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Factors Determining the Optical Activity of Coordination Compounds

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Investigations of the structure of complex compounds based on analysis of the circular dichroism spectra and the dispersion of optical rotation are surveyed. A list of 124 references is included.

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I. INTRODUCTION

The past five years have seen a tendency to a new, more differentiated use of circular dichroism spectra and the dispersion of optical rotation in the structural study of complex compounds. This approach is based on recognition that the rotational strength of d–d transitions of the complexing metal depends usually not on one but on a number of factors associated with different structural characteristics of the complex molecule. Accordingly, several contributions to the optical activity of a complex can in general be distinguished. Thus the configurational contribution is due to the helical, dissymmetric arrangement of multidentate ligands about the central metal ion. The conformational contribution is due to the asymmetry of an individual non-planar chelate ring. And the presence of asymmetric carbon atoms in the ligand molecule results in the appearance of a vicinal contribution. The establishment of asymmetry in the donor atoms of the ligand (N*, S*) on coordination with the metal can be regarded as a particular case of this last effect.

The additivity of the individual contributions to the optical activity of complex compounds has been proved quite regularly. It is fully justifiable to divide the total effect observed into component parts, and to distinguish each contribution as a differential curve (of the dispersion of optical rotation or, more frequently, of circular dichroism).

In order to study an actual property of a given compound (e.g. the configuration of an asymmetric carbon atom in a ligand) the corresponding differential curve (the curve of the vicinal effect) is, of course, immeasurably more useful than the overall spectrum observed. Moreover, analysis of the overall curve will definitely give misleading information in all cases in which the contributions of the dominant effect and of the effect under investigation are opposite in sign.

The present Review attempts to analyse some possible modes of inducing rotational strength in d–d transitions of metal complexes and to assess their relative effectiveness. Work published during 1964–1969 is covered. Earlier reviews on optically active coordination compounds summarise the literature of the preceding period[1-3]

or discuss only certain particular aspects of this new and promising field of investigation, e.g. present-day theory [4], problems of stereoselectivity [5], the nature of the Pfeiffer effect [6], etc.

Abbreviations often used in the text for various ligands are listed here for the convenience of the reader.

aa	anion of amino-acid
aaH	amino-acid
gly	glycine
ala	alanine
val	valine
leu	leucine
prol	proline
ox	oxalate
mal	malonate
tartr	tartrate
am	diamine
en	ethylenediamine
N-Meen	*N*-methylethylenediamine
pn	propylenediamine
phala	phenylalanine
o-phen	phenanthroline
IDA	iminodiacetate
EDDA	ethylenediaminediacetate
EDTA	ethylenediaminetetra-acetate
TMDTA	trimethylenediaminetetra-acetate
EDTP	ethylenediaminetetrapropionate
hmc	hydroxymethylenecamphor
$(sal)_2pn$	disalicylidenepropylenediamine
N-Meala	*N*-methylalanine
alada	alanine-*NN*-diacetate
tn	trimethylenediamine
chxn	*trans*-cyclohexane-1,2-diamine
tetraen	tetraethylenepentamine
penten	*NNN'N'*-tetrakis-2-aminoethylethylenediamine
sar	sarcosine

II. EFFECT OF CHELATION

Fundamental work on the chemistry of optically active organic compounds indicates that an asymmetric centre induces a quite measurable rotational strength, even if the chromophore is separated from it by two or three carbon atoms [7]. With complexes of unidentate ligands, such as *dextro*-s-butylamine and *dextro*-α-methylbutyric ester, however, the Cotton effect could not be observed in *d–d* transitions of a metal chromophore separated from the asymmetric centre by only one or two atoms [8].

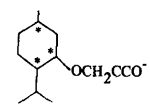
Mercury complexes containing an asymmetric carbon atom directly attached to the metal were investigated on the assumption that the asymmetrising effect falls away with distance more rapidly in coordination compounds than in organic compounds. However, measurements of circular dichroism did not reveal bands above 220 nm with *dextro*-s-butylmercuric bromide, chloride, and quinolin-8-oxide [9]. On the other hand, this was a somewhat unfortunate choice, since the Hg^{2+} ion, in which the d^{10} electron shell is complete, cannot act as a chromophore in the *d–d* range.

A series of papers on transition-metal complexes containing an asymmetric donor nitrogen atom together with other types of asymmetry (configurational, conformational) is not very useful for solving this problem owing to the difficulty of isolating the vicinal effect of the asymmetric donor nitrogen atom from the observed overall curve [10,11].

Nevertheless, it is well known that, in comparison with the above cases of unidentate ligands, bidentate optically active ligands usually induce Cotton effects of considerable amplitude in *d–d* transitions, although the asymmetric centre is sometimes very remote from the chromophore. Still earlier, in 1950, similar observations led Lifschitz [12] to suggest that the induced Cotton effect of *d–d* transitions in complexes of transition metals is of measurable magnitude only if the asymmetry ligand possesses chelating power. This rule might be extremely useful for determining the mode of coordination of potential multidentate ligands in solution. Subsequent investigations indicated that the above statement was too categorical.

From a comparison of the dispersion of optical rotation of the ions $[Co(+)\text{-tartr}(NH_3)_4]^+$ and $[Co(+)\text{-tartr}(NH_3)_5]^{2+}$, which contain bidentate and unidentate tartaric acid respectively, Bhatnagar and Kirshner showed [13] that the two curves are similar in shape, the only difference being that the complex containing the unidentate ligand exhibits half the Cotton effect in the *d–d* region.

Kirshner analysed the contradictory results of this work and that mentioned above [8], and suggested that the increase in optical activity might be due to an increase in the number of asymmetric centres in the optically active ligand. A cobalt(III) complex $[Co(-)\text{-menac}(NH_3)_5](NO_3)_2$, which contains as unidentate ligand the *laevo*-menthoxyacetate ion (I) having three asymmetric centres



(I)

was therefore prepared and examined spectropolarimetrically [14]. The sharp positive Cotton effect in the region of the absorption band due to the cobalt(III) ion in the circular dichroism spectrum is of smaller amplitude than that of the corresponding complex of unidentate *dextro*-tatrate. This result is fully understandable if it is borne in mind that the increase in the number of asymmetric centres was accompanied in this case by considerable remoteness from the chromophore, and that the latter was evidently the dominant factor.

This work was not followed by more correctly designed investigations, and the effect of the number of asymmetric centres on the magnitude of the Cotton effect which they induce remained an open question. Nevertheless, it may be supposed that increasing their number is more likely to produce mutual extinction of their individual contributions with a diminution in intensity of the overall effect.

There is probably a general tendency for the rotational strength of *d–d* transitions to decrease on passing from complexes of bidentate ligands to those of analogous unidentate ligands. This is most clearly demonstrated in an extremely detailed paper by Japanese workers, who investigated complexes of two types—$[Co(NH_3)_4L\text{-aa}]^{2+}$ and $[Co(NH_3)_5L\text{-aaH}]^{3+}$—with bidentate and unidentate amino-acids respectively [15]. The anomaly in the region of the first absorption band of the cobalt(III) ion in the dispersion of optical rotation of complexes of the second type is so weak in comparison with that of their chelate analogues that only qualitative measurements are possible with them. Several reasons may be suggested for such a sharp decrease in amplitude of the Cotton effect on rupture of a chelate ring: the most important are probably [15] the increase in distance between the asymmetric centre and the chromophore—from Co–N–C* for the chelated ligand to Co–O–C–C* for the unidentate amino-acid—and secondly the increase in the conformational mobility of the

ligand—from the rigidly fixed conformation of the chelated amino-acid to a mixture of several conformers of the unidentate ligand—which is due to free rotation of the acyclic molecule.

Since in all the above cases a Cotton effect was observed in complexes of the unidentate ligands, which were in principle capable of chelation, the question of the relation between an anomaly in the visible region and the formation of a metal-containing ring can be finally settled only by examining complexes with truly unidentate ligands. This has been done by Bosnich [16], who isolated a square planar palladium(II) complex *trans*-$[PdCl_2L_2]$ and oxidised it with chlorine to the octahedral palladium(IV) complex *trans*-$[PdCl_4L_2]$, where L represents the optically active unidentate ligand (−)-α-methylbenzylamine. It was obvious from the measured circular dichroism spectra that *d*–*d* transitions of the palladium ions possessed appreciable optical activity in both cases, although here, too, the amplitudes of the Cotton effect were considerably smaller than those usually observed with dissymmetric chelate compounds [17,18].

This result indicates that the rotational strength of *d*–*d* transitions in metal complexes is determined in considerable measure by the remote asymmetric centre of a unidentate ligand, although its interaction with the chromophore is considerably weaker than the effects observed in chelate systems. Attempts to explain the optical activity of complexes of unidentate ligands by any other types of chelation, e.g. outer-sphere chelation [19], appear to the Reviewers quite artificial.

Thus differences in the rotational strengths of *d*–*d* transitions between chelates and the non-chelate type of complexes are only quantitative, not qualitative. This is confirmed by the presence of quite measurable vicinal† effects in almost all complexes of optically active ligands which have now been studied differentially. The main reason for the decrease in rotational strength in the *d*–*d* region on the opening of a metal-containing ring is probably the sharp increase in conformational mobility of the monocoordinated ligand accompanied by considerable mutual extinction of the contributions of the various conformers. Similar effects are well known in organic chemistry [21–23].

An especially significant illustration of this hypothesis is a Japanese study [24] of the dependence of the vicinal effect due to a unidentate ligand—an *ortho*-coordinated α-amino-acid—on its conformational mobility. A substantial increase in the amplitude of the Cotton effect was observed in a series of complexes of the type *cis*-$[Co(L\text{-alaH})X(NH_3)_4]^{n+}$, where the size of the ligand X increases gradually in the sequence

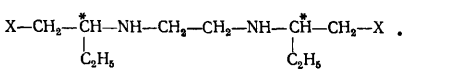
$$H_2O < \text{gly H} < \beta\text{-ala H} < \text{Sar H} < \text{L-ala H} < \text{C-prol H}.$$

This series correlates fairly closely with the restriction of the conformational mobility of optically active unidentate alanine due to its steric interaction with the adjacent ligand X. [24]

This it is evidently no longer possible to suppose that chelation is a necessary condition for the appearance of the Cotton effect in the *d*–*d* region, since it merely increases the rotational strength of these transitions by diminishing the conformational mobility of a unidentate ligand.

†The concept of a vicinal effect was first introduced by Shimura [20].

This conclusion is of both practical and theoretical importance. In practice the rigorous dependence of the induced Cotton effect on the unidentate or multidentate character of the ligand containing the asymmetric centre enables measurements of the dispersion of optical rotation and circular dichroism to be used to study the coordination of potentially multidentate ligands in complexes of undetermined structure



(II)

An example is the determination of the type of chelation of the quadridentate ligand 2,7-diethyl-3,6-diazaoctane-1,8-diol (IIa: X = OH) [25] with copper(II) and nickel(II). Bidentate behaviour of this ligand was simulated by replacing the hydroxyls by chlorine atoms (IIb: X = Cl). This took the asymmetric centres out of the chelate rings, and the centres could contribute to the optical activity mainly by their stereospecific influence on the conformation of the central ethylenediamine chelate ring. The decrease in the amplitude of the Cotton effect by more than 90% on replacement of hydroxyl by chlorine is convincing evidence of the quadridentate behaviour of the ligand (IIa).

A similar principle can be used to determine the mode of coordination of the potentially terdentate ligand cysteine as a function of the acidity of the medium [26].

The copper(II) and nickel(II) complexes of di- and tripeptides provide excellent examples for demonstrating the dependence of optical rotatory power on the number of chelate rings in a complex. Study of the dispersion of optical rotation and the circular dichroism of a series of complex ions with ligands containing a gradually increasing number of potential coordinating atoms showed that the rotational strength of *d*–*d* transitions increases in proportion to the number of chelate rings, with the most highly chelated form possessing the maximum rotational strength [27–29].

This rule is evidently quite general in character, and can be traced in the chelate compounds of metals with diamines and polyamines. The accumulation of metal-containing rings in a complex leads to an increase in optical rotation whether the chelate rings are present in one or more ligands. Thus bisbidentate complexes of the type $[MX_2am_2]^+$ give rotational strengths in the *d*–*d* region double those of the corresponding monobidentate complexes $[MCl_4am]^-$. [30] In the series of complex ions—*cis*-$[Co(NH_3)_2en_2]^{3+}$, $[Co\,en_3]^{3+}$, $[Co\,penten]^{3+}$—the amplitude of the Cotton effect, measured from the peak to the trough, increases in the sequence—2200, 7500, 16 000°—in conformity with the presence of two, three, five chelate rings [31].

All these observations demonstrate fairly clearly the same rule: the rotational strength of *d*–*d* transitions of chelate complexes of metals is a function of the number of chelate rings present [32]. This conclusion is of undoubted practical value as a means of studying the coordinating properties of optically active ligands of multidentate type.

Certain theoretical aspects of the relation between the formation of metal-containing rings and the rotational strength of *d*–*d* transitions of the metals can conveniently be noted here. The whole edifice of the modern theory of the optical activity of coordination compounds is based on the necessity of chelation, which produces the dissymmetric departures of the donor atoms in the ligands [33,34], their orbitals [35], or their charges [36] from the regular geometry that are needed for the appearance of the rotational strength of *d*–*d* transitions. Since the chelate

rings are regarded in all cases as the mechanical basis for such deviations, it is undoubtedly of interest to study the effect of the size of the chelate ring on the magnitude of the induced Cotton effect. If the theory is correct, increase in the size of the metal ring should be accompanied by an increase in its flexibility, minimum departures of the donor atoms from their normal positions, and a decrease in the amplitude of the Cotton effect.

A decrease in amplitude of the Cotton effect was actually observed with increase in the length of the carbon chain of the diamine from ethylenediamine to trimethylenediamine in complexes of the type $[Mam_3]^{3+}$, where M = Co^{III}, Cr^{III},[31,37] but this work was followed by several contradictory results[38]. Douglas compared a series of complexes containing a quadridentate ligand (ethylenediaminediacetate) together with carbonate, oxalate, and malonate anions, to give chelate rings containing 4–6 atoms respectively. Contrary to theoretical predictions, all three compounds showed almost identical circular dichroism curves[39]. Moreover, the rotational strength of the complex ion $[Co\,mal_2en]^-$ was double that of $[Co\,ox_2en]^-$, despite the diminution of distortions on the replacement of the oxalate by the malonate ion. Yet the opposite situation is found with the complexes $[Co\,mal_2gly]^{2-}$ and $[Co\,ox_2gly]^{2-}$,[40] and also in a series of complexes of the type $[CoX\,en_2]^+$, where $X = CO_3^{2-}$, ox, mal.[39]

Nor were theoretical predictions confirmed by complexes of multidentate ligands of the type $[CoEDTA]^-$. Diminishing the strain in this system by increasing the size of the chelate rings or by opening them—both diamine rings (in $[CoTMDTA]^-$ and in *cis*-$[CoIDA_2]^-$) and amino-acid rings (in $[CoEDTP]^-$)—did not lead to the expected decrease but to an increase in the intensity of all the bands in the circular dichroism spectrum[41].

These and other similar results[38,42] led to the evident conclusion that it is no longer possible to suppose that the main reason for the optical activity of coordination compounds is the deflection of metal–ligand bonds from their regular geometry as a consequence of the steric requirements of the metal-containing rings. This conclusion receives its most serious support from recent X-ray investigations of optically active complexes[43].

The unnecessary exaggeration of the role of chelation to be found in theoretical and practical papers may be ascribed to the poor sensitivity of the earlier instruments. The impossibility of measuring the Cotton effect induced by unidentate ligands made quantitative differences between chelate and non-chelate systems appear to be qualitative, so that the influence of chelation was erected into an absolute effect. The real reason for the increase of amplitude of the Cotton effect on passing to chelate compounds is the appearance of other contributions to rotation, in addition to the vicinal effect, which result from the specific character of these metallocyclic systems. Such contributions will be discussed in the following Section.

III. CONFIGURATIONAL, CONFORMATIONAL, AND VICINAL CONTRIBUTIONS

The optical activity of octahedral complexes of the type $[M(AA)_3]^{n+}$ or *cis*-$[MX_2(AA)_2]^{m+}$, if the bidentate ligand A is not itself optically active, is a consequence of the exclusively helical arrangement of the chelate rings. This has been termed the *configurational effect*. The examples most often used are cobalt(III)–ethylenediamine complexes —(+)-$[Co\,en_3]^{3+}$ and *cis*-$[CoX_2en_2]^{2+}$—although in general such compounds with non-planar chelate rings contain a contribution from the dominant conformation of these rings besides the purely configurational contribution. It would be far more correct to examine the configurational effect in complexes of planar bidentate ligands such as 1,10-phenanthroline and 2,2′-bipyridyl. Since complexes of the latter type have been known for a long time and have been well studied[44], we shall not discuss the configurational effect in greater detail. We note merely that, since in these cases the metal is both the centre of asymmetry and the chromophore, the Cotton effect in the *d–d* region usually has large amplitudes.

Asymmetric ligand atoms may also cause a Cotton effect whose amplitude is greatly dependent on the distance between the asymmetric centre and the chromophore (the metal ion). This has been termed the *vicinal effect*. It is present in purest form in complexes with optically active unidentate ligands, which have been discussed in the preceding Section. The concept of the vicinal effect includes contributions both by asymmetric carbon atoms in the ligand and by donor atoms (N* in secondary amino-groups, S* in alkylthio-groups) if they become asymmetric on coordination with the metal.

If a ligand forms a non-planar chelate ring on complex formation, an additional, *conformational effect* appears as a consequence of the asymmetry of the individual non-planar metal-containing ring. However, these last two factors are fairly difficult to separate, since formation of the preferred conformer is closely connected with the absolute configuration of the ligand. The two phenomena are often considered together under the concept of vicinal effect[45], although the conformational effect evidently predominates.

Moreover, Larsen and Olsen[8] consider the presence of a Cotton effect in the *d–d* region as proof that the complex contains a non-planar chelate ring with a single dominant conformation: i.e. they attribute the whole of the optical activity to the conformational effect. Such neglect of the vicinal effect cannot be accepted as legitimate if only because there are now sufficient experimental results indicating the presence of strong Cotton effects in the *d–d* region with four-coordinated complexes having completely planar chelate rings. Examples are provided by the dispersion of optical rotation in complexes of (+)-hydroxy methylenecamphor[46] and (–)-α-methylbenzyldithiocarbamic acid[47] containing planar six- and four-membered metal rings respectively.

We shall examine in greater detail these last two effects.

1. Vicinal Contribution

Of all the effects enumerated above the vicinal effect is usually the smallest, as would be expected from the strong dependence of optical activity on the distance between the chromophore and the asymmetric centre.

It would be reasonable to suppose that the largest vicinal effect would be produced by asymmetry of the donor atom of the ligand. Organic compounds containing an asymmetric nitrogen atom are fairly exotic and difficultly accessible owing to the rapid inversion of this centre. On coordination of a secondary amino-group, however, the nitrogen is far more basic than in organic quaternary ammonium salts. This has made possible the resolution into N* enantiomers of several coordination compounds of cobalt(III),[48–51] platinum(II), and platinum(IV)[52] with *N*-substituted diamines and amino-acids.

The optical activity of complexes of the type *trans*-$[MX_2(LL)_2]^+$ with *N*-substituted diamines and amino-acids is assumed to be due solely to the vicinal effect of the asymmetric donor nitrogen atom [48]. This is not altogether true, since it disregards the conformational contribution of the ligand, which is quite large with diamines. Separation of conformational and vicinal contributions and their separate examination is the more important as cases are known in which the absence of information on their relative roles has led to assignment of an incorrect configuration to the complex ion, as has occurred e.g. with the (−)-*trans*-*trans*-$[CoX_2N\text{-Meen}_2]^+$ ion [53].

A similar type of mistake is usually made in discussing the optical activity of *trans*-complexes of optically active diamines in which the nitrogen is unsubstituted [54]. However, this does not lead to large errors, since the C*-vicinal contribution is substantially smaller than the conformational effect, which does not apply to the N*-vicinal contribution.

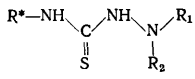
If it is supposed that the circular dichroism of *trans*-$[CoCl_2(S)\text{-pn}_2]^+$ can simulate satisfactorily the contribution of the δ-conformation of coordinated *N*-methylethylenediamine, subtraction of its circular dichroism spectrum from the circular dichroism curve of the (−)-*trans*-*trans*-$[CoCl_2N\text{-Meen}_2]^+$ ion leaves the almost pure vicinal effect of the R–N* asymmetric centre as the resulting curve. The curves obtained in this way show that the N*-vicinal and conformational effects are comparable in magnitude and opposite in sign [55].

The abrupt change in the circular dichroism spectra on passing from ordinary amino-acids to L-proline in complexes of the type $[Cu(L\text{-aa})_2]$ has been attributed to the asymmetry of the donor nitrogen atom [56]. Molecular models make it obvious that only one of the two possible enantiomeric N* configurations can be realised, owing to the steric requirements of this cyclic ligand. This assumption has since been confirmed by X-ray examination [57]. The vicinal effect of the asymmetric nitrogen atom in the coordinated L-prolinate ion results in more intense dichroic bands of certain other complexes, e.g. the $[Co(NH_3)_4L\text{-prol}]^{2+}$ ion. [58] Similar effects are observed in copper(II) complexes containing pseudoephredine and sarcosine [59].

Additional asymmetry, associated with the coordination of secondary amino-groups [60] or alkylthio-fragments of the molecule [61–63], may appear on complex formation by metals with linear multidentate acyclic ligands such as tetraethylenepentamine and also with macrocyclic multidentate ligands [64].

The vicinal effects of asymmetric centres of the carbon skeleton of the ligand which are more remote from the chromophore are substantially smaller than the contributions by asymmetric donor atoms (N*, S*), and this is fully consistent with Chugaev's vicinal rule [65]. An asymmetric α-carbon atom in such ligands as amino-acids develops a far larger vicinal effect than does a β-atom in a side-chain outside the chelate ring. A good illustration of this conclusion is the close similarity in the circular dichroism spectra of the two complexes of the type $[Cu(L\text{-aa})_2]$ in which the amino-acid is respectively L-threonine and L-allothreonine: these amino-acids are respectively *threo*- and *erythro*-isomers, having the same configurations of the α-carbon centres and opposite configurations of the β-atoms [56].

In view of the strong dependence of the vicinal effect on the position of the asymmetric centre in the ligand Lifschitz [12] postulated in 1950 that a necessary condition for the appearance of anomalous dispersion of optical rotation of inner-complex compounds is the presence of an asymmetric carbon atom in the chelate ring. This statement is shown to be too categorical by the work of Jensen [66], who investigated nickel(II) complexes of a series of optically active thiosemicarbazides of general formula

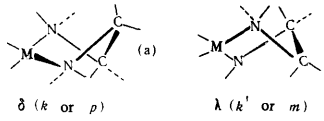

(III)

in which the optically active radical R* is isolated from the chelate ring by a nitrogen atom. Nevertheless, if the α-carbon atom in the radical R* is asymmetric, the circular dichroism spectra indicate quite large rotational strengths of *d*–*d* transitions. Although the reasons for the unusually effective asymmetrising influence of the ligand are not altogether understood [67], the optical activity may be supposed to be due mainly to the vicinal contribution, which merits the closest attention and study.

In view of the important part played by the vicinal effect it is undoubtedly useful in all cases to break down the observed curve of dispersion of optical rotation or circular dichroism into individual contributions, since it will give a clearer idea of several of the finer structural features of the molecules of complex compounds. Furthermore, in individual cases it is possible by means of the curves representing the vicinal effect to obtain a clearer resolution of the components of the *d*–*d* bands than when curves representing the configurational or the total effect are used [68].

2. Conformational Contribution

A consequence of the non-planarity of diamine and certain other chelate rings is the possible formation of at least two conformers of ions of the type *D*-$[Co\,am_3]^{3+}$. [69,70] In the most stable of them, denoted since Bailar's time as *Dkkk* or lel, all the C–C bonds of the carbon skeleton of the diamines are parallel to the axis of the C_3 complex, and a methyl group (e.g. in *laevo*-propylenediamine) is in the equatorial position. In the less stable isomer *Dk'k'k'* or ob the C–C bonds are oblique. Recently the symbols δ and λ, and also *p* and *m*, have been used most frequently in conformity with the *k* and *k'* notation for enantiomers (IVa, b). [71]



(IV)

However, the situation is evidently not so simple, as is shown by a recent theoretical calculation of conformational energies for ethylenediamine, propylenediamine, and *N*-methylethylenediamine. With ethylenediamine several energetically equivalent symmetrical and unsymmetrical conformations of minimum energy proved to be possible besides the two conformations (δ and λ) recognised by modern theory. Introduction of a methyl group attached to a carbon atom (in propylenediamine) or to a nitrogen atom (in *N*-methylethylenediamine) greatly restricts the number of possible conformations, owing to their strong steric inteacction.

The existence of two principal conformers has been brilliantly confirmed by the X-ray examination of a series

of optically active coordination compounds [43]. It is interesting that, not only the solid state but also in solution, even at room temperature, the predominant conformation of the (−)-propylenediamine chelate ring is the λ-gauche form. This has been shown by a study of the nuclear magnetic resonance spectra of certain platinum(II), palladium(II), and cobalt(III) bis-complexes [73].

Inspection of the literature indicates that the conformational effect of a ligand in a chelate ring depends mainly on the degree of distortion of the latter, on its departure from planarity. In a series of trisdiaminecobalt(III) complexes, for example, the increase in intensity of the circular dichroism bands in the series of ligands—en < pn < chxn—corresponds to the sequence of increasing distortion of the chelate ring by the substituents [74]. The spatial requirements of the ligands increase in the same sequence, and limit the number of possible conformers owing to the sharp increase in the energy differences between them. The diminution in conformational mobility leads to a smaller mutual extinction of the contributions from individual conformations, and hence an increase in intensity of the bands in the circular dichroism spectrum.

The conformational effect, together with the vicinal effect, which is difficult to separate from it, constitutes the basis of the optical activity of *trans*-biscomplexes, such as e.g. *trans*-$[RhCl_2(R\text{-pn})_2]Cl$ and $Na[RhCl_4R\text{-pn}].H_2O$. [75] The Cotton effect in the former complex is double that in the latter, in proportion to the number of chelate rings in the molecule.

An interesting system for studying conformational effects is provided by Schiff bases obtained from optically active diamines and aromatic *o*-hydroxy-aldehydes or -ketones. Examination of the optical rotatory dispersion and the circular dichroism of complexes of copper(II) and nickel(II) with quadridentate Schiff bases of general type $[MSal_2(-)\text{-pn}]$ revealed that the addition of a methyl group to the azomethine carbon atom results in inversion of the signs of the dichroic bands in the region of d–d transitions and a substantial increase in their intensity [76]. Inspection of molecular models showed that, whereas in complex ligands based on aldehydes the δ-conformation of the central diamine chelate ring, with a pseudo-equatorial position of the methyl group of the (−)-propylenediamine, is the preferred conformation, *o*-hydroxyacetophenone gives preference to the (axial-methyl) λ-conformation owing to steric interaction of the two methyl groups. The reversal of sign of the Cotton effect indicates a displacement of the conformational equilibrium $\delta \rightleftharpoons \lambda$ in favour of the latter. It is important to note that the absolute configuration of the diamine plays no part: i.e. the conformational effect predominates greatly over the vicinal effect [76].

Metal complexes of Schiff bases obtained from (−)-*trans*-cyclohexane-1,2-diamine and (−)-propylenediamine provide another example of the predominance of the conformational over the vicinal effect. The circular dichroism spectra of the two series of complexes are enantiomeric, although the configurations of the diamines are the same, RR and R respectively, so that their vicinal contributions have the same sign. The reason for the reversal of sign of the Cotton effect is that the δ-conformation is fixed in the case of the cyclic diamine, whereas the equilibrium in the second case is displaced in favour of the λ-conformation owing to steric interaction between the methyl group of (−)-propylenediamine and the radical R attached to the azomethine carbon atom. The shift in the equilibrium is greater the more bulky the substituent in the R–C(H)=N group. The decrease in such steric interactions in systems containing five-membered chelate rings formed by Schiff bases with pyrrol-2-aldehyde leads to complete similarity of the circular dichroism spectra of complexes based on the two diamines—(−)-propylenediamine and (−)-*trans*-cyclohexane-1,2-diamine [77].

Chelate rings formed by amino-acids were regarded for a long time as almost flat. However, X-ray examination revealed a slight departure from planarity, e.g. in $[Cu(D\text{-ala})_2]$. [78,98] A consequence of the almost planar character of such chelate rings is a marked decrease in their conformational contribution [79,90].

The construction of Dreiding models reveals that even these slight departures of the chelate ring atoms from planarity makes the *k*-conformation of the chelate rings more stable in $[Co(L\text{-ala})_3]$, in which the N–C–C–O chain forms a segment of a left-hand helix, while the methyl groups become quasi-equatorial, which diminishes their mutual steric repulsion [81]. In the *k*′-conformation a bulky substituent occupies an axial position, and the stability of such a conformer is lowered.

Even with greatly flattened amino-acid chelate rings the conformational contribution greatly predominates over the vicinal effect. This has been shown especially successfully by Wellman [82,83], who investigated mixed amino-acid complexes of bivalent copper of general composition Cu : gly : L-aa = 1 : 1 : 1. By displacing the equilibrium $\delta \rightleftharpoons \lambda$ towards the more stable δ-conformer (quasi-equatorial), e.g. by introducing bulky substituents R into the amino-acid or by fixing the second possible conformation λ (quasi-axial) by means of apical interactions of a third donor group with the metal in terdentate amino-acids such as L-histidine and L-$\alpha\gamma$-diaminobutyric acid, this worker demonstrated a reversal of sign and a change in magnitude of the Cotton effect depending on the conformation of the chelate ring, irrespective of the absolute configuration of the ligand, which remained constant.

Thus published results indicate that, of the two effects discussed here—the C*-vicinal and the conformational effects—the latter usually predominates strongly both in diamine and in amino-acid complexes. The vicinal effect of donor atoms (N*, S*) is probably comparable with it in magnitude.

3. Additivity of Contributions and Their Separation

All three effects discussed above—configurational, conformational, and vicinal—are essentially additive, and this applies to the most varied optically active coordination compounds, including various types of chelate rings and different metal ions [80].

The additivity of the contributions makes it entirely legitimate and justified to separate the overall curve observed—of optical rotatory dispersion or circular dichroism—into components corresponding to the individual contributions. The differential curves thus obtained are far more useful for discussing specific details of molecular structure than is the overall spectrum, which represents several such properties. For example, the C*-vicinal effect is uniquely useful for determining the absolute configuration of a coordinated ligand. No error is involved in using the observed spectrum—comprising configurational, conformational, C*-vicinal, and sometimes N*-vicinal contributions—only provided that all the contributions have the same sign, so that sometimes this method cannot guarantee freedom from errors.

Study of the conformational features of a ligand can reasonably start from the curves of the conformational contributions. However, the overall chirality of a com-

plex can be deduced absolutely rigorously only from the purely configurational effect.

Graphical methods are used to isolate individual contributions from the overall curve which is observed. This is effected most simply and conveniently by comparing the circular dichroism spectra with the optical rotatory dispersion curves.

When the circular dichroism spectra of the (+)- and (−)-$[Co\,en(laevo\text{-}pn)_2]^{3+}$ ions are added, for example, the configurational effects for right-hand and left-hand helices, equal in magnitude and opposite in sign, cancel each other out. The resultant curve represents the vicinal effect of four optically active coordinated ligands, and its reduction to one-quarter gives an idea of the vicinal effect of one *laevo*-propylenediamine chelate ring [70]. Subsequent subtraction of the vicinal effects of one, two, or three *laevo*-propylenediamine groups from the experimental circular dichroism spectra of the complex ions—(+)-$[Co\,en_2 laevo\text{-}pn]^{3+}$, (+)-$[Co\,en(laevo\text{-}pn)_2]^{3+}$, or (+)-$[Co(laevo\text{-}pn)_3]^{3+}$—will yield curves of the configurational contribution which, as was to be expected, are closely similar in form and amplitudes of the Cotton effect and resemble the circular dichroism spectrum of the (+)-$[Co\,en^3]^{3+}$ ion, whose optical activity is a consequence of the helical arrangement of the chelate rings [70].

Here, as in papers by many other authors, the vicinal effect includes the conformational effect as well as the actual vicinal effect of the asymmetric carbon atom in the diamine. The two contributions are difficult to separate, since the absolute configuration of the diamine determines the preferred conformation of the chelate ring which it forms.

The additivity of the configurational and the vicinal contributions has been shown in a similar manner, and they have been separated for complexes of the type $[Co\,aa\,en_2]X_2$, where D- and L-alanine, D- and L-leucine, and L-phenylalanine have been used as the amino-acid [84]. The good agreement between the circular dichroism spectra of complex compounds simulating individual contributions and the differential curves of these effects obtained by graphical methods can be regarded as proof of additivity. The configurational effect is represented separately in resolved complexes with optically inactive ligands, e.g. in $(+)_{546}$-$[Co\,gly\,en_2]I_2$, and the vicinal effect in racemic complexes with optically active ligands, e.g. in $[CoL\text{-}phala(NH_3)_4]I_2$. The latter contribution may be expressed also by the sum of the circular dichroism spectra of $(+)_{546}$- and $(-)_{546}$-$[CoL\text{-}leu\,en_2]^{2+}$.

Subtraction of the circular dichroism spectrum of the unresolved complex ion (±)-$[CoL\text{-}phala\,en_2]^{2+}$ from the corresponding curves of each enantiomer yields curves which are mirror images of one another and represent the pure configurational contributions of the two helices of opposite chirality. As was to be expected, these calculated curves are closely similar to the circular dichroism spectra of (+)- and (−)-$[Co\,gly\,en_2]^{2+}$ ions, which do not contain a vicinal contribution [84].

As a consequence of the additivity of the contributions the circular dichroism spectrum of $(-)_{546}$-$Ba[Co\,ox_2L\text{-}ala]$ is well reproduced by adding the circular dichroism curves of $(-)_{546}$-$Ba[Co\,ox_2gly]$ (the configurational contribution alone) and unresolved $Ba[Co\,ox_2L\text{-}ala]$ (the vicinal contribution alone). [85]

Nor are the circular dichroism spectra of dextrorotatory and laevorotatory isomers mirror images of one another with tris-amino-acid complexes of cobalt(III), owing to the additional asymmetry of the α-carbon atom of the α-amino-acid, i.e. the presence of a vicinal effect. The two contributions were shown to be additive, and they were separated for complexes with D- and L-alanine [86], L-leucine, and L-proline [67].

Configurational and vicinal contributions are additive also in the case of mixed complexes of the type $[CoL\text{-}aaL\text{-}aa']$ [87], although the considerable increase in steric hindrance in the presence of bulky side-chains, e.g. in L-valine, produces some divergence between observed and calculated curves [88].

The vicinal contributions of different optically active ligands in the same molecule of a complex are also additive and independent, as was shown in a study of a series of complex ions of general type *trans*-(*N*)-$[Co\,alada\,aa]$. [87]

In systems which are not complicated by strong steric interactions the vicinal contributions of several asymmetric centres in the same molecule of a multidentate ligand, e.g. an oligopeptide, are also independent. Evidence of their additivity is the excellent agreement between the observed value of $\Delta\epsilon$ for one of the *d*–*d* transitions of the nickel(II) complex of the tripeptide L-ala-L-ala-L-ala (−2.10) and the sum of the $\Delta\epsilon$ values for the complexes with gly-gly-L-ala, gly-L-ala-gly, and L-ala-gly-gly ($\Sigma\Delta\epsilon = -2.08$). [89]

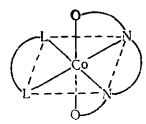
The general rule extends also to the ratio of two—N* and C*—vicinal contributions. In fact the circular dichroism spectrum of $[CoN\text{-}CH_3\text{-}L\text{-}ala(NH_3)_4]^{2+}$ can be reproduced fairly satisfactorily by adding those of the ions $[CoL\text{-}ala(NH_3)_4]^{2+}$ and $(-)_{546}$-$[Co\,sar(NH_3)_4]^{2+}$, representing the vicinal contributions due to the C* and N* centres respectively. The slight discrepancies between the observed and the calculated curve can be explained by the proximity of these two centres and the possibility of some interaction between them [90].

Although the configurational effect and the vicinal effect are far more difficult to separate on the optical rotatory dispersion curves, owing to the more complicated character of the overlapping of individual sigmoid components (inversion curves) corresponding to each optically active absorption band, such work has been undertaken by Japanese [sic] workers [68,91]. From a consideration of the series of complexes—*dextro*-$[CoL\text{-}leu\,en_2]Cl_2$, $[CoL\text{-}leu(NH_3)_4]ClO_4$, *dextro*-$[CoClNH_3en_2]Br$, and *dextro*-$[Co\,en_3]Br_3.2H_2O$—Shimura concluded that the highest molecular rotations in the first of these complexes are due to the fact that the asymmetry about the central metal atom (i.e. the configurational effect) makes a more substantial contribution to the optical rotatory dispersion in the region of *d*–*d* bands than does the asymmetric carbon atom of the coordinated ligand (the vicinal effect). [91]

In this as in most of the investigations mentioned previously the conformational effect was not considered in isolation but together with the vicinal effect. The difficulties of their separation makes even more valuable the use [92] of three complex ions—resolved *cis**-$[CoCl_2^*(NH_3)_2^*en]^+$, unresolved *cis**-$[CoCl_2^*(NH_3)_2^*(-)\text{-}pn]^+$, and optically pure *cis*-$[CoCl_2en_2]^+$—as model compounds in measurement of circular dichroism spectra. In each case the optical activity of the complex is due to mainly one cause—the conformational, vicinal, or configurational effect respectively. The rotational strengths of all three compounds in the same region of *d*–*d* transitions are of the same order of magnitude, although the vicinal effect makes the smallest contribution, and the configurational effect the largest [92].

Isolation of the vicinal contribution from the observed circular dichroism or optical rotatory dispersion spectra has permitted the investigation of the effect of interaction between ligands on the vicinal effect exhibited by the same

ligand in different types of complexes. In effect this work gives indirect information on the conformational component of the total vicinal contribution.



(V)

For example, determination of the vicinal effect of *laevo*-propylenediamine in complexes of the type *trans*-[CoEDDA(LL)]$^+$ (V: LL = en, *laevo*-pn) showed it to be insignificant, contrasting with the fairly large vicinal effect of this ligand in the $[Co(laevo\text{-}pn)_3]^{3+}$ ion [70]. Yet the curves of the vicinal effects of L-alanine in complexes of the type (V: LL = L-ala) and [CoL-ala$_3$] have the same form and differ little in the magnitude of the Cotton effects. Such differences in the behaviour of the two ligands—*laevo*-propylenediamine and L-alanine—when they pass from one type of complex to another are explained by the substantial change in the environment from almost planar amino-acid to distorted diamine chelate rings in the case of *laevo*-propylenediamine, whereas with L-alanine the environment remains almost unchanged [45].

Interligand interactions of this kind probably depend significantly on stereochemical aspects of the environment of the β-carbon atoms in the amino-acids [58].

Thus for the optical activity of d–d transitions in coordination compounds the additivity of the three principal contributions—configurational, conformational, and vicinal—can be regarded as a general rule. The individual contributions can be arranged qualitatively in the sequence —configurational > conformational $\simeq$ N*-vicinal > > C*-vicinal—according to their effect on the intensity of the Cotton effect in this region, which in general yet again emphasises the validity and universality of Chugaev's vicinal rule.

The situation is somewhat more complicated when we consider the optical activity of charge-transfer transitions. Although the individual contributions to the rotational strength of these transitions are additive even in this case, information on the relative roles of each of them is contradictory.

The circular dichroism of trisdiaminecobalt(III) complexes in the visible region (d–d transitions) is an indication mainly of the stereochemistry of the chelate rings arranged about the metal ion (configurational effect). [93] Several investigations suggest that the sign and the amplitude of the Cotton effect due to charge-transfer transitions in the ultraviolet region are given by the sum of the conformational and the configurational contribution, where the former is strongly predominant [39,71,94]. Such predominance was deduced from the fact that the sign of dichroic bands in the region of charge-transfer transitions is determined in many cases solely by the chirality of the diamine chain, irrespective of the absolute configuration of the chelate rings about the metal ion [95]. The presence of both contributions—conformational and configurational—was assumed from a consideration of the optical activity of trisdiamineplatinum(IV) complexes in the region of charge-transfer transitions [96].

The exactly opposite conclusion was reached by Japanese workers [97]. From the opposite signs of the circular dichrosim in charge-transfer transitions ($\sim$ 215 nm) for (+)- and (–)-$[Copn_3]^{3+}$ ions having opposite configurations they assumed that the configurational effect is strongly predominant at shorter wavelengths, whereas the vicinal effect predominates at longer wavelengths.

Although the factual information is clearly insufficient to settle this question finally, the conclusions of the first group of investigators seem more reasonable. Actually, Chugaev's vicinal rule indicates that the asymmetry of the metal should determine the optical activity of the internal transitions in the metal (d–d) to a greater extent than transitions of the metal–ligand type (charge-transfer transitions). And conversely, the chirality of an individual chelate ring in the ligand should play the more important part for these latter transitions.

The resolution of the experimental curves representing optical rotatory dispersion and circular dichroism into differential curves corresponding to the individual contributions to the rotation is of undoubted practical value, since it will permit a more correct exploitation of the opportunities offered by spectropolarimetry.

For example, a well known method for determining the absolute configuration of chelate complexes of metals involves comparing their rotatory dispersion or circular dichroism curves with the spectra of complexes whose absolute configuration has been established by means of X-rays. It is quite obvious that, since the configuration of the central metal atom affects only the configurational contribution, the vicinal effects of optically active ligands must be subtracted from the total curve to avoid errors.

On the other hand, vicinal curves obtained by subtracting the configurational contribution from the experimental curve are closely connected with the absolute configuration of an optically active ligand and may provide a means for its determination. Thus the curves of the vicinal effect for *laevo*-propylenediamine and L-alanine have the same general shape, but are mirror images of one another. From this it was concluded that these molecules had opposite absolute configurations [45].

IV. GEOMETRICAL ISOMERISM

Geometrical isomerism is another factor influencing the optical activity of coordination compounds. The elucidation of some generalisations in this field is not only of intrinsic value but also useful as a means for detecting and characterising such phenomena in new systems.

Geometrical isomerism arises in complex compounds of bidentate ligands when the latter are of the unsymmetrical type AB. The possibility of two *cis*- and *trans*-isomers is already apparent in bisamino-acid complexes, although it is rarely taken into account owing to the substantially greater stability of the *trans*-isomer. It is especially interesting that *cis*-[Cu(D-ala)$_2$] has recently been isolated in the solid state, and its structure has been analysed by means of X-rays [98]. However, comparison of the circular dichroism spectra of crystals and solutions of complexes of similar types with other amino-acids showed that the predominant isomer in solution is nevertheless the *trans*-isomer [99].

With amides of amino-acids such geometrical stereospecificity was not so rigorous, and both isomers—*cis* and *trans*—could be isolated in the case of the nickel(II) and palladium(II) complexes of these ligands. The structure of each isomer was assigned on the basis of a study of the effect of solvents on the magnitude, sign, and position

of certain components in the circular dichroism spectrum [100].

The possibility of two geometrical isomers—meridional (mer or 1,2,6) and facial (fac or 1,2,3)—is well known for the trisamino-acid complexes of cobalt(III), rhodium(III), and other metals. Every possible geometrical and optical isomer has been isolated e.g. in the case of the alanine complex $[Co(L\text{-}ala)_3]$. [101]

The differences in the spectropolarimetric behaviour of geometrical isomers are due to their belonging to different symmetry types, resulting in different ways of splitting the bands characteristic of O_h symmetry. For example, the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition is split into two components—of A_2 and E symmetry—in the β-isomers, but into three components—of A_2, B_1, and B_2 symmetry—in the less symmetrical α-isomers. In conformity with this the violet α-isomer of the complex $[Co(L\text{-}ala)_3]$ gives three extrema in the region of the T_1 band in the circular dichroism spectrum, whereas the red β-isomer gives two dichroic components of opposite sign in the same region [81]. The assignment of structures to the α- and β-isomers is supported by nuclear magnetic resonance spectra [67].

Each geometrical isomer exists as two optical isomers, in which the chelate rings are arranged in opposite helices about the metal ion [102]. Thus the total number of isomers of trisamino-acid complexes is increased to four, although this may be greatly diminished by steric hindrance. Thus coordination of the L-prolinate ion yields only one isomer, the fac-Λ-isomer, whose structure has been established by the combined application of electronic spectra, optical rotatory dispersion, and circular dichroism. Similar geometrical and optical selectivity has been observed also with L-hydroxyproline [103].

With terdentate amino-acids the number of geometrical isomers which are theoretically possible is increased to three, each of which occurs as two enantiomers in which the chelate rings are arranged in opposite spirals about the metal atom. Here too, however, steric hindrance reduces the total number of geometrical and optical isomers—to three in the case of D- and L-aspartic acid [104].

Such a terdentate ligand as $\alpha\beta$-diaminopropionic acid, on coordination with cobalt(III) to form a bis-complex, is able theoretically to give five geometrical isomers, three of which are possible only when the two ligands in the complex molecule have the same absolute configuration. In fact it has proved possible to isolate all five isomers with the DL-acid and three isomers with each optically active ligand (D and L). [105]

Geometrical isomerism has hitherto been ignored in connection with bis- and tris-hydroxymethylenecamphor complexes, although the molecule of the chelated ligand has no second-order axis of symmetry and belongs to the AB type of ligands. The most stable was the 1,2,3-isomer, whose structure was confirmed by measuring the nuclear magnetic resonance spectra [106].

Complexes of multidentate ligands of polyamine type [107,108], whose chemistry has been actively developed during recent years, are especially interesting for the investigation of geometrical isomerism. The topology of the coordinated ligand can be in considerable measure controlled by introducing substituents into different parts of the molecule, and the substantial differences in the circular dichroism and optical rotatory dispersion spectra of the various geometrical isomers make these methods, together with nuclear magnetic resonance spectroscopy, especially valuable for structure assignments to individual isomers. However, the number of publications on this topic has recently increased so greatly that the stereochemistry of complexes of multidentate ligands may constitute a subject for a special review.

V. OUTER-SPHERE COORDINATION

The first observations that the molecular rotation of ions of dissymmetric metal complexes depends on the properties of the gegenion were made by Werner as early as 1912. [109] In general this effect is not very large in comparison with those already discussed, but in some cases it plays an important part. An example is the almost tenfold increase in intensity of the dichroic bands due to the (+)-$[Co\,en_3]^{3+}$ ion produced by its outer-sphere interaction with nitrosonaphthoxide ions. The probable reason is strong interaction of the formally forbidden d–d transitions with the charge-transfer transitions which appear on outer-sphere coordination, from which the d–d bands obtain most of their intensity [110].

Most work in this field has been done on the effect of optically inactive ions on the rotatory dispersion or the circular dichroism of optically active complex ions. It is interesting that different transitions are subject to this effect in different degrees depending on their symmetry. Thus the intensity of the positive dichroic maximum corresponding to the $^1A \rightarrow {}^1E_a$ transition in the complex $(+)_{546}$-$[Co\,en_3]Cl_3$ is increased by the addition of all electrolytes other than trisodium orthophosphate, which diminishes the intensity. The negative peak in the circular dichroism spectrum of the same complex ion ($^1A \rightarrow {}^1A_2$ transition) increases in intensity in the presence of all electrolytes, and the orthophosphate anion produces the maximum effect [111].

The effects of trigonal and tetrahedral anions on the optical activity of octahedral complexes of diamines are quite regular. Increase in the concentration of such anions in solution leads in general to a decrease in the rotational strength R of the E_u transition, a compensating increase in that of the A_2 transition, an increase in the rotational strength of the E_g band, and the appearance of a new dichroic component caused by charge transfer from anion to cation.

Quantitative analysis of this latter band has demonstrated the formation in solution of a 1 : 1 ion-pair with complex ions such as (+)-$[Co\,en_3]^{3+}$ and (+)-$[Co(+)\text{-}pn_3]^{3+}$. The main factor in the structure of such an outer-sphere complex is assumed to be a system of hydrogen bonds involving the NH groups of the coordinated diamine molecules [112]. The fact that a similar 1 : 1 outer-sphere complex is not formed with the (−)-$[Co(+)\text{-}pn_3]^{3+}$ ion can be regarded as indirect confirmation of this suggestion. The reason for the marked differences in behaviour of complexes of (+)-propylenediamine having opposite absolute configurations may be the enantiomeric character of the conformations of the chelate rings, only one of which [in the (+)-complex] enables three NH groups to lie in the same direction, parallel to the C_3 axis and convenient for the formation of three NH...X hydrogen bonds with an anion located on the C_3 axis [112].

As a result of this advantage of one of the two conformations the association constants of the lel-$[Co(\textit{dextro}\text{-}pn)_3]^{3+}$ ion were significantly higher than those for the ob-isomer. For example, the values on interaction with the SO_4^{2-} ion were respectively 70 and 43, with *dextro*-$tartr^{2-}$ 30 and 7, and with *laevo*-$tartr^{2-}$ 28 and 16. [113] The differences in the behaviour of *dextro*- and *laevo*-tartrate ions are explained by different relative configurations of the

$^{-}OCO-C-C-COO^{-}$ chain, on its outer-sphere coordination through the two carboxy-groups [114].

The dimeric complex $[Co_2(L\text{-}amO)_3(L\text{-}amOH)_3]^{3+}$ represents a type of association which is rather more complicated than that described above. It is formed by three O–H...O hydrogen bonds between coordinated amino-alcohol molecules L-amOH and their anions $L\text{-}amO^{-}$. [115]

However, the number of possible outer-sphere complexes is not restricted to 1 : 1 products. The above change in the rotational strengths of the components of an octahedral T_{1g} transition is entirely regular for complex ions of many metals—cobalt(III), chromium(III), rhodium(III)—and several anions, such as arsenate, phosphate, selenite, thiosulphate, etc. [116] However, the sign of this effect may be reversed when the concentration of the anion rises above a certain limit. Larsson and his coworkers used similar changes in the circular dichroism spectra to determine formation constants for a series of outer-sphere complexes of general type ML_n, where n = 1–4 when L represented the thiosulphate ion, and n = 1, 2 for the hexacyanoferrate(II) ion. The presence of a maximum effect in the 1 : 1 and 1 : 3 complexes was explained by the fact that formation of a centrosymmetric outer coordination sphere leads to the smallest change in optical activity of the complex cation with even values of n. [117]

In some cases an abrupt change in the circular dichroism spectra is observed only in the third-stage of the formation of outer-sphere complexes, e.g. with *dextro*-$\{[Co\,en_3](SeO_3)n\}^{3-2n}$, [118] or at the third and fourth stages [119].

Analysing possible mechanisms of the effect of outer-sphere coordination on the optical activity of complex ions, Larsson considers that the direct effect of anions on the *d*-orbitals of the metal would be quite small in comparison with the effects observed with inner-sphere coordination. It is most probable that the effect of outer-sphere coordination is indirect—through the mixing of *d*–*d* transitions with the very intense charge-transfer transitions which then arise [117,119].

A second aspect of the same problem is the effect of cations on the optical activity of complex anions. In a study of the molybdate complexes of tartaric and mandelic acids Brown observed that increase in the concentration of simple singly charged alkali-metal cations in the solution was accompanied by an increase in the optical activity, which reached saturation at a certain stage [120]. According to their relative effectiveness the metal ions can be arranged in the sequence

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$

which is also the sequence of diminishing cationic radius [120].

In order to ascertain which characteristic of an optically inactive ion governs its effect on the optical rotatory dispersion of a complex ion, Albinak [121] made a detailed comparative investigation of the effectiveness of anions (F^-, Cl^-, Br^-, I^-, PF_4^{3-}, SO_4^{2-}, PO_4^{3-}) and cations (Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}) for a series of salts of two optically active cations (*laevo-cis*-$[Co\,ox\,en_2]^+$ and *laevo*-$[Cr\,en_3]^{3+}$) and two anions (*dextro*- and *laevo*-$[Rh\,ox_3]^{3-}$). Comparison of the rotatory dispersion curves within a series showed a clear tendency for the intense long-wavelength rotation maximum to vary with the ratio of ionic charge to ionic size (i.e. the ionic potential) and the polarisability of the optically inactive ion. The plot of molecular rotation against ionic potential is a straight line [121].

A second possibility—coordination of an optically inactive complex ion with an optically active gegenion—has been far less investigated. Mason studied the outer-sphere coordination of hexa-amminecobalt(III) in aqueous solution containing excess of the (+)-tartrate ion, (+)-tartaric acid, or (+)-diethyl tartrate. A completely unexpected result of this work was the discovery of a appreciable Cotton effect in the region of the $^1A_{1g} \rightarrow {}^1T_{1g}$ band, exceeding in magnitude the effect induced in this band by inner-sphere unidentate and even bidentate coordination of the same ligands in the complex ions $[CoL(NH_3)_5]^+$ and $[CoL(NH_3)_4]^+$ respectively. The Cotton effects accompanying inner-sphere and outer-sphere coordination are of opposite sign. The reason for this effect is supposed to be orientation of the species on the surface of the complex ion without elements of symmetry [122].

A similar phenomenon has been noted in the systems formed by the hexa-amminecobalt(III) ion with (–)-α-methylbenzyl acetate [123] and by the tetrachloroplatinate(II) ion with *dextro*-butane-2,3-diol [124].

Outer-sphere coordination is obviously also the cause of the Pfeiffer effect (change in the rotatory dispersion of certain optically active organic compounds, e.g. *dextro*-α-bromocamphor-π-sulphonate and *dextro*-tartaric acid, in the presence of racemic mixtures of certain optically active coordination compounds, e.g. DL-$[Zn(o\text{-}phen)_3]$). This effect was the subject of a recent review by Kirshner [6], and therefore will not be discussed here.

Thus the progress made in recent years in research on optically active coordination compounds gives grounds for hoping that the application of circular dichroism and rotatory dispersion to inorganic chemistry will become increasingly effective, and provide inestimable help in the investigation of those finer aspects of the spectroscopy and the structure of complex molecules to which other present-day methods are insensitive.

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