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SOME APPLICATIONS OF CIRCULAR DICHROISM MEASUREMENTS TO PROBLEMS IN METAL ION COMPLEXES, USING Ni^{II} AND LANTHANIDES AS EXAMPLES*

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A. INTRODUCTION

It has been known since 1832 that not only did certain organic compounds of biological origin, such as tartaric acid, rotate the polarization plane of light, but that a marked alteration in rotatory dispersion properties was found when these substances were incorporated into compounds with an inorganic material, *e.g.*, tartaric acid with boric acid[1]. It was demonstrated by Cotton almost 75 years ago that when tartaric acid reacts with colored metal ions such as Cr^{III} or Cu^{II}, the absorption bands characteristic of the metal ion now demonstrate an unequal absorption for right- and left-circularly polarized light, a phenomenon named circular dichroism (CD)[1]. In these bands there is also a characteristic pattern for the rotatory dispersion, which is called the Cotton effect, and there exists in fact

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a mathematical relation between these two equivalent, though different, expressions of the same physical phenomenon.

It was pointed out by Cotton that the CD induced in metal complexes represented a consequence of covalent binding. Lesser forms of interaction, such as simple propinquity in solution, were incapable of activating dichroism in the metal ion absorption. In other terms, it results from incorporating the metal ion chromophore into an optically active unit through binding it to an optically active ligand. This fundamental message has apparently had to be repeated at various times (*e.g.*, Ref. 2). Two correlates have also had a varied history—that the influence of an optically active ligand on the metal ion is not restricted to some fixed relative position of an "asymmetric carbon" and the metal ion (*e.g.*, in a chelate ring), and that ligands need no more than a single ("monodentate") bond to induce some degree of dichroism in the metal ion absorption.

Our original aim was to apply the above CD relations in an attempt to map the factors which determine the responses of the metal ion spectrum to the asymmetric field introduced by binding the metal to the optically active ligand. Experience with the technique showed that it represented an almost unique indicator for certain fine details of the chemistry of the systems, and to some degree, of structural details, even before theoretical spectroscopic relations may be fully unravelled.

Some of the technical relations which underlie the usefulness of the method may be outlined as follows With modern recording instruments, one is able to follow the CD spectrum directly in the absorption bands of interest, free of the background from other parts of the spectrum, or in general from the reagent itself, which inevitably accompanies rotatory dispersion studies. One is also free of the ambiguities of interpreting overlapping Cotton effects, and of resolving them from the background It has also turned out in the course of the work that the resolution and separation of components in the CD spectrum are generally better than in the ordinary absorption spectrum. This is a combination of various factors: the dichroic ratio ($\Delta\varepsilon/\varepsilon$) varies between components of a band, giving a different perspective than that of the absorption envelope; the neighboring components may be of opposite sign (either the right- or the left-circularly polarized beam may be absorbed the more strongly); and there exists a definitely greater sharpness in the dichroic components, which implies a selection between the contributions of different rotational states. Technical limitations in the application of the technique, other than spectral range (195–800 nm is the present reasonable maximum for commercial instruments), are principally the limitation of maximum optical density of 2.5–3 through which measurements can effectively be made, and detection sensitivity approximating 1×10^{-5} optical density units. Allowing for increased noise and decreased sensitivity above optical density 2, a value of about 1×10^{-5} represents an order of magnitude for measurable $|\Delta\varepsilon/\varepsilon|$. For contrast, the largest $\Delta\varepsilon/\varepsilon$ value that the author has encountered[3] (for

a spectral component in the 300-nm region absorption of 3-methyl pentanone vapor) is about 0.25.

There is a body of literature, deliberately not cited in this summary, which deals primarily with stable or robust complexes, of Co^{III}, Cr^{III}, and various heavier elements. The largest part of this is concerned with the isomeric asymmetry and optical activity consequent to *tris*-chelation of six-coordinate ions (*bis*-chelation for four-coordinate species). When an optically active ligand is included, the presumed effects of the two sources of activity must be dissected out, which is at best difficult indeed. The approach chosen in the work reviewed here has been to attack first the effects of a variety of simple optically active ligands upon metal ions that equilibrate rapidly, and for which a variety of complexing relations (monodentate and chelate, single and multiple complexes) can readily be compared. One can also compare different coordination numbers. We have thus restricted our attention in this discussion to yield an independent body of information, which may in future be applied to the robust complexes and perhaps to the general problem of over-all symmetry effects.

In what follows, reference to α-, β- or γ-chelates means chelates formed through action of a functional group on the carbon atom α-, β- or γ- to the carboxyl group involved. These form respectively 5-, 6- and 7-membered chelate rings. Formulae of the amino acids are summarized in Table 1, and those for the hydroxy acids are shown in Fig. 1.

TABLE 1

AMINO ACID REAGENTS (ZWITTERION FORMS)

Alanine	$^-OOC-HC(NH_3^+)-CH_3$
Serine	$-CH_2OH$
Valine	$-CH(CH_3)_2$
Aspartic acid	$-CH_2-COOH$
Asparagine	$-CH_2-CONH_2$
Glutamic acid	$-(CH_2)_2-COOH$
Ornithine	$^-OOC-HC(NH_2)-(CH_2)_2-CH_2NH_3^+$
Arginine	$^-OOC-HC(NH_2)-(CH_2)_2-CH_2NH-C(=NH)-NH_3^+$

B. CHEMICAL USES

(i) Signal for bonding

The appearance of circular dichroism in the absorption of a metal ion is as definite an indicator that a new species has been formed as is the appearance of a new absorption band. With more than one potential ligand present (*e.g.*, NH_3, OH^-) it becomes a definitive confirmation that the optically active candidate

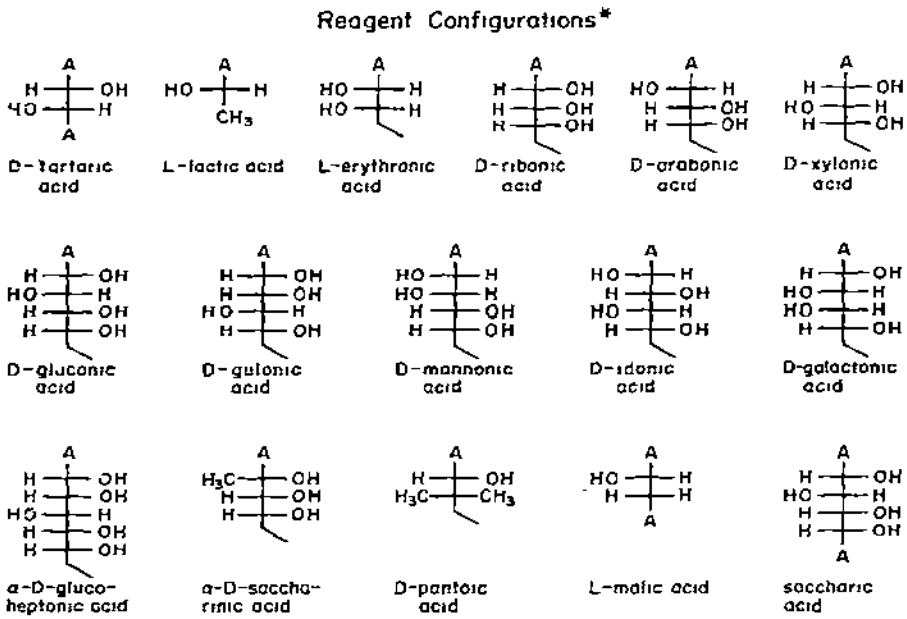

Fig 1 Structural configurations of hydroxy-acid reagents

is in fact bound. In certain cases, the absorption and the CD together give useful information. This may be exemplified in the interaction of Eu^{III} and alanine[4]. In the presence of the alanine zwitterion, the "hypersensitive" transition to the $^5D_2$ upper state of Eu^{III} is intensified several-fold over the simple water spectrum. This results from binding of the amino acid rather than, say, a change in water coordination state alone, as verified by the circular dichroism seen in the band at about 527 nm ($^5D_1$ upper state). Monodentate binding through the carboxyl group is present as seen in the CD change accompanying chelation at higher pH.

As another example[5], 0.16 M $NiCl_2$, with an equal concentration of L-lactic acid (pK 3.87), shows no CD in the Ni^{II} absorptions at 495 and 660 nm. Addition of concentrated NaOH, raising the pH to 3–4, promotes the presence of a definite CD in both absorptions. Attempts to achieve a higher pH precipitate the nickel. Twice the concentration of lactic acid gives approximately twice the CD intensity. More lactic acid increases the intensity somewhat further, and also makes it possible to obtain stable solutions at higher pH.

Similar pH-related variations of the onset and intensity of CD are found for other hydroxy-acids, and for the amino acids, with[5,6] Ni^{II} and with the rare earths (Pr^{III}[7,8] and Eu^{III}[4]) and have been tested in detail. It is also possible to demonstrate binding in the cases of certain favorable uncharged ligands. Experiments with nicotine and Ni^{II} have demonstrated interaction between these[9]. The

equilibrium conditions are less favorable for this demonstration in water than in alcohol. The test material has been both the simple salt (chloride, nitrate) and mono- and bis-chelates with optically inactive ligands.

(ii) Changes of species

Not all alterations in species or stoichiometry of complexes are accompanied by obvious absorption spectral indicators. The CD is usually, however, very sensitive to such changes Thus, for sugar acid chelates of, say, Ni^{II} there is no significant alteration in absorption spectrum between the acid-region form in which the hydroxyl group of the anion is coordinated as a whole, and the neutral-region form in which it has been deprotonated to give a doubly-charged ligand moiety[5]. The alteration is, however, signalled by a change in CD pattern (Figs. 2 and 3) and a considerable increase in CD component intensity. Similar relations are found in the rare earth complexes[4,7]. Sharp differences are also seen between mono- and bis-complexes (Figs. 4a, 5 and 6) and between monomeric and (pos-

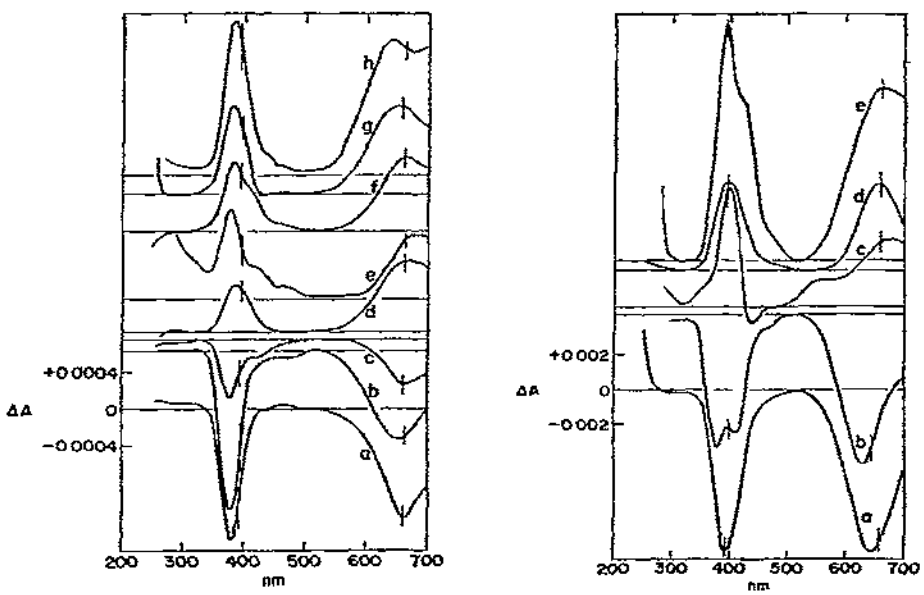

Fig. 2 CD spectra of low-pH complexes of Ni^{II} with hydroxy acids Ni^{II} about 0.16 normal, 10-mm cell Dichroism in absorbancy units, scale indicated Vertical bars, location of maxima of absorption bands (a) Lactic acid, 5 1, pH 7, (b) arabonic acid, 3:1, pH 7; (c) arabonic acid, 1.1.1, pH 6; (d) gluconic acid, 2 1, pH 4; (e) galactonic acid, 3:1, pH 6; (f) xylonic acid, 1 5.1, pH 6; (g) gulonic acid, 5.1, pH 3, (h) ribonic acid, 3 1, pH 6.

Fig 3 CD spectra of higher-pH (deprotonated) complexes of Ni^{II} with hydroxy acids. Ni^{II} about 0.16 normal, 10-mm cell. Dichroism in absorbancy units, scale indicated. Vertical bars, location of maxima of absorption bands (a) Ribonic acid, 1 25:1, pH 7, (b) gulonic acid, 3:1, pH 6–7; (c) arabonic acid, 1 1.1, pH 7 (scale multiplier, 0 5); (d) galactonic acid, 1 5.1, pH 7; (e) gluconic acid, 2.1, pH 7 (scale multiplier required, 0.2).

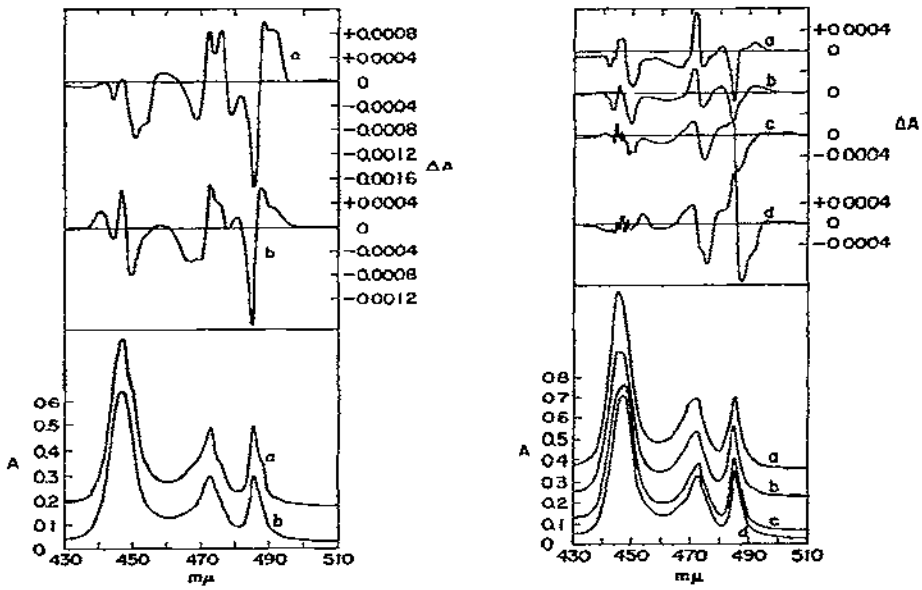

Fig 4 CD and absorption spectra, 430–510 nm spectral region, 1·1 complexes of Pr^{III} with (a) alanine and (b) asparagine CD pathlengths, 30 mm, absorption, 5 mm Pr^{III} *ca* 0 1 normal

Fig. 5. Alterations of CD and absorption spectra for 3·1 valine–Pr^{III} mixture, pH increasing from pH 7+ (a) to pH 8+ (d) At about pH 7, spectra would be those of Fig 4a. CD pathlengths, 30 mm; absorption, 5 mm

sibly) dimeric species[7]. In systems such as Eu^{III}–alanine[4], it is possible to follow the change from monodentate attachment through the carboxyl group to chelation through the carboxyl and amino groups, as the acid proton is titrated off of the $-NH_3^+$ group of the zwitterionic ligand

(iii) What groups of a polyfunctional ligand are used?

Aspartic acid in water tends to transfer a proton from one carboxyl (pK 2 0) to the α-amino group ($-NH_3^+$ pK 10.0), and only partially to ionize the second carboxyl group (pK 3.9)[10]. If one equivalent of NaOH is added to a 1:1 mixture of Ni^{II} with aspartic acid[6], the resulting pH is only 3.8, and it takes a full second equivalent to reach neutrality. The Ni–aspartic acid complex therefore involves a ligand with a bare amino group, as well as two ionized carboxyls. The binding can be deduced from the following accessory information. Ni^{II} with an equimolar concentration of alanine, serine, valine, arginine, or ornithine, in the pH range 4–7, shows essentially a single CD pattern (Fig. 6, a–e), which may be taken as the α-chelate pattern. The CD pattern of the aspartic acid complex is very different (Fig. 7d), so that complex is not the α-chelate. Asparagine, with a single carboxyl, like the simple amino acids, also gives a single titrable proton,

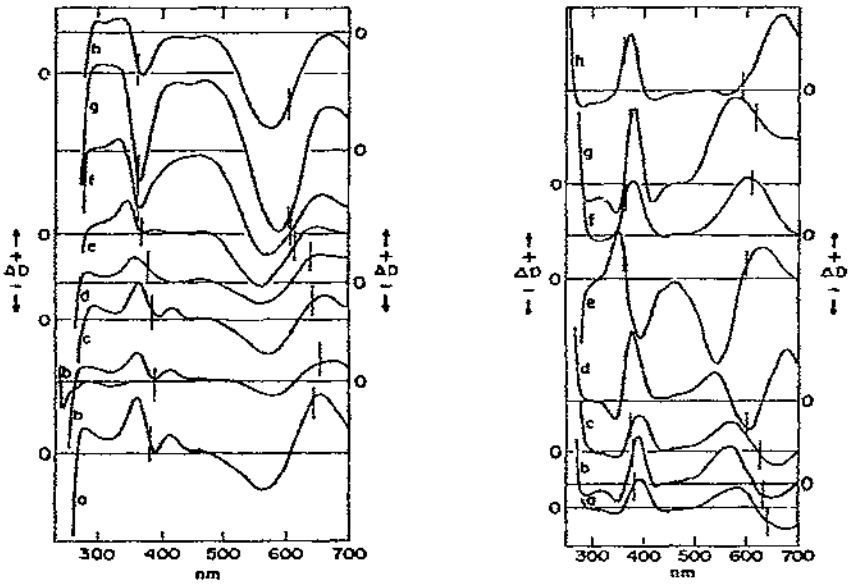

Fig. 6 CD spectra of Ni^{II}–amino acid systems Vertical bars indicate positions of maxima in the absorption spectra of the given solutions; (b'), (b), (a) valine–Ni^{II}, 1:1, at pH 3, 5, and 6, respectively; (c) arginine, 1:1, pH 6, (d) glutamic acid, 1·1, pH 6; (e) alanine, 2:1, pH 8, and (f) 3·1, pH 8; (g) arginine, 3:1, pH 7, (h) ornithine, 3·1, pH 7

Fig 7. CD spectra of Ni^{II} with asparagine and aspartic acid. Vertical bars indicate positions of maxima in the absorption spectra of the given solutions, (a) asparagine–Ni^{II}, 1·1, pH 4; (b) aspartic acid, 1 1, pH 6, (c) asparagine, 1 1, pH 8, (d) aspartic acid, 1·1, pH 9; (e) asparagine, 3·1, pH 8 and (f) 2 1, pH 7, (g) aspartic acid, 2.1, at pH 6, and (h) pH 10

but the 1·1 CD pattern is the aspartic acid CD pattern and not that of the simple acids. If the aspartic acid pattern were due to bidentate β-chelation, asparagine should not give the same relation, as the effect of the carboxyl α to the amino group should outweigh the weakly binding amide group, and result in α-chelation. One concludes that both aspartic acid and asparagine act as tridentate chelating ligands. A symmetry argument based on the number of components in the CD spectrum (see below) corroborates this and suggests further that the actual attachments are *cis*. Interestingly, glutamic acid, with one additional methylene group, gives the CD pattern of α-chelation. Manipulation of a model suggests that it might actually be very difficult to achieve tridentate chelation with the additional methylene intercalated.

In the Pr^{III}-amino acid system[8] we see another behavior. (As with the Ni^{II} example, the absorption spectra alone are not helpful). At about pH 6, 1:1 complexes with amino acid are found. The CD spectra for complexes with simple amino acids (alanine, valine) are sharp, relatively intense, and the same (Fig. 4). The serine and asparagine complexes give some modifications of this characteristic pattern, but are essentially indistinguishable from each other. Aspartic acid,

however, gives still a third CD spectrum, weak, and unaffected by high ratios of ligand except at quite elevated pH (Fig. 8). If the CD spectrum characterizing the serine and asparagine complexes differs from that of the simple acids because of tridentate chelation, as seems a possibility, then the same explanation seems improbable for the aspartic acid. The weakness of the CD for the aspartic acid complex, and the general behavior, suggests here the possibility of simply bidentate carboxyl–carboxyl chelation.

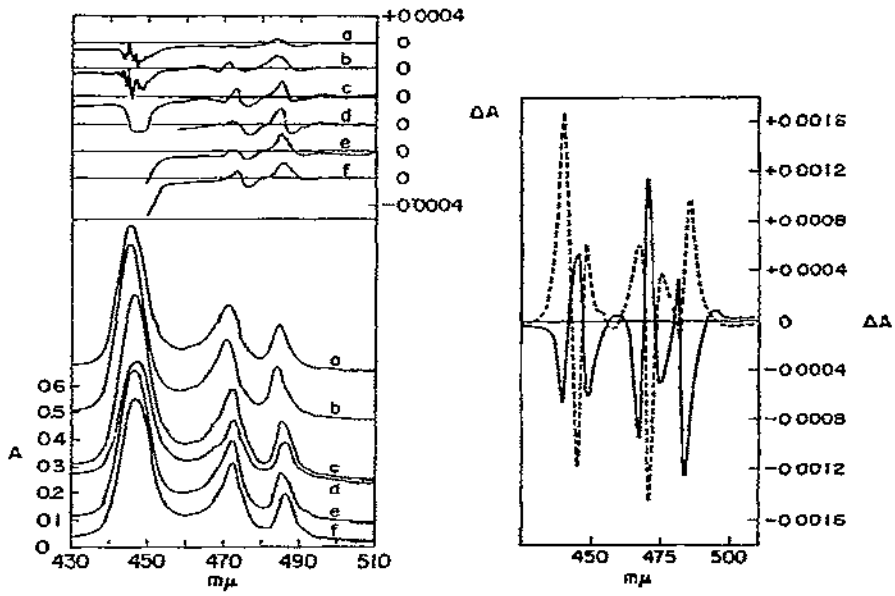

Fig 8 CD and absorption spectra for aspartic acid–Pr^{III} mixtures, with increasing pH, (a) 2 1, pH 6, (b)–(d), 3:1, pH 6, 8, 9, respectively; (e), (f), 5 1, pH 8, 9, respectively. CD pathlengths, 30 mm, absorption, 5 mm

Fig 9 Pr–sugar acid "neutral" complex CD spectra for gluconic (dashed) and galactonic (full) acids, showing inverse signs

The polyhydroxylic sugar acid systems give another sort of example in which assignment of interacting functional groups can be made through CD spectroscopy. Eu^{III} forms 1:1 complexes with a number of these acids[4], but for the moment attention will be concentrated on gluconic and galactonic acids, monocarboxylic acids from the respective aldoses. In the relatively acid pH range, say, 3–5, CD confirmation is seen that complexing has occurred. Observation at certain isolated absorptions (*e.g.*, the one at 526 nm for the $^7F_0 \rightarrow {}^5D_1$ transition) shows opposite signs of CD for the two complexes. When the pH is raised to 6–7, marked changes and intensification take place in the CD spectrum, signalling deprotonation of a hydroxyl and replacement by the metal ion in the chelate. In the new CD spectrum, the signs of the CD for the 526 nm absorption are still

opposite for the two ligands. Structurally, the two aldonic acids differ only in configuration (*l- vs. d-*) at the γ-carbon. The inference is that chelation involves the carboxyl and the γ-hydroxyl groups, both before and after deprotonation of the latter.

The higher-pH, deprotonated sugar acid complexes of Pr^{III} follow the same correlation of sign with configuration (Table 2, Fig. 9) at the γ-carbon[7], so it may tentatively be assumed that the rare earth ions generally will tend to form 7-membered rings in their chelates with these ligands. The acid-region complexes

TABLE 2

CORRELATIONS OF CD SIGN AND LIGAND STRUCTURE FOR Pr^{III}–HYDROXY ACID COMPLEXES

Ligand acid	*CD sign (~482 mμ)*	*α-Hydroxide configuration*	*Neutral-region complex CD type ($^3P_0$ band)*[a]	*γ-Hydroxide configuration*
D-tartaric	—	*d*	T	—
L-lactic	neg	*l*	—	—
L-erythronic	neg	*l*	anti-T	—
D-ribonic	pos	*d*	T	*d*
D-arabonic	neg	*l*	T	*d*
D-xylonic	pos	*d*	T	*d*
D-gluconic	pos	*d*	T	*d*
D-gulonic	pos	*d*	anti-T	*l*
D-mannonic	neg	*l*	T	*d*
D-idonic	neg	*l*	anti-T	*l*
D-galactonic	pos	*d*	anti-T	*l*
α-D-glucoheptonic	pos	*d*	anti-T	*l*
α-D-saccharinic	pos	*d*	T	*d*
D-pantoic	pos	*d*	—	—
L-malic	neg[b]	*l*	anti-T	—
D-saccharic	—	*d, l*	T	*d*[c]
Glucuronic	pos	*d*	—	

[a] T = sign pattern of tartrate complex, anti-T = sign pattern inverted from tartrate complex
[b] at pH 2–3 [c] Viewed as *either* D-gluco-saccharic or L-gulo-saccharic acid

with Pr^{III}, however, show signs correlating with configuration at the α-carbon. This does not mean α-chelation for this complex, and γ-chelation for the higher-pH one, but means that the field from the carboxyl group (which is attached to the α-carbon) has more effect on the sign of the CD than does that of the γ-hydroxyl group, so long as the latter retains its proton.

The same ligands form complexes with Ni^{II} that have some of the same general characteristics as the complexes with the rare earths[5]. There is one complex in the acid region, and a second, deprotonated complex at higher pH. The CD spectra for the two are different in appearance and in intensity, as for the rare earths (Figs. 2 and 3). As with Pr^{III}, the sign of the CD spectrum of the acid-region complex correlates with configuration at the α-carbon. The signs of the CD spectra for the deprotonated complexes also show a correlation with con-

figuration, but it is with the configuration at the β-carbon, in contrast to the rare earths (Table 3). The stable Ni^{II} complex in these environments, therefore, is the 6-membered ring. Nevertheless, with arabonic acid as reagent, the CD spectra (Fig. 3c) indicate some other, as yet undefined, structure for the high-pH complex.

TABLE 3

CORRELATION OF CD SIGN WITH CONFIGURATION OF LIGAND HYDROXYL, Ni^{II}–HYDROXY ACID SYSTEMS

Reagent acid	*CD sign, Ni^{II} complex*		*–CHOH-configuration at carbon indicated*		
	low pH	*higher pH*	α	β	γ
Lactic	neg	—	*l*	—	—
Ribonic	pos	neg	*d*	*d*	*d*
Arabonic	neg	[a]	*l*	*d*	*d*
Xylonic	pos	pos	*d*	*l*	*d*
Gluconic	pos	pos	*d*	*l*	*d*
Galactonic	pos	pos	*d*	*l*	*l*
Gulonic	pos	neg	*d*	*d*	*l*
Malic	neg	[a]	*l*	—	—
Tartaric	pos	[a]	*d*	*l*	—

[a] CD spectra not comparable to majority

C. SPECTRAL INFORMATION

(i) Correspondence between absorption and CD spectra

To be able to reason back and forth between data from absorption spectra, and data from CD spectra, requires some feeling for the nature of the interrelations. As an example for the need one may consider the band of Nd^{3+} which lies at 340–360 nm in water, in which three sharp absorption components are visible, and the presence of a fourth is suggested[11]. Data from atomic spectroscopy and absorption in solids indicate that four upper states contribute to this band. The absorption in the tartrate complex shows a slight broadening of components, but the relations are recognizably like those for the hydrated ion. The CD spectrum of this band, thanks to variations in component sign, shows not less than 10 distinct components (Fig. 10), and the shapes of some of these imply that they may be compound.

A partial answer to some of the questions such observations raise can be obtained from a detailed study of a favourable part of the Pr^{III} spectrum. This region, about 430–500 nm, contains in the water spectrum the three sharp peaks of transitions to the $^3P_{2,1,0}$ upper levels, and buried at the base of one of them, the weak $^1I_6$ upper state. In a series of three tartrate complexes which have been studied[7], it has been possible to perform detailed resolutions of the resulting

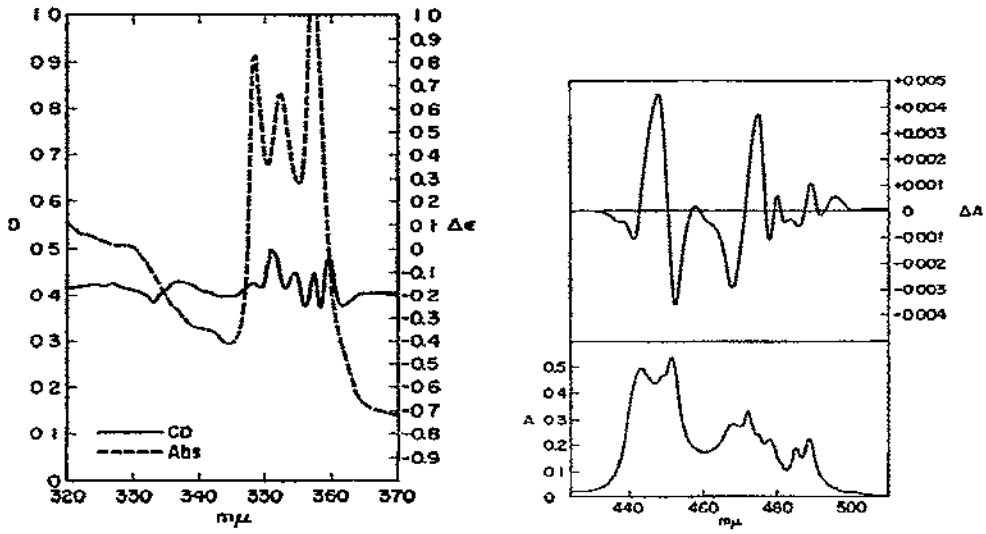

Fig. 10. Absorption and CD spectra of Nd^{III} in alkaline tartrate, 320–370-nm region.

Fig 11 Absorption and CD spectra of alkaline Pr–tartrate complex. A, ΔA in absorbance units. CD pathlength, 50 mm; absorption, 10 mm

TABLE 4

ABSORPTION AND CD SPECTRA OF THE ALKALINE Pr^{III}–TARTRATE COMPLEX COMPONENT ANALYSIS

Absorption		*CD*		
λ(nm)	*A*[a]	*λ(nm)*	*ΔA* (×10⁴)[a]	*Δε/ε* (×10³)[b]
433	0 3	—	(neg)	—
438	0 07	437	−0 76	−1 1
443	0 45	441 5	−2 0	<−0 45
		444 5	+2 8	>+0 62
446 5	0 09	447	+4 6	+5.1
449 5	0 30	449 5	+6 8	+2 3
452	0 40	452	−7 4	−1.85
455 5	0 18	455 5	−1 6	−0 89
459	0.10	459	+0 40	+0 40
462 5	0 01	463	−0 8	−8.
468	0 27	468	−5 6	−2.1
472 5	0 14	474	+5 6	+4 0
475 5	0.115	476	+5.2	+4 5
478 5	0 14	477 5	−7 4	−5 2
		481	+1 2	>+1 25
482	0 095	483	−1 45	<−1.5
485 5	0 15	487	−1 3	−0 87
489	0.16	490	+2 25	+1.4
491 5	0 06	492.5	−0 86	−1.4
498	0 01	497	+0 92	+9
502	0 01	501	−0 2	−2.

[a] Absorbance units, per 10-mm path. [b] $\Delta A/A = \Delta\varepsilon/\varepsilon$.

spectra, both absorption and CD. In one of the complexes no fewer than 21 components have been separated (Fig 11, Table 4). With exceptions which seem to be technical, each absorption component is apparently associated with a CD component, and *vice versa*. It seems reasonable to assume as a start that this is a general characteristic of electronic spectra.

(ii) CD spectra as indicators of symmetry field effects

The $^3P_0$ upper level of Pr^{III}, as a $J = 0$ state, retains its single character under all fields. When the corresponding absorption peak broadens, and the CD shows four or five components for amino acid or hydroxy acid complexes (Figs. 4, 5 and 11), the reasonable conclusion is that one is seeing consequences of some splitting in the $^3H_4$ ground state. The CD patterns in the $^3P_0$ region are essentially the same (except for sign inversion) for all the hydroxy acid complexes, whereas the $^3P_1$ and $^3P_2$ regions show effects suggesting a rather variable splitting of these upper levels, depending on details of the ligand The ground state of Eu^{III}, $^7F_0$, gives sharp single peaks with all upper levels, even in the amino acid and hydroxy acid complexes, while the $^7F_1$ and $^7F_2$ lower levels lead to complex absorption and CD patterns[4]. There are several limitations on the sort of information which can be obtained from such data, however. One, perhaps more specific to the rare earths than some other sorts of ions, is that the splitting patterns of the states are not sensitive to the details of the local symmetry[12]. A second is that the selection rules which determine how many components appear are not clear for the low symmetries of the complexes, and in particular there is not yet a clear explanation for how signs of individual CD components are determined In the CD pattern of the $^3P_0$ praeseodymium band, for instance, the highest energy component is of different sign than the others. More generally, through the rare earths, and the 3*d* elements also, "splittings" to give CD components of opposed signs are very common, and not clearly explained.

One point at which detailed symmetry information has apparently been obtained will perhaps serve to illustrate further theoretical problems. The Ni^{II}–aspartic acid complex already referred to has in the 650-nm spectral region a broad absorption which represents the $\Gamma_4(^3F)$ upper level[6]. In complexes of Ni^{II} with simple amino acids, two CD components are found in this peak (Fig. 6), corresponding to two components with magnetic moments under conditions of C_{2v} symmetry. The aspartic acid complex shows three CD components here (Fig. 7d), which could he obtained under C_s symmetry, for example. But to decide which factors determine the symmetry to be used involves a certain arbitrariness. On the basis of the fact that hydroxy acids give CD effects related to those of amino acids insofar as components are concerned, we have chosen (*a*) to consider coordinated oxygen and nitrogen to be symmetry-equivalent, (*b*) to consider the linkage of two coordination positions by a chelating agent to be a symmetry

differentiator, and (*c*) to consider the exact number of atoms in the chelate ring to be unimportant. Thus, any 1:1 Ni^{II}–chelate, with optically active ligand, can be considered to have C_{2v} symmetry, justifying two CD components in the 650-nm band. Similarly, aspartic acid, acting as a tridentate, would also be expected to show C_{2v} symmetry if the attachment were *trans*, while *cis* coordination would justify designating the symmetry C_s, which in turn agrees with three components in the CD. The question, say, of how many water molecules in the coordination sphere are replaced by ammonia molecules, becomes irrelevant to the symmetry question, and in practice apparently does not affect the number of CD components, though the frequency location and intensity of the absorption peak may be affected. Exploration of these relations should be more widely extended.

(iii) Signs of CD components

There are some who feel confident that they understand theoretically how to predict at least the sign of the rotation of, say, a methylcyclopentanone, given obtainable structural parameters. In the vapor spectrum of (+)-3-methyl-cyclopentanone already alluded to, the 300-nm carbonyl absorption shows a number of electronic transitions, including also components of vibrational fine structure. All of these are of a single sign (Fig 12) We have seen already that in the inorganic

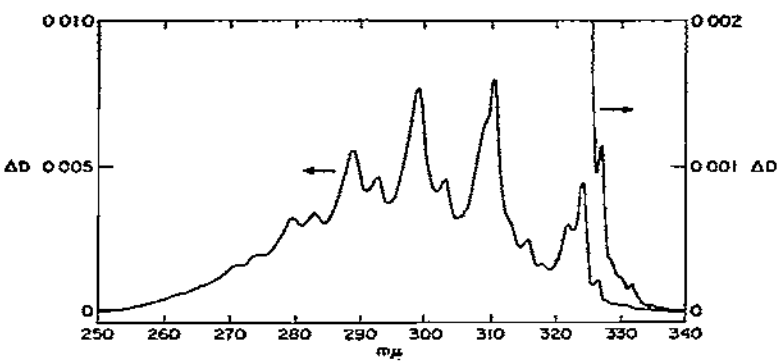

Fig 12. Circular dichroism spectrum for carbonyl absorption band (250–340 nm) of (+)-3-methylcyclopentanone vapor

complexes components of differing signs are present. For systems in which the ligand-complex structural difference is that of a simple isomerism—*e.g.*, between the gluconate and galactonate complexes of Pr^{III}—the corresponding CD components are of opposite sign, as expected. For Eu^{III}, the signs of the comparable CD components for the complex with L-alanine are the same as those for the complex with L-lactic acid, with the same structural configuration for the ligand. The CD spectra for Ni^{II} complexes with L-alanine and with L-lactic acid do *not*

show this relationship (Figs. 2 and 6a). Single transitions, such as that at 375 nm, are of opposite sign; and split transitions, such as in the 660-nm region, which show two components of opposite sign with the amino acid, show a uniform sign with lactic acid or the other hydroxy acids. In this case at least more influences than simple geometrical symmetry relations are operative, and one is justified in talking about the effects of detailed bonding relations.

In addition to the effects of detailed bonding on the sign of a given CD component, a good explanation is still needed for the opposed signs of splitting components so commonly found in the metal complexes. One would like to speculate on a possible internal Zeeman effect of the asymmetric field of the ligand, for example. There is further the obviously differential effect on sign and intensity between different transitions of the spectrum, as a function of ligand. One would like, say, to find some relation between spatial orientation of the orbitals involved and the axes determined by the bonds to the coordination positions linked by the chelating ligand, for it seems reasonable to assign to the latter the role of setting up a fixed net vector field of some sort, by virtue of its asymmetry.

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