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Circular Dichroism Spectral Studies on Cobalt(II)–Carboxylic Acid Systems[1]

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Complexes were investigated, in acid solution, between Co(II) and ions of alanine, valine, serine, methionine, proline, hydroxyproline, lysine, arginine, ornithine, aspartic acid, glutamic acid, and asparagine; L-lactic, L-malic, and D-tartaric acids; and L-erythronic, D-ribonic, D-arabonic, D-gluconic, D-gulonic, D-galactonic, D-idonic, D-mannonic, D-pantoic, α-D-glucoheptonic, and α-D-saccharinic acids. CD was seen in both the main $^4T_{1g}(O_h)$ and the lesser $^2T_{1g}(O_h)$ components of the absorption peak in the visible spectrum. For the 1:1 complexes between Co(II) and the anions of the α-hydroxymonocarboxylic acids, the signs of the CD for both O_h upper states were negative for ligands levo (*S*) at the α carbon and positive for dextro (*R*). The sign for the α-amino acids showed similar correlation. Whereas the CD components for the hydroxy acids were compatible with O_h first-shell symmetry, the amino acid case was describable as C_{4v} effective symmetry. The dicarboxylic acids, L-malic and L-aspartic acid, and also L-asparagine, showed a positive CD, the components of which could be attributed to C_{2v} effective symmetry. L-Glutamic acid was like the monocarboxylic amino acids. D-Tartaric acid, in the intermediate pH range, yielded a Co(II) CD superficially like that of the L-dicarboxylic acids, but with some irregularity in sign of CD components. Deprotonated hydroxy acid complexes produced at pH 5–7 do not give a uniform CD spectrum, but there is a strong suggestion that it is the β-hydroxyl that is coordinated, as in the case of the Ni(II) complexes. Here also different components in the same spectrum may differ in sign. All complexes of lowered effective symmetry showed CD in the very weak optical transitions to $^4A_{2g}$ and to various ^2T levels.

In preceding studies of the systems Ni(II)-optically active ligand,[2-5] it was demonstrated that from circularly dichroic absorption spectra (CD) structural relations in the resultant complex can sometimes be deduced. A combination of the selection rules for optical activity of the metal ion d-d transitions with group theoretical considerations furnishes the essential theoretical leverage.

The ion Co(II) is very similar chemically to Ni(II). Spectrally, in octahedral coordination its absorption in the visible region shows a single peak (though this clearly includes at least two transitions—*e.g.*, ref 6 and 7). The major component is a T_{1g} upper state, as in Ni(II), though the relevant electron complement is d^7 rather than d^8. We have therefore investigated its CD spectral behavior with many of the same reagents with which Ni(II) was tested, to attempt to sort out general relations between metal ions and optically active ligands from those which might be specific to the details of the electronic transitions.

Experimental Section

Aliquots (1.0 ml) of a stock 0.68 *M* $CoCl_2$ solution were added to excess organic reagent which had been treated with appropriate amounts of concentrated NaOH, and the mixture was made to 5.0 ml. In some instances, additional drops of concentrated NaOH might be added after mixing. In preparing solutions, final alkaline preparations were avoided, to obviate difficulties of precipitation or of oxidation of the cobalt to Co(III).

CD and absorption spectral observations on the solutions were made with the Jasco UV/CD-5, as previously.[2-5] A few absorption spectra were repeated on the Cary spectrophotometer, when component analysis was desired. Resolution of absorption and CD spectra into gaussian components was accomplished with the help of the Du Pont curve resolver.

Optically active reagents used included[2,3] alanine, valine, serine, methionine, proline, hydroxyproline, lysine, arginine, ornithine, aspartic acid, glutamic acid, and asparagine; L-lactic, L-malic, and D-tartaric acids; and the lactones of L-erythronic, D-ribonic, D-arabonic, D-gluconic, D-gulonic, D-galactonic, D-pantoic, α-D-glucoheptonic, and α-D-saccharinic acids. Idonic acid was available as the strychnine salt, and D-mannonic acid as the brucine salt, from which the alkaloid was extracted away with carbon tetrachloride.

A few preliminary measurements on the tartaric acid and alanine systems were made with the Cary CD apparatus of Dr. Gideon Hausner, while the author was on a visiting appointment to the Hebrew University, Jerusalem. Indebtedness for the technical assistance of Mrs. Josefina Silfen in those measurements is gratefully acknowledged.

Results

At a pH well below the carboxyl pK_a, the appearance and spectra of the Co(II)-reagent mixture may be indistinguishable from those for $CoCl_2$ without reagent. As the hydroxy acid carboxyl is ionized at higher pH, the solution may become more or less red or magenta tinged with respect to the unmodified Co(II), as the complexation takes place. Zwitterionic forms of the simple amino acids may show no effect with Co(II) until alkali is added, while the basic amino acids may signal interaction prior to addition of external alkali. These amino acid complexes have a slight orange shading compared to the unmodified Co(II). The dicarboxylic acids give the most highly colored (magenta-tinged) solutions as the pH is raised. The color changes come from two or three rather minor alterations in the absorption spectrum, which does not change its intrinsic appearance. One effect is a small wavelength shift from the 512-nm maximum of the Co(II)(aq) at that concentration. This shift is to 510 nm for the orange-tinted amino acid complexes, and to 515 nm or so for the red-toned hydroxy acid complexes. The latter may be accompanied by an extinction enhancement to perhaps double or slightly more in the extreme. The amino acid complexes show only fractional intensification. There may also appear, particularly with the hydroxy acid systems, an absorption increase to the long-wavelength side of the peak, from say 575 or 600 to 700–800 nm, which at most approaches 10% of the intensity of the peak. The spectra of all these solutions are clearly those of six-coordinate Co(II), and there is no indication of tetrahedrally coordinated species.

All such color-modified solutions show a CD spectrum. The discussion will be centered on these CD spectra, which have characteristic features not *a priori* to be inferred from the absorption spectra. From pH values at which the first

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) L. I. Katzin and E. Gulyas, *J. Amer. Chem. Soc.*, 91, 6940 (1969).
(3) L. I. Katzin and E. Gulyas, *J. Amer. Chem. Soc.*, 92, 1211 (1970).
(4) L. I. Katzin, *Coord. Chem. Rev.*, 5, 279 (1970).
(5) L. I. Katzin and E. Gulyas, *Inorg. Chem.*, 10, 2411 (1971).
(6) L. I. Katzin and E. Gebert, *J. Amer. Chem. Soc.*, 72, 5455, 5464 (1950).
(7) R. L. Carlin, *Transition Metal Chem.*, 1, 1 (1965).

spectral changes are seen, and the CD spectrum first appears, to the essentially complete neutralization of the reagent acids, at the concentrations used in these experiments, a single CD spectrum is seen in each system. The changes are solely of increasing intensity as more complex is formed. With the amino acids, in which release of the acid proton occurs generally only above the zwitterion pH, titration of the mixture of Co(II) and amino acid indicates not more than one proton per metal ion is released. Considered together with the fact that the reaction is substitutional, chelating complexing of a metal ion which undergoes no coordination number change, and with our prior studies on other metal ion systems,[2-5] there is no serious doubt that we are studying 1:1 chelate complexes.

Monocarboxylic Hydroxy Acids. This group gives the simplest CD spectrum to the Co(II) complex. Two CD components become visible in the Co(II) absorption peak. The differences between complexes, beside overall intensity, appear in the relative intensity of the two components and their spectral spacing. These two quantities were obtained by resolving the CD spectra into gaussian components. With two or three exceptions (see below), the curves were satisfactorily representable by only two such components. The peak wavelength, width at half-maximum, and intensity ratio of the two derived components are given in Table I. Several spectra are illustrated in Figure 1.

The spectrum of the system with idonic acid is modified in the longer wavelength CD component, while a totally new CD has appeared in the 570–700-nm spectral region (Figure 2c). Resolution shows that the major component at 477 nm is accompanied by a weak satellite at 450 nm, while the 500–570-nm region shows three CD components, at 517, 535, and 553 nm, respectively. These drop successively about 10% in intensity from the 517-nm component, which also seems to be the narrowest. The 570–700-nm CD is also composed of three rather similar components, but appreciably broader than the 500–570 nm group and spaced further apart.

With α-D-saccharine, even the low-pH CD spectrum is complex, and at moderately higher pH there is a distinct change (Figure 2a, b).

Monocarboxylic Amino Acids. The amino acids differ from the hydroxy acids in the zwitterionic form of the former, which requires a proton to be displaced from the $-NH_3^+$ group before it is available for chelation. If alanine is added to $CoCl_2$, originally at pH 4.5, the pH still reads 4.5–4.6, and only a very weak indication of a CD is detected. If NaOH is slowly added, an appreciable fraction of an equivalent can be added without the pH rising over 6, and a strong negative CD is now present. The behavior for the other monocarboxylic amino acids is similar, with hydroxy-L-proline possibly showing a stronger interaction prior to addition of NaOH. The basic amino acids also show a strong CD without requiring NaOH to be added, as the proton resides at least partially on the terminal basic group, rather than the α-amino group.

The CD spectra for the amino acid complexes bear a superficial resemblance to the CD for the lactate complex, with the extreme CD intensity coming at 530–534 nm (Figure 3). One characteristic difference is the clear indication of more than two components even in the main CD peak. A second is the low, long-wavelength extension of the CD to 650 nm and higher. For example, the valine complex has its major component at 534 nm, the next most significant (55%) at 492 nm, and smaller ones at 452 and 510 nm. There are a component at 549 nm and a pair of broad components at about 592 and 632 nm which give the long-wavelength tailing of the envelope.

Table I. Characteristics of CD Spectra of Cobalt(II)-Hydroxy Acid 1:1 Complexes for the Visible Peak[a]

Acid	CD sign	λ_1	λ_2	$\Delta\lambda$	Δ_1	Δ_2	I_1/I_2
Arabonic	Neg	469	514	45	44	44	0.93
Galactonic	Pos	467	512	45	38	50	0.72
Mannonic	Neg	471	520	49	46	60	0.72
Gluconic	Pos	466	514	48	42	52	0.65
Gulonic	Pos	468	518	50	42	52	0.59
Pantoic	Pos	463	512	49	33	70	0.53
α-Glucoheptonic	Pos	467	518	51	44	58	0.62
Erythronic	Neg	471	522	51	42	56	0.55
Ribonic	Pos	472	526	54	40	56	0.47
Lactic	Neg	473	527	54	43	62	0.37
		472	530	58	42	58	0.40

[a] $\lambda_{1,2}$ = wavelengths of component maxima (nm); $\Delta\lambda = \lambda_2 - \lambda_1$ (nm); $\Delta_{1,2}$ = width of component at half-maximum (nm); $I_{1,2}$ = intensity of components, arbitrary units.

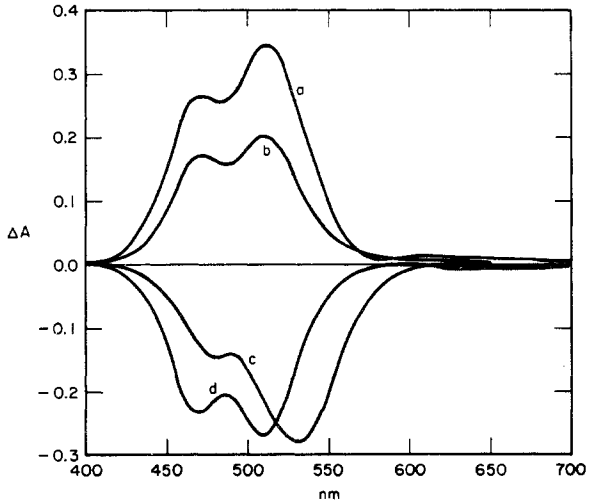


Figure 1. Sample of CD spectra of 1:1 cobalt(II)-hydroxy acid anion complexes (multipliers to nominal ΔA scale in parentheses): (a) gluconic acid (×0.004); (b) galactonic acid (×0.010); (c) lactic acid (×0.010); (d) arabonic acid (×0.004).

The other amino acid systems show basically the same components (Table II), with minor differences in part due to component resolution variations on curves of this nature. The complex with hydroxy-L-proline uniquely shows a *positive* CD for the 575–700-nm region. The proline complex, in contrast, seems to be flat through this region, without 600–700-nm dichroism, but it is possible this appearance is based on an extremely weak positive component rather than total absence. The hydroxyproline CD intensity may possibly be significantly greater than that for the other amino acids.

Asparagine technically is a monocarboxylic acid, but its CD spectrum is opposite in sign to that of the other monocarboxylic L-amino acids, and in general it appears like the dicarboxylic acids (see below).

Dicarboxylic Amino Acids. Addition of $CoCl_2$ to aspartic acid solutions gives a bare indication of CD. Addition of NaOH brings up a strong CD which is *positive* in sign (Figure 4). The main components are at 524 and 480 nm (75%), with small ones at 452, 498, 549, 570, and about 625 nm.

Glutamic acid, with an additional methylene group between the carboxyls, complexes Co(II) with a weak CD spectrum, essentially that which characterizes the monocarboxylic L-amino acids.

Though asparagine is a monocarboxylic acid, its complex

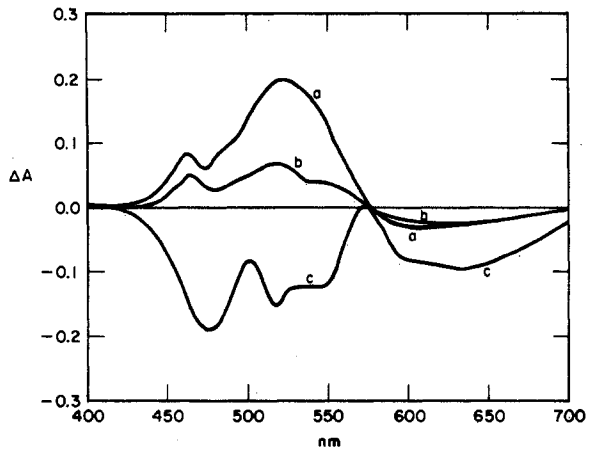


Figure 2. Nontypical CD spectra of cobalt(II)-hydroxy acid anion complexes (multipliers to nominal ΔA scale $\times 0.004$): (a) α-D-saccharine, intermediate pH; (b) α-D-saccharine, low pH; (c) idonic acid.

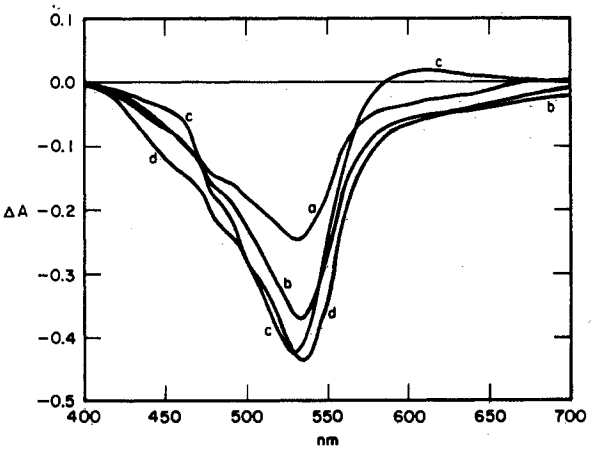


Figure 3. Typical CD spectra of cobalt(II)-monocarboxylic amino acid complexes (multipliers to nominal ΔA scale in parentheses): (a) alanine ($\times 0.010$); (b) serine ($\times 0.004$); (c) hydroxyproline ($\times 0.010$); (d) valine ($\times 0.010$).

with Co(II) shows a positive CD spectrum which is quite comparable with that for the aspartic acid complex. The difference visible to the eye (Figure 4) is primarily the wavelength shift of the higher energy components to 440 and 464 nm (Table III). A component comparable to that at 549 nm in the aspartic acid spectrum is not resolved.

Dicarboxylic Hydroxy Acids. $CoCl_2$ in the presence of malic acid gives a weak negative CD of the general appearance shown by the monocarboxylic hydroxy acids. A small amount of NaOH, to ionize the stronger carboxyl more, intensifies this spectrum, delineating extrema at about 472 and 514 nm (Figure 4). With addition of still more NaOH and appreciable ionization of the malic acid, the CD spectrum changes radically, to a positive spectrum resembling that of the aspartic acid complex (Figure 4), with extrema at about 480 and 535 nm. The components are essentially the same as for the aspartic acid complex (Table III).

The dissociation constants of tartaric acid differ less than those for malic acid, so separation of the dissociation stages is less definite. A cobalt-tartaric acid complex seen with the very minimal addition of NaOH shows a positive extremum at 470 nm and a second at 509 nm, as might be anticipated for a monocarboxylic hydroxy acid of D configuration. The novel and unique phenomenon is appearance of a negative extremum at about 550 nm (Figure 5). Resolution shows positive components at 440, 468, and 509 nm, and a

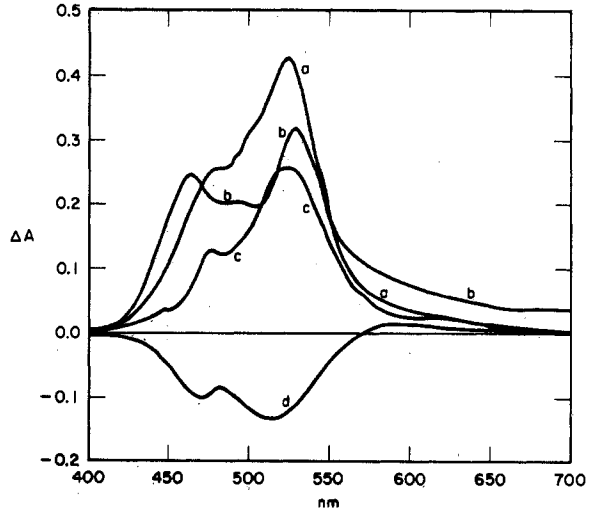


Figure 4. CD spectra of Co(II) complexes with asparagine, aspartic acid, and malic acid (multipliers to nominal ΔA scale in parentheses): (a) aspartic acid ($\times 0.010$); (b) asparagine ($\times 0.004$); (c) malic acid, intermediate pH ($\times 0.020$); (d) malic acid, low pH ($\times 0.004$).

Table II. Wavelengths of CD Spectral Components in the Visible Spectra for Cobalt(II)-Amino Acid Complexes[a]

Ligand	Upper state (O_h)									
	$^2T_{1g}$		$^4T_{1g}$		$^2T_{1g,2g}$		$^4A_{2g}$
Alanine	450	483	511	530	541		600
Valine	452	492	510	534	549	592	632
Serine	451	489	508	533	551	590	638
Proline	447	487	508	533	557	590 (?)	
Hydroxyproline	450	482	502	526	550		610*
Arginine	451	484	505	529	550	580	625, 675
Ornithine	448	482	501	528	552	582	625
Lysine	452	480	502	528	552	592	625
Methionine	450	478	500	529	555		

[a] All components negative except asterisk-marked hydroxyproline component. Wavelengths in nm.

Table III. Wavelengths of CD Spectral Components for Visible Absorption of Co(II) Complexes with Asparagine and Dicarboxylic Acids[a,b]

Ligand		Upper state (O_h)							
		$^2T_{1g}$		$^4T_{1g}$		$^2T_{1g,2g}$		$^4A_{2g}$
Asparagine		440	464	496	528		574	612
Aspartic acid		452	480	498	524	549	570	626
Malic acid	c	472*		514*				
	d	445	478	498	526	549	575	620
Tartaric acid	c	440	468	509	542*			
	d	449	473	504	543*		570	633*

[a] Wavelengths in nm. [b] All components positive except those asterisk marked. [c] Low-pH complex. [d] Higher pH complex.

negative component at 542 nm. More NaOH brings dissociation of both carboxyls, and the color of the solution darkens and reddens strongly. The process is limited in that precipitation sets in before tartaric acid is half-neutralized. A stable solution below this pH shows a CD which is principally modified by the addition of new dichroism between 575 and 700 nm, and here also components of both signs are to be seen (Figure 5). A unique resolution of this spectrum into components is difficult, as there seems to be more than one possibility. One difficult area is the 500–550-nm region, where there is the possibility of hidden components, between the positive 504-nm and negative 543-nm components of the resolution given in Table III. There exists also the possibility of a small negative component in the 495-nm region, between

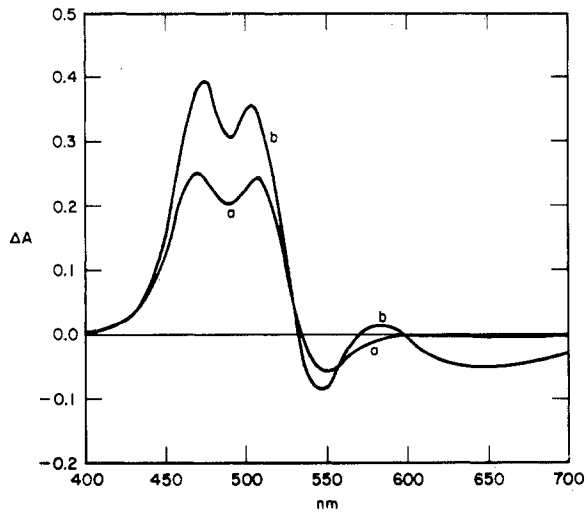


Figure 5. CD spectra of Co(II) complexes with tartaric acid (multipliers to nominal ΔA scale $\times 0.004$).

the prominent extrema. The new positive extremum near 575 nm probably also is made of two components, while the negative CD to longer wavelength is also probably compound. The complexity might relate to multiple species, since precipitation is close.

The cobalt(II)-saccharic acid CD spectrum is weak and suggests strongly that it represents a difference between the two monocarboxylic acid spectra of opposite sign expected from the two ends of the molecule.

Discussion

The most detailed theoretical analysis of the spectrum of Co^{2+} is that of Liehr.[8] The ground state of Co(II) (chemical notation) is ^4F. In octahedral crystal field this splits to $^4T_{1g}$ (ground level), $^4T_{2g}$, and $^4A_{2g}$ components for the electronic d-d transition levels. The characteristic absorption peak at just below 20,000 cm^{-1} (*ca.* 505-515 nm) most probably involves the $^4P(T_{1g})$ upper level. However, at values of the crystal field parameter, $-Dq$, of 700-1000 cm^{-1}, which is the range in which fittings to octahedral Co(II) are generally computed, the $^4A_{2g}$ component from the free-ion ground state is not too distant, and there are a number of levels from the doublet terms (^2G, ^2P, ^2H, ^2D) also in the vicinity. In the Dq range indicated, the relative positions of some of these are changing rapidly, and some care must be taken in making identifications.

Ferguson, Wood, and Knox[9] have reported and analyzed crystal spectra for Co(II) in octahedral and near-octahedral sites. Most relevant for us are the data on Co(II) "doped" into the octahedral cation sites of $KMgF_3$. The room-temperature absorption spectrum for the crystal is very like the spectrum of Co(II)(aq). The main absorption at about 19,500 cm^{-1} (513 nm) is attributed to the $^4T_{1g}(P)$ upper state. The shoulder at about 21,500 cm^{-1} (465 nm) represents components identified at low temperature with a $^2T_{1g}$ upper state. The $^4A_{2g}$ upper state is identified with a transition at *ca.* 15,200 cm^{-1}, at about 5% or less the extinction of the main peak. Some additional $^2T_{1g}$ and $^2T_{2g}$ levels are expected between 15,000 and 20,000 cm^{-1} but were not identified in this solid.

The absorption spectrum of Co(II)(aq) (as 0.136 M $CoCl_2$) between 390 and 750 nm has its peak at about 512 nm. This decomposes into a major component at 517 nm and a lesser (56%) at 467 nm. These may be attributed respectively to the $^4T_{1g}$ and the $^2T_{1g}$ upper states from the solid-state assignments.[9] There is a foot extending to longer wavelength from the peak, terminating before 750 nm, which seems made up of a 646-nm component, and one appearing to be assignable to about 582 nm. The former presumably represents the $^4A_{2g}$ upper state. The correct location of the second may not be 582 nm, as it falls under the end of the strong 517-nm component, but it has presumably one of the doublet upper states mentioned earlier.

In O_h symmetry, a $T_{1g} \rightarrow T_{1g}$ transition is expected to have four components, A_{1g}, E_g, T_{2g}, and T_{1g}, of which the last satisfies the selection rule for optical activity and hence exhibits circular dichroism. $T_{1g} \rightarrow A_{2g}$ should not be active. The two CD components seen in the spectra for the simple hydroxy acid complexes of Co(II) (Figure 1 and Table I) are consistent with the identification of the lower wavelength component with the $^2T_{1g}$ levels and the longer wavelength one with the $^4T_{1g}(P)$, under essentially O_h conditions. The variations in relative intensity and position relative to the absorption maximum respond to factors beyond the first-order identifications of the moment (*e.g.*, to variations in Dq and other parameters, such as $\Delta\epsilon/\epsilon$). In these spectra, the sign of the CD correlates with the configuration of the hydroxyl group at the α carbon—negative for L configuration and positive for D.

If instead of effectively approximating O_h first-shell symmetry around the Co(II), as seems to be the case above, one of the bonds (say, to carboxyl) were different enough from the others, the symmetry might be reduced to C_{4v}. In this case, the $^4T_{1g}$ of both the ground level and the upper state would be split to $A_2 + E$. If the ground level is now E, interaction with the E derivative of the upper $^4T_{1g}$ will give four components, one of which (the A_2) should be dichroic. Interaction of E with the A_2 derivative from the upper $^4T_{1g}$ should give a single, dichroic component. The $^2T_{1g}$ and $^2T_{2g}$ may be expected to respond similarly, so far as these criteria are concerned. The $^4A_{2g}$ (O_h) is now labeled B_1, but transition to it from the E ground state should now also be dichroic. If the ordering of the split ground levels is reversed, then only the transitions to the E upper states, of those indicated above, would be dichroic.

In the event that both binding sites of a chelate ligand are differentiated equally from the water binding sites, approximate C_{2v} symmetry might be realized. In this case, the $T(O_h)$ levels are split to three one-dimensional levels, of which two may be expected to be dichroic. The transition to the $^4A_{2g}(O_h)$ upper level will also be dichroic, as in the C_{4v} case.

The idonic acid and α-D-saccharinic acid complexes, with their more involved CD spectra, clearly represent a departure from O_h relation, probably linked with stronger binding of the ligands to the metal ion. In the idonic acid case there may be deprotonation of the coordinated hydroxyl. The detailed CD spectra will be discussed in connection with some of the later items. It need only be pointed out here that the negative CD of the saccharinic system at 600 nm and higher and the strong, multicomponent CD at 575-700 nm in the idonic acid system represent contributions from $^2T_{1g,2g}$ and $^4A_{2g}$ upper states not seen in the other hydroxy acid systems.

The Co(II) complexes with the monocarboxylic amino acids, in contrast to most of the simple hydroxy acids, definitely show four CD components in the main absorption peak (Table II). Broad CD also appears in the 600-nm region, corresponding to the $^2T_{1g,2g}$ and $^4A_{2g}$ levels. This

(8) A. D. Liehr, *J. Phys. Chem.*, 67, 1314 (1963).
(9) J. Ferguson, D. L. Wood, and K. Knox, *J. Chem. Phys.*, 39, 881 (1963).

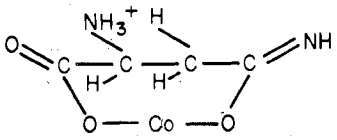
overall CD spectral behavior justifies considering these complexes to have approximate C_{4v} symmetry, though it is not possible *a priori* to assign definite labels to the levels seen. Thus it may be assumed that the components at approximately 505 and 530 nm both derive from $^4T_{1g}(O_h)$, without more closely identifying them, and that the two lower wavelength components are associated with $^2T_{1g}(O_h)$.

The apparent absorption maximum for the complexes of Co(II) with the basic amino acids or with hydroxyproline, for example, is shifted to 510 nm, and the components are typically at 515 and 461–462 nm, respectively (*cf.* Co(II)-(aq) above), though for methionine the latter still seems to be at about 467 nm. Hydroxy acids, as α-D-saccharine and tartaric acids, have the absorption maximum shifted to 515 nm or higher and the main component to perhaps 521 nm. These shifts are presumably reflections of alterations in the *Dq* parameter. The profile of the long-wavelength "toe" changes slightly, but whether 590 nm is a representative value for the closer component and how this would be altered if there is an unresolved 550 nm component buried under the main peak (as the CD suggests) cannot be settled unequivocally. In any event, it seems improbable that the apparent absorption component at 515 nm for the amino acids or at 521 nm for the dicarboxylic acids can be reconstructed entirely from components only at the wavelengths of the CD peaks. Thus one or more intermediate components lacking CD are required, as the above reduced-symmetry arguments imply.

A number of the monocarboxylic acid complex systems listed in Table I show CD components which correspond closely to the absorption components resolved from the Co(II) spectrum, further underpinning the essentially O_h response to the coordination environment. It is possible to resolve the lactic acid complex CD to indicate the presence of a very small 508-nm component accompanying a major 532-nm component, but this is the extreme in Table I. The difference between most of the hydroxy acids and the C_{4v} character of typical amino acid complex CD suggests that the symmetry difference revolves around the effect of the amino group. This implies that the bonding difference between one amino group and, say, water is greater than those between carboxyl oxygen, water, and hydroxyl oxygen, with ^{oct}Co(II) as the partner. An interesting item is the apparent repression of the CD in the 600-nm region with the proline complex and clear appearance of the CD with *reversed* sign for hydroxyproline, compared to the nonring acids. This has an analog in the higher pH spectrum of the saccharinic acid complex, which has a negative CD in this region against a positive main spectrum (which incidentally has a 487-nm component like the amino acid spectra do).

The malic acid–cobalt(II) system in the more acid region shows the negative CD spectrum characteristic of the L-monocarboxylic acids and so corresponds to first ionization of the α-carboxyl group. As ionization of the β-carboxyl commences, the CD spectrum changes to a completely positive one. A very similar positive CD spectrum is seen with aspartic acid, as its β-carboxyl ionizes. Since in both instances the pH is much too acid to anticipate deprotonation either of the malic acid hydroxyl group or of the $-NH_3^+$ group of the amino acid, in preference to ionization of the second carboxyl, it seems most reasonable to consider these CD spectra to result from chelation of Co(II) through two carboxyl groups.

The asparagine complex shows a CD spectrum differing only in detail from those for the malic acid or aspartic acid systems which leads to the inference that the proton lost in forming this complex from the zwitterion comes from the amide group rather than from the $-NH_3^+$—possibly to leave the structure



This would be analogous to what is believed to happen in the metal ion binding of peptides.[10-12] Alternative attribution of the positive CD spectra to tridentate chelation might be reasonable for the malic acid, perhaps even the asparagine, but would seem very difficult to justify in the case of the aspartic acid.

In the main absorption peak region, all three of the above show a small CD in the 495–500-nm region and a major peak at 526–528 nm. With the absorption peaking at 512–514 nm, this could be considered compatible with expectation for C_{2v} effective symmetry, as might be predicted for binding of two carboxyls. The $^2T_{1g}(O_h)$ for the second malic acid spectrum shows components of similar relation—weak absorption at 445 nm, strong absorption at 478 nm, and an absorption that is probably centered at 465–470 nm. All three complexes show similar components to longer wavelength, where $^2T_{1g,2g}$ and $^4A_{2g}(O_h)$ are expected. These could also reflect C_{2v} effective symmetry.

In the more acid range, the CD spectrum of the Co(II) complex with D-tartaric acid has a positive CD at about 470 nm, which is opposite in sign to that for the acid-range L-malic acid complex and the L-α-hydroxy monocarboxylic acid complexes, as would be expected. The negative 542-nm component is novel. The shape of this portion of the CD spectrum shows no sign of $^2T_{1g,2g}$ or $^4A_{2g}(O_h)$ components in the 575–700-nm range, such as in the amino acid spectra or dicarboxylic acid spectra of aspartic or malic acid. There is no criterion by which to decide whether this 542-nm phenomenon represents sign inversion of a doublet level which is normally not resolved from the $^4T_{1g}(O_h)$ CD or whether it results from splitting into positive and negative daughters of the $^4T_{1g}$ itself. Further ionization of the ligand, making both carboxyls available, brings in the CD components at longer wavelength, as with the other dicarboxylic acid systems. Again, however, there is nonuniformity of sign—the 575-nm component is positive while the longer wavelength ones are negative. There is also an intimation that there may be a weak negative component at 490–495 nm. Resolution difficulties may be compounded by the probability that a mixture of species is present, since precipitation of cobalt tartrate may intervene before complete conversion to the second form is obtained, or else a third species may already be in formation.

Besides differing from the other hydroxy acid complex spectra, the cobalt(II)-idonic acid CD has a unique separation of $^2T_{1g}(O_h)$, $^4T_{1g}(O_h)$, and long-wavelength $^2T_{1g,2g}$ and $^4A_{2g}$ regions of the spectrum. The apparently null CD at 500 nm and at 575 nm, where components have been found in the other spectra, leaves open the question whether there may actually be components with null or possibly positive CD at these wavelengths. Three components are found in the ostensible $^4T_{1g}(O_h)$ region. The 550-nm one could per-

(10) W. L. Koltun, M. Fried, and F. R. N. Gurd, *J. Amer. Chem. Soc.*, 82, 233 (1960).
(11) R. B. Martin, M. Chamberlin, and J. T. Edsall, *J. Amer. Chem. Soc.*, 82, 233 (1960).
(12) J. D. Bell, H. C. Freeman, and A. M. Wood, *Chem. Commun.*, 1441 (1969).

haps belong to a masked ^2T state, as mentioned above. If it does not, then the $^4T_{1g}$ is in a low-symmetry environment such as C_1, C_s, or C_2, in which all three states are optically active.

Notwithstanding uncertainties in some such details, certain useful conclusions can be drawn. Chelation of lactic acid or of a simple amino acid obviously forms a five-membered ring. With such a carboxylic acid ligand asymmetric at the α carbon, the sign of the Co(II) CD is determined by the α-carbon configuration (positive for *d*, negative for *l*). In the absence of hydroxyl deprotonation, this correlation holds even when further potentially coordinating and asymmetric hydroxyls are present, as in the sugar acids. As prior studies have pointed up,[3,13,14] in the latter case this does not necessarily designate the hydroxyl involved—only that the effect of the carboxyl binding predominates. Malic acid and aspartic acid show that if a second carboxyl is present on the β carbon, so that chelation involves the two carboxylate groups, with formation of a seven-membered ring, the sign of the CD is inverted from the case where only one carboxyl is involved. The CD of the Co(II) complex with D-tartrate suggests that this dicarboxyl effect may be independent of the configuration at the asymmetric carbon, since L-malic and D-tartaric complexes apparently give the same sign. Within these generalizations there are individual clues to details of metal ion environment difference in the differing details of individual complex CD spectra.

The difference in sign of CD between the five-membered ring involving a single carboxyl and the seven-membered ring involving two carboxyls, without change in the structure or configuration around the asymmetric carbon, points up again that the sign effect of a ligand on the metal ion CD depends intimately on the details of its bonding to the metal ion.[15] We cannot say in this case whether it is the negative charges on the carboxylates which are effective or some difference in geometrical bond angle strain due to the difference in ring size, or still some other factor. As there is no good reason to doubt that chelants occupy two cis coordination positions, this potential for differentiated behavior should be reasonably independent of the other occupants of the residual coordination positions, except insofar as these may influence the bonding itself, or introduce additional fields or symmetry effects that interact with those due to the active ligand.

The greater complexity of the CD spectra for complexes with tartrate, compared to malate, seems to be a general characteristic (*cf.* the Ni(II) and rare earth complexes[3,13,14]). The behavior of glutamic acid like a monocarboxylic amino acid, exhibited here with Co(II), has been remarked on with Ni(II)[2] and other cations and apparently reflects a geometrical influence attributable to the additional methylene group.

For Ni(II) and some rare earths, it has been possible to localize the hydroxyl coordinated in a polyhydroxylic sugar acid, by correlating the CD sign following hydroxyl deprotonation with the configurations at the several hydroxyl positions (α, β, γ).[3,13,14] The necessity to avoid alkaline solutions which might lead to Co(III) formation, as well as Co(II) precipitation, restricts the area of experimentation in which a similar test may be made. By using large excess of ligand and converting almost all lactone to anion before adding Co(II) to the solution, it was possible to demonstrate deprotonation in the pH range 5–7, depending on the ligand, and to find CD spectral changes appropriate to such a binding change. Under such conditions, however, a variety of molecular species may form, other than the 1:1 complexes, and comparison must be tentative. There is in fact a variety of CD spectral forms found, and in some systems (*e.g.*, gluconate) a change in spectrum with time, indicating equilibration to some slower forming species.

Of the reagents available to us, four had the configuration *d,d* for the α- and β-carbon atoms, namely, the ribonic, gulonic, α-D-glucoheptonic, and α-D-saccharinic acids. Two had the *l,l* configuration—L-erythronic and D-mannonic acids. Four of these six systems showed Co(II) CD spectra in the deprotonated complex pH region which were of the same sign as the low-pH spectra, though being different from those low-pH spectra and showing individual differences from each other (Figure 6). One of the four showed a negative component in the 585-nm region in an otherwise positive spectrum (α-D-saccharine). Of the other two systems, the gulonic inverts from a positive low-pH spectrum to a negative one with considerable overt indication of individual components, through the 600–700-nm region CD. This new ribonate CD is unprecedentedly intense, at least twice the erythronate intensity and probably 5 times or more that of other complexes.

Reagents with *l,d* or *d,l* configuration at the α- and β-carbon atoms were arabonic, gluconic, and galactonic acids. The latter two, both *d,l*, showed a tendency for a strong negative component in the 530-nm region, though with time the gluconic acid system changed to a completely different spectrum, with mainly positive components, and a marked 400-nm dichroism (Figure 7). Arabonic acid (*l,d*) developed a Co(II) CD spectrum in the pH 6–7 form which was strongly positive in the 530-nm region, but also had a marked positive 400-nm component like the second gluconate spectrum. Idonic acid is also *l,d* but it is not certain how "pure" the main peak CD obtained was. The 575–700 nm portion is more like an inverse to the α-D-glucoheptonate (*d,d*) than the generally two-signed spectrum of the other *x,y* types.

If one assumes that the first gluconic acid spectrum and the arabonic and galactonic spectra represent 1:1 complexes with Co(II) and that four *d,d* and *l,l* systems that behaved similarly to each other also represent 1:1 complexes, one can make the following deductions. First, both groups cannot simultaneously represent deprotonation at the α hydroxyl, since one group retains the CD sign of the spectrum with the low-pH complex, while the second does not. If one then makes the simplifying (but not necessarily correct) assumption that all of the 1:1 complexes deal with the same position on the carbon chain, then this must represent the β carbon, with sign retention between the *x,x* reagents from the low-pH to the higher pH complexes and sign inversion for the *x,y* group. This would accord with the relations for the Ni(II) complexes,[3] in which the β hydroxyl was used. It would however differ in that for the Ni(II) systems the CD sign for *d* configuration was positive for the α carbon, but negative for the β hydroxyl. Another significant conclusion from the higher pH complexes is that the field of the ligand does not affect all transitions the same, since the CD of different transitions in the same spectrum may differ in sign. This allows the possibility that the portion of the ligand outside of the chelate ring may still exert an influence (*e.g.*, the γ or δ substituents). Resolutions of the main CD peaks of these deprotonated complexes suggest that there are probably three components derived from $^4T_{1g}(O_h)$, thus less than C_{2v} effective symmetry, but the nonuniformity of the spectra makes these resolutions and their interpretation un-

(13) L. I. Katzin, *Inorg. Chem.*, 7, 1183 (1968).
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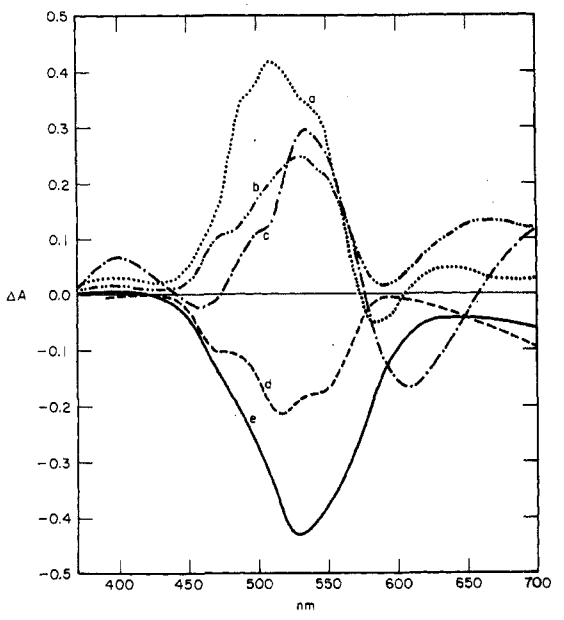

Figure 6. CD spectra of Co(II)-deprotonated hydroxy acid anion complexes with similar configurations on α and β carbons (multipliers to nominal ΔA scale in parentheses): (a) α-D-saccharine (×0.010); (b) α-D-glucoheptonate (×0.010); (c) D-arabonate (×0.010); (d) D-mannonate (×0.004); (e) L-erythronate (×0.020).

certain. Neither the absorption spectra nor the CD spectra for these complexes are like those for the cobalt(II)-dipeptide systems recorded for pH 9 and above.[16,17]

Registry No. L-Alanine, 56-41-7; L-valine, 72-18-4; L-serine, 56-45-1; L-methionine, 63-68-3; L-proline, 147-85-3; L-hydroxyproline, 51-35-4; L-lysine, 56-87-1; L-arginine, 74-79-3; L-ornithine, 70-26-8; L-aspartic acid, 56-84-8; L-glutamic acid, 56-86-0; L-asparagine, 70-47-3; L-lactic acid, 79-33-4; L-malic acid, 97-67-6; D-tartaric acid, 147-71-7; L-erythronic acid, 20703-66-6; D-ribonic acid, 642-98-8; D-arabonic acid, 488-30-2; D-gluconic acid, 526-95-4; D-gulonic acid, 20246-33-7; D-galactonic acid, 576-36-3; D-idonic acid, 488-33-5; D-mannonic acid, 642-99-9; D-pantoic acid, 1112-33-0; α-D-glucoheptonic acid, 87-74-1; α-D-saccharinic acid, 13962-35-1; cobalt, 7440-48-4.

(16) M. S. Michailidis and R. B. Martin, *J. Amer. Chem. Soc.*, 91, 4683 (1969).
(17) P. J. Morris and R. B. Martin, *Inorg. Chem.*, 10, 964 (1971).

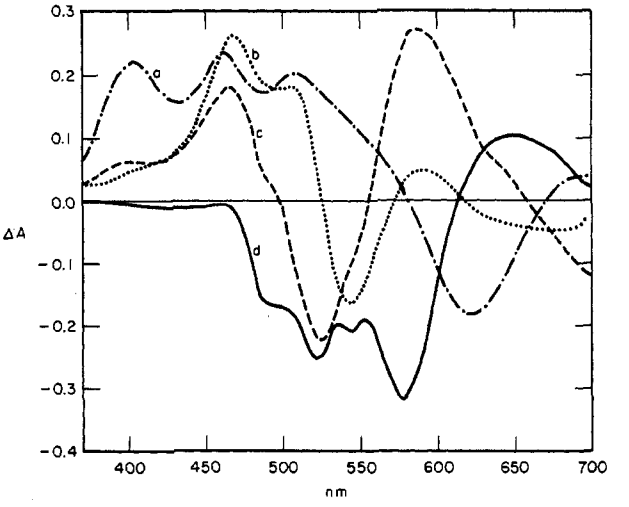

Figure 7. CD spectra of Co(II)-deprotonated hydroxy acid anion complexes with dissimilar configurations on α and β carbons (multipliers to nominal ΔA scale in parentheses): (a) D-gluconate, after 24-hr equilibration (×0.010); (b) D-galactonate (×0.004); (c) D-gluconate, on preparation (×0.010); (d) D-gulonate (×0.004).

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μ-Oxalato-cobalt(III) Complexes

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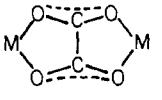
Binuclear, trinuclear, and tetranuclear cobalt(III) complexes containing a single bridging oxalate ligand have been prepared and characterized. Elemental analyses and ultraviolet–visible and infrared spectra are reported. Behavior on reduction with Cr^{2+} and V^{2+} is consistent with the structures proposed.

Binuclear complexes in which both metal centers are linked to a planar tetradentate oxalate ligand to give two five-membered rings



have been known for some time. Well-established examples are the tri-*n*-butylphosphinepalladium(II) complex $[(n\text{-}Bu_3P)(Cl)PdC_2O_4Pd(Cl)(P\text{-}n\text{-}Bu_3)]$[2] and the pyridineruthenium(II) complex $[(C_5H_5N)_4RuC_2O_4Ru(C_5H_5N)_4](BF_4)_2$.[3] The mineral humboltine contains iron atoms linked by oxalate ligands to give planar polymeric chains, two water molecules completing the coordination about each iron.[4] The oxalate is similarly tetradentate in β-[Cu-

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