are mirror images one of the other. Replacement of one amino-acid residue by another of the same configuration and without additional donor groups leads merely to an unimportant quantitative change in the optical rotatory dispersion. These two properties are undoubtedly of use for determining the configuration of an amino-acid involved in coordination.

Further, the form of the optical rotatory dispersion curve is strongly dependent on the type of complex present at a given pH. Addition of one, two, and three equivalents of alkali to a solution of a 1 : 1 mixture of the Cu^{2+} ion and a dipeptide (L)yields the complexes CuL^+, CuL, and $Cu(OH)L^-$, corresponding to successive stages of proton elimination from terminal amino-nitrogen, amide nitrogen, and a coordinated water molecule. The most marked changes in optical rotatory dispersion are observed on passing from the free ligand to the CuL^+ and CuL complexes, obviously owing to formation of the first and second chelate rings [138].

Similar titration with alkali with simultaneous determination of the circular dichroism spectra showed for amides of dipeptides the existence of two main types of complexes—CuL (protons dissociated from amide and peptide groups) and $CuOHL^-$ (third proton dissociates from coordinated water molecule). [139]

The position of the optically active amino-acid residue in the dipeptide molecule has a significant influence on the dispersion of optical rotatory dispersion. On passing from the Cu^{2+} complex with *L*-alagly to the complex with gly-*L*-ala, for example, the rotation increases sharply in absolute magnitude, and the curve passes into the negative region. Together with the close similarity in the dispersion of the gly-*L*-ala and *L*-ala-*L*-ala complexes, this presupposes that the carboxy-terminal amino-acid residue plays the dominant part, probably as a consequence of different degrees of non-planarity of the two types of chelate rings [138,140].

Investigations of the octahedral complexes of dipeptides with Co^{3+} are interesting because this ion activates certain

enzymes in reactions involving hydrolysis. Stereoselectivity in such systems is probably due to easier coordination of the metal with one of the enantiomorphs of the substrate, whose configuration is determined by the stereochemical requirements of the enzyme. Indeed it has been shown that, when dipeptides made up of amino-acids of *L*-configuration are coordinated with Co^{3+}, the preferred isomer of the complex also has always the *L*-configuration [141].

The optical rotation depends significantly on the position of the optically active amino-acid residue in the peptide chain also in complexes of copper(II) and nickel(II) with tripeptides. Thus we have the sequence

$$L\text{-ala-}L\text{-ala-}L\text{-ala} > \text{gly-}L\text{-ala gly} > \text{gly gly-}L\text{-ala} > L\text{-ala gly gly}$$

for the amplitude of the Cotton effect induced in $d-d$ transitions of the ions Cu^{2+} and Ni^{2+} (at 550 and 475 nm respectively) depending on the structure of the ligand in complexes of the type ML^-. Maximum rotatory power is thus obtained by introducing the optically active fragment into the middle chelate ring of the three. This is probably due to maximum departures from planarity in this metal ring, which contains two trigonal nitrogen atoms of deprotonated amide groups.

It is interesting that the contributions to the rotatory power of transitions made by asymmetric centres in each of the three chelate rings in tripeptide complexes are not only additive in magnitude but also identical in sign, which is readily explicable only within the framework of the hexadecadic (or double octant) rule [142]. Thus in a comparison of the integral circular dichroism areas in a definite region for the series of complexes of type NiL^- with the above four tripeptides containing the *L*-ala residue in different positions, for example, it was shown that the rotatory power of the complex with the first tripeptide constitutes 103% of the sum of those of the complexes with the other three tripeptides [141].

Tripeptides containing an *L*-histidine residue are already potentially quinquedentate ligands, and their complexes have considerably greater optical activity than those of simple tripeptides. This complicated ligand coordinates with metals through four nitrogen atoms—an imidazole, an amine, and two amide atoms. The circular dichroism data indicate that the optical rotatory dispersion curves represent the superposition of two Cotton effects (at 590 and 490 nm), the signs of which depend on the relative position of the histidine residue in the tripeptide molecule [143].

Detailed investigations of the coordination of model compounds—di- and tri-peptides—have permitted the study of more complicated systems. Thus the interaction of the polypeptide of apomyoglobin with Cu^{2+} and Ni^{2+} shows that it coordinates four metal ions—one at the terminal amino-portion and the other three at histidine portions inside the polypeptide chain [144]. Examination by means of circular dichroism of two copper-containing proteins—one of which acts as an electron-transmitting fragment in the cytochrome chain, while the other catalyses the oxidation of various aromatic structures by molecular oxygen—revealed a sharp increase in the rotatory power of $d-d$ transitions in these natural complexes compared with the models, perhaps as a consequence of a charge-transfer band between Cu^{2+} and Cu^+ located side by side [145].

Determination of the sites of coordination with a metal (Cu^{2+} and Ni^{2+}) in a series of proteins, such as lysin, vasopressin, conalbumin, α-chymotrypsin, etc., became possible as a result of preliminary investigation of the circular dichroism spectra characteristic of complexes of these metals with terminal amino-groups, histidine, and thiol-containing groups in model oligopeptides [146].

The circular dichroism spectra of rubredoxin (an iron-containing protein) have yielded evidence of the quasi-tetrahedral geometry of the environment of the metal (the chelate unit $[FeS_4]$, with the sulphur atoms from four cysteine residues) in this protein [147].

An interesting problem is the effect of metal ions on the secondary structure of polypeptides. Some metals stabilise a helical conformation of the macromolecules; others, on the other hand, break it down [148]. A model process—the interaction of copper ions with polyglutamic acid—has been examined by means of optical rotatory dispersion. Calculation of the spiral content from the rotation at 233 nm showed that the spiral structure is apparently preserved even at relatively high pH-values if a sufficient quantity of Cu^{2+} ions is added. The latter probably act as bridges stabilising the spirals [149]. A similar stabilising effect of metals on the structure of nucleic acids was suggested [150] from the dependence of the melting point and certain other properties of deoxyribonucleic acid on the content of metal ions. On the assumption that the sugars of DNA were involved in metal fixation, an investigation was made of equimolecular complexes of manganese, cobalt, nickel, and copper with adenosine triphosphate; their optical rotatory dispersion indicated that 2′,3′-hydroxy-groups of ribose were involved in coordinating the metal with the ATP molecule [151].

A further use of the optical activity of complex compounds is to establish the identity of natural and synthetic macromolecules from the optical rotatory dispersion of their metal complexes. For example, the optical rotatory dispersion curves of the natural antibiotic polymyxin B and its synthetic analogue, which are smooth up to 260 nm, carry too little information, in contrast to the complexes of these cyclic decapeptides, which exhibit clearly defined Cotton effects in the vicinal region. Analysis of the form of the curves for the complexes of the two substances showed their general qualitative similarity, with slight quantitative differences that disappear completely with time owing to denaturation of the natural macromolecule; this enabled the decapeptides to be regarded as identical [152].

Hitherto the discussion has been concerned mainly with complexes of metals with natural macromolecules. Such complexes are probably responsible for certain aspects of the functioning of enzymes containing a "labile metal". Another group of natural metal complexes contain various porphyrin systems, where the metal is firmly bound in a square planar complex with an $[MN_4]$ chelate unit, examples of which are haemoglobin, myoglobin [153], plastocyanin [154], cytochrome c [155,156], and other natural products, which have also been investigated by optical rotatory dispersion. The Fe^{2+} ion present in haem becomes asymmetric on coordination at the apical position with two different ligands (e.g. with two polypeptide chains, as in cytochrome c [155]). As a consequence both forms—oxidised and reduced—of this important respiratory pigment of blood have a sharp Cotton effect of great amplitude in the region of 530 nm. The optical rotatory dispersion results from the superposition of three effects—due to the asymmetric carbon atoms of the amino-acid residues, to the helical portions of the polypeptide chain, and to the asymmetric metal atom—and is quite complicated to interpret exhaustively. Nevertheless it was concluded, in view of the reversibility of the changes occurring in the dispersion on passing from the oxidised to the reduced

form of cytochrome c, that this process involved a change only in the electronic state of the metal, while the structure of the natural ligand remained unchanged [156]. Study of the concentration and temperature dependence of the circular dichroism spectra of ferrihaem octapeptide (a fragment of cytochrome c) has yielded information on the relative orientation of the haems; the results obtained on model systems are used to interpret certain structural features of haemoglobin and of cytochrome-c oxidase [157].

Several chlorophylls and protochlorophyll pigments have also been investigated by means of circular dichroism and magnetic circular dichroism [158]. A quite detailed study has been made of the effect of complex formation with several bivalent metals (zinc, copper, nickel) on the optical activity of bile pigments, which can also be included structurally among porphyrin ligands [159].

V. DETERMINATION OF THE ABSOLUTE CONFIGURATION OF ORGANIC COMPOUNDS

For many classes of organic compounds the transitions responsible for optical activity are at too high an energy level for direct observation of the Cotton effect to be possible without appropriate apparatus for the vacuum ultraviolet. This applies to alcohols, amines, carboxylic acids, hydroxy-acids, and most amino-acids [160]. The problem can be solved also by introducing into the molecule a chromophoric group, which absorbs in a spectral range convenient for measurement. Thus Djerassi and his coworkers achieved considerable success in using $n \rightarrow \pi^*$ transitions of C=S groups in so called "chromophoric derivatives" of hydroxy-acids, amino-acids, and steroids to establish their absolute configurations [66]. Yet complexes of transition metals are especially convenient as such "chromophoric derivatives", both spectroscopically (because of the position of their $d-d$ transitions in the visible range) and practically (thanks to the simplicity of preparation of the complexes and the possibility of working in solution without isolating them).

Since the first attempts at using the Cotton effects of metal complexes to study dissymmetric organic molecules [161-163] several papers have appeared on the use for these purposes of the vicinal effect in various types of complex compounds. The rational basis for such configurational comparisons is the hypothesis that similar ligands having the same configurations in related complexes should induce rotatory forces of the same sign in corresponding transitions of the metal ion. As the same ligand may form part of several types of complexes, e.g. trisbidentate and bisbidentate, this provides an opportunity for checking the accuracy of the assignment of a configuration. The absolute configuration can be postulated by comparison with complexes of a ligand of known absolute configuration. The identity of the configurations of a series of diamines—(−)-pn, (−)-bn, (−)-chxn, (−)-phenen, (+)-stien—has been established in this way [164].

Configurations have been assigned to a series of hydroxy-acids related to mandelic acid by use of the sign of the Cotton effect of the copper(II) complexes of the amidines of these acids, which is positive for complexes obtained from amidines of the $L(R)$ series and negative for those of the $L(S)$ series [165]. Since the amidines themselves also have a Cotton effect at 270 nm, it is recommended that the two optical rotatory dispersion curves of the ligand should be subtracted from the curve observed for the complex [166].

The absolute configurations of different asymmetric carbon atoms in polyhydroxy-carboxylic acids can probably be determined from the optical activity of complexes formed at definite pH-values. Thus the signs of the circular dichroism of praseodymium(III) complexes with hydroxy-acids obtained in acid and neutral medium correlate with the configurations of the α- and γ-carbon atoms respectively [45]. Europium(III) complexes of hydroxy-acids differing only in the configuration of the α-carbon atom have circular dichroism spectra of mirror-image type [48]. When hydroxy-acids coordinate with nickel(III) at low pH, the sign of the circular dichroism correlates with the absolute configuration of the α-carbon atom, whereas at higher pH the deprotonation of the β-hydroxyl and ring formation with the metal enable the sign for the neutral complex to be related to the configuration of the β-carbon of the ligand (aldonic acid) [167].

The sign of the Cotton effect in the visible range for biscomplexes of copper(II) and nickel(II) [30,168] with amino-acids also depends on the configuration of the ligand, rotatory powers of opposite sign being induced in transitions of these two metals [168]. Probably here too, on coordination of the metal with ter- and multi-dentate amino-acids under certain conditions, individual types of complex compounds can be distinguished by differences in the optical rotatory dispersion and circular dichroism. Thus L-asparagine on coordination with copper(II) induces in the region of 600 nm Cotton effects of opposite sign depending on the pH. [169] The circular dichroism spectra of 1 : 1 complexes of praseodymium(III) with potentially terdentate amino-acids have been used to study aspects of the chelation of these ligands in various media [47].

Torchinskii and Koreneva [170,171] proposed a method for determining the absolute configuration of α-amino-acids and their derivatives (including N-terminal amino-acid residues in peptides) by measuring the optical rotatory dispersion of chelate compounds of several metals—copper(II), nickel(II), zinc(II), cobalt(III), aluminium(III)—with Schiff bases of the amino-acids with certain aromatic o-hydroxy-aldehydes. The sign of the Cotton effect was shown to be determined by the absolute configuration of the α-amino-acid and to be independent of the sign of rotation of the free ligand: a negative Cotton effect corresponded to compounds of the L-series, and a positive effect to those of the L-series. The complexes do not need to be isolated in the free state.

We have been discussing the use for configurational correlations of the sign of the rotatory power of definite $a-a$ transitions in metal complexes. The use of charge-transfer bands has been proposed for the same purposes. In copper complexes of amino-acids this band is located at ~250–270 nm and is of the L→M type. The coordination of amino-acids of the L-configuration with copper(II) at pH 8–10 gives a charge-transfer band of negative rotatory power. It is supposed that correlations based on the rotatory power of these bands may be more generally applicable, since both possible conformations of five-membered chelate rings induce Cotton effects of the same sign in the charge-transfer bands for biscomplexes with copper [169].

A second possible way of eliminating additional effects due to conformational contributions is to use for the determination of configurations complexes in which the compound occurs as a unidentate ligand L, e.g. of the type $[CoL(NH_3)_5]^{2+}$, where L represents an amino-acid [160] or a hydroxy-acid [172]. Cobalt(III) complexes have the advantages of kinetic inertness and the fact that the spectroscopy of Co^{3+} has been well studied. There is no difficulty

in obtaining the above complexes under controlled conditions (pH ≃ 5, below 40°C), although in the case of potentially bidentate ligands raising the temperature may lead to loss of ammonia and chelation. The optical activity of complexes with unidentate ligands is due solely to the vicinal contribution by an asymmetric carbon atom: if the dominant Cotton effect of the long-wavelength spin-allowed transition in it is negative, the acid has the *L*-configuration, related to *L*(+)-lactic acid[160]. This method is obviously applicable only to carboxylic acids with an asymmetric centre in the α-position with respect to the carboxyl, since the increase in distance between this centre and the chromophore (here the metal) in β- and γ-substituted carboxylic acids produces a sharp decrease in the relatively small vicinal effect. Complexes of the same type $[CoLX_5]^{n+}$ but with more bulky optically inactive ligands X may be more useful in these cases. Even in a series of complexes $[CoLX(NH_3)_4]^{n+}$ increase in the volume of the optically inactive ligand X is accompanied by a significant increase in the vicinal effect of the *O*-coordinated unidentate α-amino-acid L, caused by the diminution in the conformational mobility of the optically active ligand L with growth in the steric requirements of the neighbouring group X.[173]

A further important advantage of using the non-chelate type of complexes consists in the possibility of making configurational comparisons between different classes of substituted carboxylic acids of general type R.CHX.COOH (X = Alk, OH, NH_2, etc.), since all $[CoL(NH_3)_5]^{n+}$ complexes have the same microsymmetry C_{4V} when the acids are coordinated through the carboxyl, so that the way in which the *d*-levels are split and the energetic sequence of the transitions should be the same independently of R and X. Such comparison of the configurations of amino- and hydroxy-acids cannot be based on the optical activity of chelate complexes of the type $[Co(R.CHX.COO)(NH_3)_4]^{2+}$, since their microsymmetry changes from C_{4V} when X = NH_2 to C_{2V} when X = OH. In conformity with this the splitting of the triply degenerate octahedral $^1T_{1g}$ level is different in the two cases: $^1T_{1g} \rightarrow {}^1A + {}^1E$ with C_{4V} microsymmetry, but $^1T_{1g} \rightarrow {}^1A + {}^1B + {}^1B$ with C_{2V}.

Nevertheless, monochelate complexes can be quite useful for comparing the configurations of a series of ligands of the same type. For example, an intense circular dichroism band in the region of the absorption band II of Co^{3+} at 342–335 nm may be useful for comparing amino-acids, its Cotton effect being negative for compounds of the *L*-configuration and positive for *D*-amino-acids in the complexes $[Co\,aa(NH_3)_4]^{2+}$.[8,22]

Complexes of other metals can also be employed for configurational comparisons. Thus the absolute configuration of the β-carbon atom of (+)-pseudoephedrine has been established[40] from the analogy of the circular dichroism and absorption spectra in the region of *d*–*a* transitions of copper biscomplexes of this ligand and of the related *L*-(+)-2-aminopropanol of known absolute configuration.

The effect of complex formation with copper (in the form of cuprammonium solutions) on optical rotatory dispersion is used widely for the stereochemical analysis of amino-sugars[174], cyclic diols and amino-alcohols[175], and their acyclic analogues[174]. The molecular rotation of sugars is significantly increased by complex formation with molybdate ions, and the anomaly in the dispersion at 345 nm has been proposed for the analysis of sugar isomers[176]. The conformation of the first three hydroxyls of the pyranose ring is significant for complex formation. Molybdate solutions of sugars show three or four Cotton effects in the range 220–350 nm if the hydroxyls are arranged in a *cis*–*cis* configuration, and two Cotton effects in the same wavelength range if they are in the *trans*–*trans* positions[177].

The configurations of alcohols and amines can be determined from the sign of the rotatory power of the bands at 480 and 420 nm due to dichelates of nickel with xanthate or dithiocarbamate ions obtained from these alcohols and amines respectively. Both the Cotton effects are negative when the alcohol or amine has the *l*-configuration, as has been shown for *l*-menthol, *l*-2-methylbutanol[178], and secondary amines obtained from *l*-phenylethylamine[179,180].

Another interesting application of the circular dichroism of metal complexes is to determine the configuration of alkenes, whose own π–π* and n–σ* absorption occurs in the fairly remote ultraviolet (190–200 nm). Existing methods for obtaining chromophoric derivatives—osmates and episulphides—disturb the geometry of the ethylenic bond and therefore are not always acceptable. The formation of π-complexes of platinum(II) with alkenes is free from this defect, so that chromophoric *d*–*a* transitions of Pt^{2+} have been successfully used for configurational comparisons.

When ethylenic compounds undergo π-type coordination with a metal, the substituted carbon atom of the double bond becomes asymmetric. Monosubstituted ethylenes acquire one asymmetric centre, and *trans*-disubstituted ethylenes acquire two such centres having the same configuration; *cis*-disubstituted ethylenes yield a *meso*-form on coordination, since the two asymmetric centres have opposite configurations[181]. In complexes of mixed type $[PtCl_2LL']$, containing an optically active amine L and an alkene L', the sign of the low-energy transition of Pt^{2+} is independent of the relative positions (*cis* or *trans*) of amine and alkene, and indicates only the configuration of the coordinated alkene. This conclusion is confirmed by applying the quadrant rule[182–189].

VI. DETERMINATION OF THE COMPOSITION AND THE STABILITY OF COMPLEX COMPOUNDS

As a consequence of the presence of an additional parameter—the sign of the optical rotation—optical rotatory dispersion and circular dichroism should be far more effective than ordinary spectrophotometry for determining the composition and the stability of complexes. Nevertheless, very little work has been done on these lines, and most investigators, even when working with optically active ligands, use only potentiometry or absorption spectra[190–192]. However, a few examples of the application of spectropolarimetry can be mentioned. A group of French workers have developed methods for determining the composition and the stability of complex compounds, in particular of copper(II), zinc(II), cobalt(II), nickel(II), and cobalt(III) with optically active amino-acids[193–196], and of iron(III) with tartaric acid[197]. The formation of complexes by molybdate, tungstate, and uranyl ions with hydroxy-acids[198], by zinc(II), cobalt(II), and nickel(II) with *L*-mandelic acid[199–201], and by arsenic acid with *d*(–)-mannitol[202] has been investigated by means of the optical rotatory dispersion or even simply by measuring the specific rotations at a single wavelength[203]. Similar results were obtained when the stability constants were determined by other methods, e.g. potentiometric pH measurement[200].

Circular dichroism can also be used to investigate complex formation [204], although the apparatus is less accurate [205]. However, determination of the stability constants of complexes of oxovanadium with lactic acid showed not only good agreement with those obtained by the independent method of absorption spectra over a wide range of values of $\bar{n}$ (the formation function) but also that circular dichroism is even more sensitive at low values of $\bar{n} \simeq 0.2$. [206]

The spectropolarimetry of complex compounds can be useful in determining not only their composition [207-209] and their stability [207,210] but also for the quantitative determination both of metals [211-214] and of organic compounds [212,215,216].

Measurement of the optical rotatory dispersion and the circular dichroism of coordination compounds will yield the most valuable information on the finest structural features of the environment of the metal. Thus a diminution in the rotatory power of $d-d$ transitions may indicate flattening of the chelate unit, e.g. by interaction with a donor solvent [217] or as a consequence of fewer steric interactions within the molecule of the complex [218-220].

Many other applications of spectropolarimetry—such as e.g. study of the reactions of coordination compounds by means of optical rotatory dispersion and circular dichroism [221-224], analysis of conformational equilibria in complex compounds [225], investigation of geometrical and optical stereoselectivity in the coordination of metals with optically active ligands, and certain other aspects—are not dealt with here, since they may form the subject of separate reviews.

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In conclusion it may be stated that the wide application of spectropolarimetry in the field of inorganic chemistry during recent years has in effect provided a new method for studying the structure of coordination compounds, the possibilities of which have been by no means fully revealed so far.

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