in the same way as $MSBenNEt_2$ (I, Y = S) in its interaction with cobalt(II) halides in giving only tetrahedral complexes, whereas $MABenNEt_2$ (I, Y = NH) gives only pentacoordinate complexes. This must reflect on the donor strength of oxygen and sulfur as compared with nitrogen, since to all intents and purposes the steric factors in the three ligands are identical.

Acknowledgments.—Thanks are expressed to Mr. F. Zanobini for assistance in the preparation of the compounds. We are indebted to Dr. J. Gelsomini for microanalyses and to Mr. F. Nuzzi for the metal analyses. The financial support of the Italian "Consiglio Nazionale delle Richerche" is gratefully acknowledged.

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Absorption Spectral and Circular Dichroic Studies of Complexes of Hydroxy Acids with Praeseodymium Ion[1]

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Received February 16, 1968

Complexes of three types were characterized, according to the general pH range in which they were obtained, as acid, neutral, and alkaline complexes. All three could be obtained with many of the ligands. Spectra obtained could be attributed to effects of splitting both ground and excited states of the central metal ion. Each spectral transition apparently exhibited circular dichroism, so that a transition could be identified by either an absorption or dichroism component, as convenient. In the 430–510-mμ wavelength band, in which Pr(III) normally shows only three peaks of the $^3P_{2,1,0}$ multiplet and also has a buried $^1I_6$ transition, as many as 21 transitions could be recognized for the 1:1 alkaline tartrate complex. Correlation of the various spectra led to the following conclusions of chemical interest: acid complexes showed a sign of the CD defined by hydroxyl configuration at the α carbon; neutral complexes showed a sign of CD correlated with the sign of the lactone rotation which in turn is correlated with the sign of the hydroxyl configuration at the γ carbon, where this is an asymmetric center. Further conclusion was that seven-membered rings would form where the internal levels of the ligand favored this, six-membered rings would also form readily where this was the available choice, and under certain conditions, five-membered rings could form. Ligand acids used were tartaric, lactic, erythronic, ribonic, arabonic, xylonic, gluconic, gulonic, mannonic, idonic, galactonic, glucoheptonic, saccharinic, pantoic, malic, and saccharic acids.

Introduction

It has been shown[2] that rare earths form stable complexes with tartrate, with marked effects on the absorption spectra of the rare earth ions. Gray[3] has reported observing Cotton effects in the optical rotatory dispersion of alkaline tartrate solutions containing Nd(III), in the region of the Nd(III) absorption bands. Similar data have been obtained in this laboratory[4] for the Pr(III) complex, but it was obvious that the ORD technique was not suited to the fine-scale studies which the spectral alterations[2] made evident were needed.

The recent availability of a sensitive circular dichroism (CD) instrument has made it practical to reinvestigate the properties of rare earth complexes with optically active ligands and to map the correlations of the absorption and CD spectra. This paper will report the results of such a study with tartaric acid and a series of other hydroxy carboxylic acids as the ligands. Results with amino acids as the ligands will be reported separately.[5]

In addition to information on the spectral correlations mentioned, it has been possible to obtain considerable valuable information on chemical relations in the complex formation. Preliminary observations in this laboratory on the complexes of Nd(III), Er(III), etc., indicated fine-scale CD effects (*e.g.*, the 350-mμ band of neodymium(III) tartrate complex) which showed much more structure than was overt in the absorption spectrum. Investigations to be reported here are restricted to complexes of Pr(III), as the spectrum of this rare earth ion is simple enough to allow alterations to be followed in considerable detail.

Experimental Section

Spectral measurements were made with the Durrum–Jasco spectropolarimeter ORD–UV–CD-5. With Pr(III) concentrations of approximately 0.1 *M*, it was generally convenient to use 50-mm cells for the CD measurements, and 10-mm cells for the absorption spectra.

Most of the organic acids used in the study were available in the form of lactones, whose hydrolysis in water was quite variable with time and pH. The following procedure was therefore generally adopted. An amount of solid lactone sufficient almost to saturate 2 ml of water was dissolved to about that volume, and 2 or 3 drops of 5 *M* NaOH were added. When the pH of the mixture had settled back to pH 4 or less, indicating that anions had been formed, 1 ml of 0.3 *M* praeseodymium chloride solution (slightly acid) was added. Further additions of NaOH, as desired, increased the concentration of acid anion by further hydrolysis of lactone and ionization of the hydrolyzed acid.

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.
(2) L. I. Katzin and M. L. Barnett, *J. Phys. Chem.*, **68**, 3779 (1964).
(3) F. Gray, *Phys. Rev.*, **7**, 472 (1916).
(4) L. I. Katzin and R. W. Anderson, unpublished work.
(5) L. I. Katzin and E. Gulyas, in preparation.

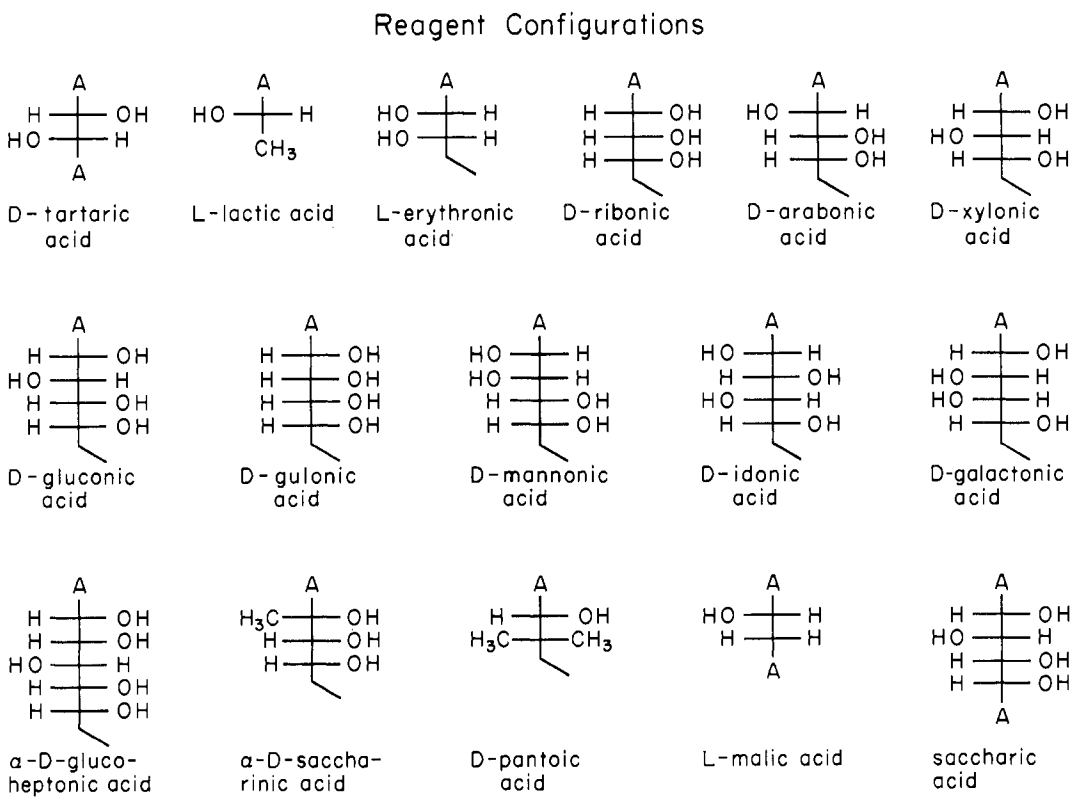

Figure 1.—Structures of ligand acids, where A is the carboxyl group and the tail is the conventional designation of a terminal $-CH_2OH$ group.

Where hydrolysis was slow, a precipitate sometimes formed, which redissolved as more acid anion was generated. Hydrion paper served to monitor the pH.

Of the hydroxy acids used, the tartaric acid and lactic acid were Baker Analyzed and were the same lots characterized in previous ORD and CD studies.[6] The *α-gluco*-heptonic lactone, γ-galactic lactone, and L-malic acid (the last also previously used[6c]) were Pfanstiehl products. (−)-Pantoyl lactone, gulonic lactone, and saccharic acid (K salt) were supplied by Nutritional Biochemicals Co. Glucono-δ-lactone (Matheson Corp.) and D-arabonic acid γ-lactone and D-ribonolactone (K & K Laboratories) were the other commercial products used. Laboratory-prepared samples of L-(+)-erythronic lactone, xylonic lactone, α-D-(+)-saccharinic acid, idonic acid (strychnine salt), and mannonic acid (brucine salt) were available and were attributed to original preparations by J. W. E. Glattfeld. One or two ambiguities in labeling which made it unclear whether a given preparation was the D or the L isomer, in current sugar chemical nomenclature, were resolved by checking the sign of the lactone rotation against the literature.[7]

Both CD and absorption spectral traces of the tartrate complex spectra were analyzed into Gaussian components with the aid of a Du Pont Model 310 curve resolver, with 10 channels. As each channel has peak height and width as parameters, in addition to wavelength, it was possible to obtain (with visual matching) slightly different relative intensities and peak widths for some of the spectral components, on repetition of curve analysis, but such variations did not significantly modify the analysis. Components found were recorded on an X–Y plotter incorporated into the apparatus, and parameters were read from this plot.

The Fisher convention configurations of the reagents used, which are relevant to the succeeding discussion, are shown in Figure 1.

(6) (a) L. I. Katzin and E. Gulyas, *J. Phys. Chem.*, **66**, 494 (1962); (b) L. I. Katzin and E. Gulyas, *J. Am. Chem. Soc.*, **88**, 5209 (1966); (c) L. I. Katzin and E. Gulyas, *ibid.*, **90**, 247 (1968).

(7) C. S. Hudson, *ibid.*, **32**, 339 (1910).

Results

Tartrate Complexes.—This system, with no complications due to lactone and with a stability for the 1:1 complex which allows detailed analysis, furnishes a reference against which the findings for the other reagents can be compared.

As reported before,[2] precipitation commences in a mixed solution of tartaric acid and $PrCl_3$ as neutralization of the acid is initiated. On attainment of pH ~7, allowing time for equilibration, a clear solution is obtained in the presence of a few per cent excess of tartrate. The absorption in the spectral region of the $^3P_{2,1,0}$ multiplet, at pH 7–8, is shown in Figure 2, together with the corresponding circular dichroism spectrum. In this pH region the tartrate concentration may be varied from 1.05 to at least 3.2 times the Pr(III) concentration with no effect on these spectra. From about pH 8 up, however, they undergo a slow change, which is faster the higher the pH and the greater the excess of tartrate. With a 3.2 ratio of tartrate to Pr(III), the change might be complete in 1 hr. With only a few per cent excess of tartrate and probably considerably more NaOH, several days to 1 week might be required for completion. This second spectrum, which will be referred to as the "alkaline spectrum," is shown in Figure 3, together with its associated CD spectrum. It is identical with the absorption already reported[2] for the 1:1 complex, but the earlier pH designation is incorrect.

Addition of HCl to the alkaline complex solution, with precautions to avoid irreversible precipitation in

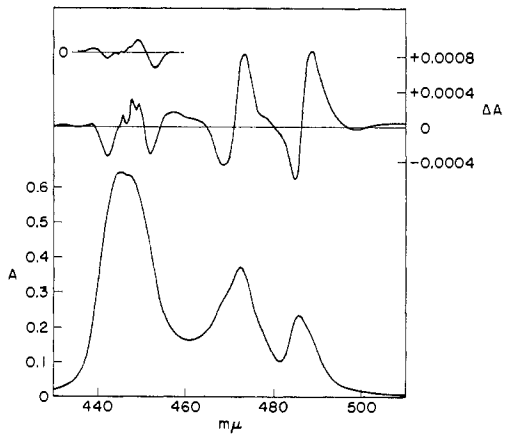

Figure 2.—Absorption and CD spectra of the neutral praeseodymium tartrate complex. A, ΔA in absorbance units; CD path length, 50 mm; absorption, 10 mm; CD inset, 30-mm path; Pr(III), 0.10 M.

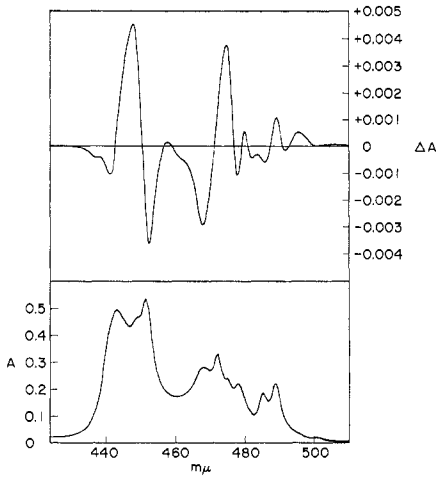

Figure 3.—Absorption and CD spectra of alkaline praeseodymium tartrate complexes. A, ΔA in absorbance units; CD path length, 50 mm; absorption, 10 mm; Pr(III), 0.10 M.

portions of the solution momentarily acid (excess tartrate helps), to bring it down to pH 7.5–8, regenerates a spectrum which looks very much like that of the original neutral complex, but with differences which are brought out by superposition of the two spectra. The difference in the $^3P_2$ band is perceptible without this (Figure 4). There are very marked differences in the CD pattern, most obvious (Figure 4) in the region of the $^3P_1$ band. Addition of acid to the alkaline complex must give a regenerated neutral complex which is different in structure than the one freshly formed from the acid precipitate.

Visual inspection of the alkaline absorption spectrum (Figure 3) between 460 and 510 mμ suggests the presence of ten or eleven components, and in fact the resolution demonstrates just these eleven. Differences between different trials in this spectral band are not significant, except possibly for the component at about 463 mμ. Below 460 mμ, with favorable traces, the eye can see indications of perhaps five components, and the analysis can locate at least seven or eight. Here

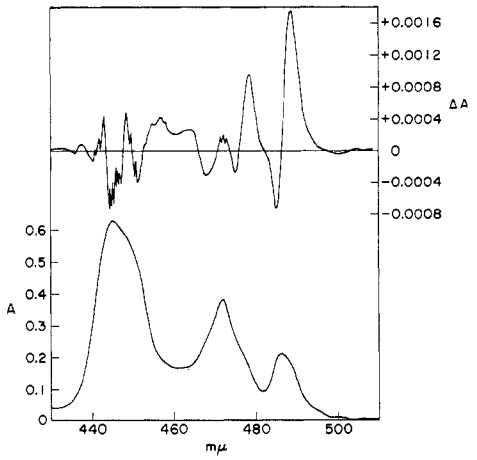

Figure 4.—Absorption and CD spectra of the reconstituted neutral praeseodymium tartrate complex. A, ΔA in absorbance units; CD path length, 50 mm; absorption, 10 mm. Noise in CD at 445–455 mμ and at 470 mμ owing to high absorbance; Pr(III), 0.10 M.

the congestion and intensity range of the components makes the resolutions less definitive, so some variation in component parameters can occur between trials. The intensity of the 463-mμ component, lying between much stronger transitions, in a relatively featureless minimum of the envelope, may also suffer in this respect. The occurrence of both positive and negative signs in the CD makes much of that resolution more definitive, though it is possible to "lose" components in the places where there are strong positive–negative swings.

In the final results, Table I, there is essentially a 1 to 1 correspondence between circular dichroism and absorption spectral components. The negative CD to match the 433-mμ absorption is probably buried in the 437-mμ component. There are two instances where a single absorption component (443, 482 mμ) is linked to a pair of CD components which are unmistakable, as they are of opposite sign. In both of these cases the absorption component is over twice the usual width (about 4 mμ at half-height, CD components slightly narrower), with the inference that two close and fairly equally intense transitions are unresolved. The 468-mμ absorption is also relatively broad but is apparently related to a single CD, about 4.5 mμ in width. The conclusion, therefore, is that the spectrum which consists of the ^3P trio in aqueous Pr^{3+} (and the weak, buried $^1I_6$ at about 462 mμ) has been split into at least 21 components in the alkaline spectrum.

The $^1D_2$ peak, with absorption at around 590 mμ in water, is rather broader than the individual ^3P peaks. In the tartrate complex it broadens more (primarily to the long-wavelength side), with visual indications of six components. The CD pattern shows broad components correspondingly (Figure 5), but no resolution of them was undertaken.

Resolution of the components in the neutral-complex spectrum from about 455 mμ up is straightforward, and a single trial each on the absorption and CD spectra yielded the concordance shown in Table I. The

TABLE I

ABSORPTION AND CD SPECTRA OF THE PRAESEODYMIUM(III) TARTRATE COMPLEXES: COMPONENT ANALYSIS

Pr^{3+} absorption	Neutral complex					Alkaline complex					Regenerated neutral complex				
	Absorption		CD			Absorption		CD			Absorption		CD		
λ, mμ	λ, mμ	A^a	λ, mμ	ΔA ($\times 10^4$)[a]	$\Delta\epsilon/\epsilon$ ($\times 10^3$)[b]	λ, mμ	A^a	λ, mμ	ΔA ($\times 10^4$)[a]	$\Delta\epsilon/\epsilon$ ($\times 10^3$)[b]	λ, mμ	A^a	λ, mμ	ΔA ($\times 10^4$)[a]	$\Delta\epsilon/\epsilon$ ($\times 10^3$)[b]
						433	0.3	...	(neg)	...					
	436	0.055				438	0.07	437	−0.76	−1.1	438	0.03			
443.5 ($^3P_2$)	444–	0.57				443	0.45	441.5 444.5	−2.0 +2.8	<−0.45 >+0.62	444	0.57_5			
						446.5	0.09	447	+4.6	+5.1					
	450	0.41	(449)	(Pos)		449.5	0.30	449.5	+6.8	+2.3	450	0.33			
						452	0.40	452	−7.4	-1.8_5					
			(453)	(Neg)		455.5	0.18	455.5	−1.6	−0.89	454	0.10	455	+0.52	+0.52
	457+	0.13	457	+0.28	+0.2	459	0.10	459	+0.40	+0.40	457.5	0.13	459	+0.64	+0.49
(462) ($^1I_6$)	462	0.12	462	+0.16	+0.1	462.5	0.01	463	−0.8	−8	463	0.11	461.5 465	+0.32 +0.48	>+0.3 >+0.45
468.8	468	0.235	468	−0.92	−0.39	468	0.27	468	−5.6	−2.1	468.5	0.20	469	+0.68	−0.34
($^3P_1$)	471.5	0.185	473	+1.64	<+0.89	472.5	0.14	474	+5.6	+4.0	472.5	0.29	473	+0.96	+0.33
	474	0.24			<+0.68	475.5	0.11_5	476	+5.2	+4.5	477	0.16	475	−0.72	<−0.45
	478	0.16	478	+0.20	+0.1	478.5	0.14	477.5	−7.4	−5.2			479	+1.84	+>1.15
	481	0.09	481	−0.20	−0.2			481	+1.2	>+1.25					
						482	0.09_5	483	−1.45	<−1.5	482	0.08	(482)	(Pos)	...
482.0	485	0.19	485	−1.40	−0.74	485.5	0.15	487	−1.3	−0.87	486.5	0.17_5	486	−1.68	−0.96
($^3P_0$)	488.5	0.15	488	+1.80	+1.2	489	0.16	490	+2.25	+1.4	490	0.10	489	+3.6	+3.6
						491.5	0.06	492.5	−0.86	−1.4					
	494	0.03	492	+0.36	+1	498	0.01	497	+0.92	+9	494	0.025	493	−0.24	+1.0
	499	0.01	499	−0.08	−0.8	502	0.01	501	−0.2	−2	500	0.005	499	−0.12	−2.5

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

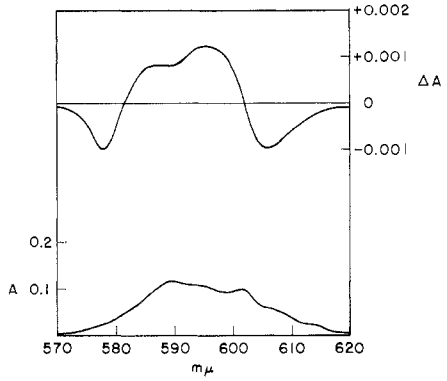

Figure 5.—Absorption and CD spectra of the alkaline praeseodymium tartrate complex, $^1D_2$ band. A, ΔA in absorbance units; CD path length, 50 mm; absorption, 10 mm; Pr(III), 0.10 M.

weakness of the CD below 455 mμ, in conjunction with the absorption intensity (good measurements are limited to absorbancies less than 2.5) inhibits detailed resolution. With a 30-mm rather than a 50-mm cell path, there is an unambiguous negative extremum at about 453 mμ, a positive one near 449 mμ, and a further poorly defined negative one near 442 mμ and positive one near 439 mμ, as is suggested in the noisier 50-mm-cell trace (Figure 4). The apparent 450-mμ component in the absorption spectrum therefore covers two (or possibly even three) actual components.

Comparison of both the absorption and CD intensity relations between the neutral and alkaline spectra suggests strongly that nevertheless the six transitions between 440 and 457 mμ in the latter spectrum are best characterized as derivatives of the 444-, 449-, and 453-mμ components of the neutral spectrum by some sort of splitting-related transition change and are not directly the same components, with altered intensities. This is even more clearly the case between the 478- and 481-mμ transitions of the neutral complex, and the 477.5-, 481-, and 483-mμ components of the alkaline spectrum. It also seems probable that the 488.5-mμ transition of the neutral complex is split in giving the 489- and 491.5-mμ components of the alkaline spectrum, with the apparent 498-mμ alkaline component possibly being a superposition of a third member of this splitting on the original 494-mμ neutral component (note the very high ΔA and $\Delta\epsilon/\epsilon$ values).

Visual differences in the absorption spectra of the reconstituted and original neutral complexes are expressed in the component analysis by the weakness of the 450-mμ component of the reconstituted complex compared to that in the original (444-mμ component strength equal), the shift and greater strength of the 472-mμ component, and essential absence of the 474-mμ component relative to the spectra of the original neutral complex. The wavelength difference between 486- and 485-mμ components also reflects real differences in the spectra. Strongest characteristic individualities are shown in the CD spectrum: there are sign reversals from the original neutral spectrum for the 454- and 482-mμ components; the strong negative–positive pair at 475 and 479 mμ are opposite in sign to the corresponding pair in the alkaline spectrum, and the original neutral species has only weak dichroism here; and the 486- and 490-mμ components (especially the last) are stronger than the corresponding members of either of the other two spectra.

Although there is variation in the $\Delta\epsilon/\epsilon$ (dissymmetry ratio) values for the individual components, there is a reassuring amount of consistency and recognizable pattern. Particularly in the $^3P_0$ band, transitions (such as the 485-mμ component) which are largely constant through the three species are about equally constant in the dissymmetry ratio. This verifies its nature as a characteristic parameter. The changes in the $^3P_2$ and $^3P_1$ bands in consequence of alkaline complex formation give $\Delta\epsilon/\epsilon$ values that form a reasonable pat-

tern. The differences seen in the regenerated neutral complex give a useful differentiating criterion. The characteristic $\Delta\epsilon/\epsilon$ values for the strong components in these praeseodymium(III) tartrate spectra are still only 0.1–0.2 those found for organic carboxyls[6c] and are a still smaller fraction of the carbonyl values.

Monocarboxylic Acids.—Unlike tartaric acid, these reagents do not precipitate Pr(III) in acid solution. It is, therefore, possible to anticipate a series of stepwise equilibria. In the acid region, where Pr(III) hydrolysis should not be a factor, anionic ligand should penetrate the coordination sphere by displacing water, favored by chelation coordination of a hydroxyl group to displace a second water molecule. A second or even a third group might follow, under favorable conditions. In the neutral region, in which tartrate complexed to Pr(III) undergoes deprotonation of a hydroxyl, a similar reaction may take place with the monocarboxylic anions. This reaction may involve elimination of the other organic ligands from the sphere or, if retained, they may undergo the reaction successively. Where the complexing is relatively weak and the deprotonation difficult, competition from the hydroxyl ions in the alkaline range may lead to precipitation of Pr(III), in the extreme perhaps as low as, say, pH 6.

Parallel observations on the CD and absorption spectra, as with the tartrate system, in fact demonstrate the fundamental stages of the above processes in the systems studied. Though, as with the tartrate, very marked and intense changes may occur in the CD of the $^1D_2$ absorption, data here will be limited to the more revealing ^3P peaks. In dilute HCl these latter are narrow and sharp, and appear at about 443.5, 468.8, and 482.0 mμ (*cf.* Table I) with extinction ratios 2.35:1.0:0.857.

Acid Region.—In the most acid conditions, *ca.* pH 1, all of the organic acids used in this work are essentially completely associated, and no CD or spectral indications of interaction between Pr(III) and organic ligand are observed. For some, decreasing the acidity just to pH 3 produces a change. Others, with higher pK, or difficulty in lactone hydrolysis, may require a higher pH to show an initial effect. The signal that there is interaction with the ligand anion is the appearance of a CD pattern of a fairly characteristic kind (Figure 6).

When a sufficient fraction of the Pr(III) is involved, a marked broadening of the absorption peaks occurs, with an apparent decrease in the peak intensity. Peak wavelength shifts are small but definite, to limits of about 444.5, 470, and 483 mμ, respectively. For the $^3P_1$ component the maximum intensity decrease is about 15%, but it is more for the other two, since the limiting intensity ratios are now about 1.90:1.0:0.62.

The CD effects are relatively weak, the characteristic $\Delta\epsilon/\epsilon$ value for the extremum at 482–483 mμ being $\pm(0.2\text{–}0.4) \times 10^{-3}$. The significant difference between patterns for different ligands is the sign of the extremum at 482 mμ. This is positive for a majority of the acids in this study but is negative for lactic, erythronic, arabonic, idonic, and mannonic acids of the monocarboxylic group and for malic acid in the pH 2–3 range (Table II). With acids for which the complexing demonstrating this "acid" form of interaction is strong and for which the next stage is brought about with difficulty, the pattern may be maintained in full strength even to pH 7—pantoyl acid is an example.

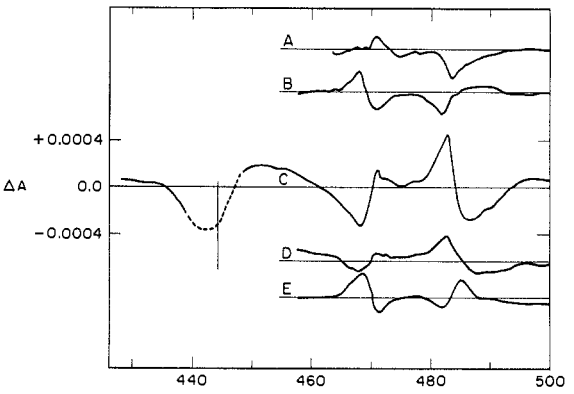

Figure 6.—Specimen praeseodymium–sugar acid "acid" complex CD spectra: A, lactic acid; B, arabonic acid; C, galactonic acid (dashed section reconstructed from measurements with 10-mm path length; vertical bar indicates location of absorption maximum); D, ribonic acid; E, arabonic acid (higher ligand concentration than B); Pr(III), 0.10 *M*; 50-mm path.

TABLE II
CORRELATIONS OF CD SIGN AND LIGAND STRUCTURE FOR PRAESEODYMIUM(III)–HYDROXY ACID COMPLEXES

Ligand acid	CD sign (~482 mμ)	α-Hydroxide config	Neutral complex, CD type ($^3P_0$ band)	Lactone rotation sign[a]	γ-Hydroxide config
D-Tartaric	...	*d*	T	...	...
L-Lactic	Neg	*l*	...	...	...
L-Erythronic	Neg	*l*	Anti-T	Pos	...
D-Ribonic	Pos	*d*	T	Pos	*d*
D-Arabonic	Neg	*l*	T	Pos	*d*
D-Xylonic	Pos	*d*	T	Pos	*d*
D-Gluconic	Pos	*d*	T	Pos	*d*
D-Gulonic	Pos	*d*	Anti-T	Neg	*l*
D-Mannonic	Neg	*l*	T	Pos	*d*
D-Idonic	Neg	*l*	Anti-T	Neg[b]	*l*
D-Galactonic	Pos	*d*	Anti-T	Neg	*l*
α-D-Glucoheptonic	Pos	*d*	Anti-T	Neg	*l*
α-D-Saccharinic	Pos	*d*	T	Pos	*d*
D-Pantoic	Pos	*d*	...	Neg	...
L-Malic	Neg[c]	*l*	Anti-T	...	...
D-Saccharic	...	*d*, *l*	T		*d*[d]
Glucuronic	Pos	*d*	...		

[a] C. S. Hudson, *J. Am. Chem. Soc.*, **32**, 339 (1910). [b] K. Rehorst and A. Naumann, *Ber.*, **77B**, 24 (1944). [c] At pH 2–3. [d] Viewed as *either* D-*gluco*-saccharic or L-*gulo*-saccharic acid.

Neutral Region.—For the stronger complexers and ligands more readily deprotonated (*e.g.*, xylonic and galactonic acids), raising the pH to 6 changes the CD pattern drastically. It becomes much more intense, structured, and detailed (*e.g.*, Figure 7). The pattern in the region of the original $^3P_0$ peak most often resembles that for the neutral tartrate complex (or its sign-inverted image), though occasionally it may have the feature of the alkaline tartrate CD (equivalent of 492-mμ component of sign opposite to 490-mμ component).

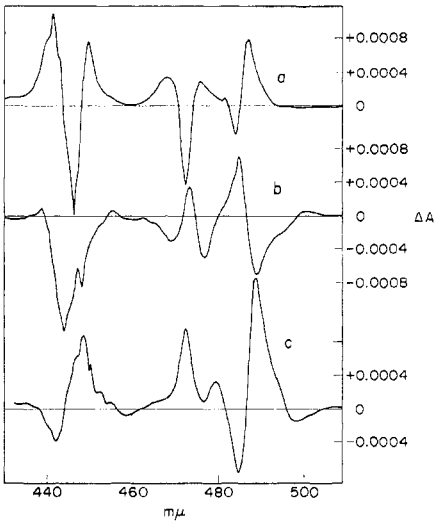

Figure 7.—Specimen praeseodymium–sugar acid "neutral" complex CD spectra: A, xylonic acid; b, gulonic acid; c, ribonic acid. (440–450 mμ region noisy in b and c.) Pr(III), 0.10 *M*; 50-mm path.

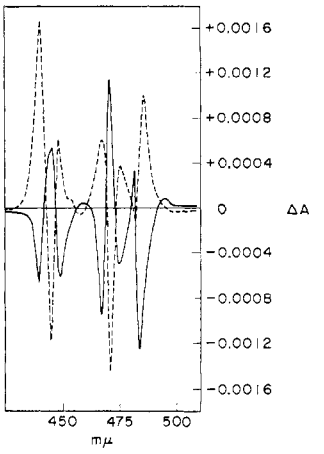

Figure 8.—Praeseodymium–sugar acid "neutral" complex CD spectra for gluconic (dashed) and galactonic (full) acids, showing inverse signs.

An occasional spectrum may seem to present other variants, but in general these can be ascribed to the presence of multiple species or to a difference in apparent intensity of a component. This last is often the equivalent of the shortest wavelength member of the $^3P_0$ group (negative 486-mμ component in the tartrate system). Sometimes the CD in the $^3P_1$ band will show structure as detailed as for the neutral tartrate complex, but most often the pattern for that, and for the $^3P_2$ band also, will be best represented by superposition on a single, broad component of a much narrower, more intense one of opposite sign, centered at a slightly longer wavelength (see Figure 7).

When there is considerable excess of ligand, the absorption spectra come to resemble that for the neutral tartrate complex (Figure 2), with some minor differences, principally in the $^3P_2$ band. Where there is a lower ligand ratio, the absorption peaks tend to be at slightly lower wavelength, and the presence of a mixture of acid form and neutral form is signaled by separated peaks for both, particularly within the $^3P_1$ and $^3P_0$ bands. In some cases a possible proportion of Pr(III) may exist in uncomplexed form also, but no separate recognizable spectral peak is seen.

As already suggested, the CD patterns differ in sign as well as in more detailed points. For convenience, spectra having $^3P_0$ CD components that correspond to the tartrate pattern (485-mμ component negative, 488-mμ component positive) will be designated T type, and those with components of the opposite sign will be called anti-T. This nomenclature is followed in Table II. It will merely be pointed out here that the signs of the acid-region complex CD and this neutral-region complex do not necessarily correlate. Thus, the neutral-region CD patterns for gluconic and galactonic acid complexes are seen to be opposite in sign (indeed, essentially sign-inverted images) in Figure 8, whereas their acid-region complexes have CD patterns of the same sign.

Alkaline Range.—Not all systems are equally tolerant of pH values above 8. Where the systems can be followed without interruption by precipitation, more alkali broadens the spectral peaks further than in the neutral range and lowers their maximum extinction. Sometimes, however, there is an increase in the extinction of the $^3P_0$ absorption, suggesting a sharpening of the peak. The wavelength of the maximum comes fairly uniformly to about 485 mμ; that of the $^3P_1$, to about 473 mμ. The most noticeable change is in the original $^3P_2$ peak, which now shows two definite components, roughly at 448 and 444 mμ, though they are not resolved. The absorption is often greater at the 448-mμ maximum than at the lower wavelength, differing from the neutral tartrate spectrum.

The CD spectrum in all cases loses intensity and complexity. There tends to be a single, broad CD peak approximately coincident in wavelength with each of the 485- and 473-mμ absorption peaks. Each of the components of the 444–448 mμ pair seems generally to have a broad, weak CD peak, the signs being opposite. Variations from this basic pattern are prevalent, *e.g.*, confluence of the 473- and 485-mμ components. The 440–450-mμ region may again, as in the neutral range, show a broad CD with an overlapping sharper peak of the opposite sign, but the signs may be inverted from the corresponding pattern of the neutral-range spectrum. Some of these phenomena may represent mutual interference of the patterns for a mixture of species in solution, since after some days or weeks solid phases may be deposited from the solution. However, alterations of the ligands on long exposure to alkali are known to occur.[8] Formation of alkaline complexes may in some cases indicate involvement of a second molecule of ligand.

For some ligands (*e.g.*, ribonic acid), it is necessary to go to pH 8 and even perhaps pH 10 to obtain the "neutral-region" spectra. These are often ligands whose

(8) W. W. Pigman and R. M. Goepp, Jr., "Chemistry of the Carbohydrates," Academic Press Inc., New York, N. Y., 1948.

lactones are most stable and difficultly hydrolyzed. A concentration of these ligands sufficient to hold the Pr(III) in solution at pH 7, where the "acid-region" spectrum is still shown, will form some solid phase immediately on addition of NaOH, which, after some time, will revert to a clear solution at the higher pH. With gulonic acid, the CD pattern obtained is apparently the alkaline type, the neutral type being skipped.

Dicarboxylic Acids.—As with tartaric acid, a Pr(III) precipitate is formed with saccharic acid at low pH, which dissolves at pH 7–8. The CD pattern is relatively weaker than for tartrate, but of the T type. The absorption is like that of the neutral complex. On raising the pH to 9–10, the CD intensity is diminished. The absorption peaks shift and the $^3P_1$ shows indication of fine structure, like that seen in the early stages of generating the alkaline tartrate complex spectrum. Adding more alkali and allowing time for slow reaction (as with the tartrate) finally yield a more intense CD than the pH 7 pattern. Differences in sign at critical points explain the apparent initial decrease in intensity. The final intensity is not equal to that of the alkaline tartrate complex CD, nor is the complexity of the pattern. The absorption shows overt splittings of the $^3P_1$ and $^3P_2$ bands which are smaller than in the tartrate complex. No splitting is visible in the $^2P_0$ band (Figure 9). The CD for the $^3P_2$ is of the narrow band–broad band combination type noted earlier, in correlation with the appearance of the absorption peak.

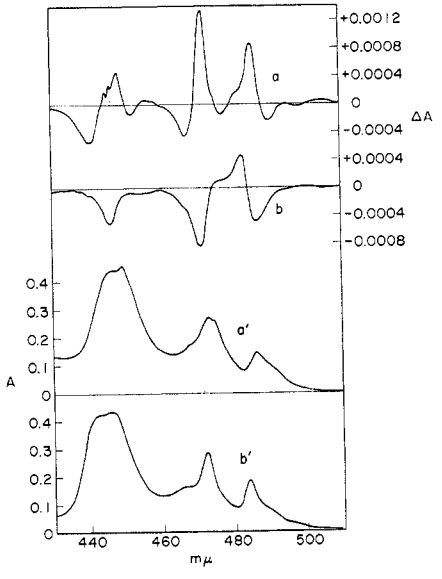

Figure 9.—Praeseodymium–dicarboxylic acid absorption and CD spectra: a, a′, alkaline complex, saccharic acid; b, b′, neutral complex, malic acid. Pr(III), 0.10 *M*.

With a sufficient concentration of malic acid, the solution containing Pr(III) remains homogeneous irrespective of pH, so it is possible to follow the details of the low-pH region. At pH 2–3, a weak, negative, acid-type CD is seen. At pH 5, at which the second carboxyl is largely ionized, a weak, positive CD is seen at about 485 mμ, and a second one is seen at about 470 mμ (the corresponding absorption peaks are at just under 484 mμ and just over 470 mμ). At pH 8 or higher there is a change (complete in 1 or 2 min) to a typical neutral CD pattern, which is anti-T (Figure 9). The $^3P_1$ absorption band looks most like the regenerated neutral tartrate, but there are two components in the $^3P_2$ band (Figure 9), which seems most general in the alkaline region. At gross NaOH concentrations (0.1 *N* and higher) slow precipitation takes place. Spectra taken in the early stages show further splitting of the $^3P_2$ band, among other changes.

Discussion

Restricting our attention for the moment to purely electronic transitions, the following general observations may be made. The chelate structure of the 1:1 neutral tartrate complex, for example, would be expected to distort and otherwise alter the distribution of the oxygen atoms around the Pr(III) ion, from that of the simply hydrated ion. One possible configuration would be that of an approximate equilateral triangular array at the ionic equator of the two charged oxygens of the tartrate (one carboxyl, one deprotonated hydroxyl) and one free hydroxyl ion. Additional water oxygens, say, three in each layer, might be arranged above and below this plane. On the other hand, considerably less symmetric arrangements might be seen. In any event, field distortions from those in the simple hydrated cation would be expected, lowering the symmetry. Splittings of the $^3H_4$ ground state will be expected, also of the upper states. The exact effect on each level and the resultant absorption spectrum could vary from ligand to ligand, as a function of degrees of splitting and quantum factors in the transitions.

A second basic point involves the appearance of circular dichroism because of the asymmetry in the ligand. It will be assumed that in all cases, as has been demonstrated for the tartrate complexes (Table I), the presence of a CD component implies the existence of a corresponding absorption component and *vice versa*, *i.e.*, all transitions are dichroic. The sign of the CD will be a function of the quantum factors, for a given complex species.

Practical use of these considerations will most often involve the $^3P_0$ upper state, which should suffer no splitting under the above field changes. Fine structures which appear in this absorption band must therefore primarily reflect the splittings and alterations in the ground state. Possible involvement of vibrational levels in determining the observed fine structure could make the $^3P_0$ level itself a more active factor in the results seen.

Almost all of the neutral-region complex CD spectra have envelopes for the $^3P_0$ band region which correspond to that for the neutral tartrate complex, which has been resolved into four components. The shorter wavelength pair are uniformly the most intense and opposite to each other in sign. The weaker, long-wavelength pair are again usually of opposite sign to each other, though the malate spectrum may differ. In a few cases (low-ligand mannonate, low-ligand alka-

line arabonate, alkaline pantoylate) there is a suggestion of the alkaline tartrate pattern, rather than that of the neutral tartrate. These similarities and variations, and those in the ratio of CD to absorption intensity, do not seem unreasonable within the range of similarity expected in binding of the central metal ion, for these related ligands.

The chemical implications of the data give further evidence of the often unique power of polarized-light studies in optically active chemical systems. The sign of the CD in the acid complex region correlates with the configuration at the α-carbon (Figure 1, Table II). This is compatible either with a monodentate carboxylate attachment or with weak chelation through an additional organic hydroxyl group. The author favors the latter view. It may not be evidence but is certainly suggestive that the CD of the lactate complex, with only an α-hydroxyl group available, lacks the broad CD at longer wavelength, neighboring to the 482–483-mμ peak, which most of the compounds having additional hydroxyls show. A chelate structure at this stage also furnishes a rationale for the rapidity with which the transition to the neutral complex takes place.

There is a voluminous literature on the reactions of tartaric acid with a very large variety of metal ions (including some reports of compounds of lanthanides isolated[9,10]) to justify the deduction that, when the praeseodymium tartrate precipitate of acid environment is dissolved on bringing it to pH 7–8 with NaOH, it is because deprotonation of a hydroxyl group gives rise to a strong chelate complex of the metal ion. As such deprotonation is difficult to achieve in the absence of metal ion, it is reasonable to assume that prior formation of a chelate with the neutral hydroxyl is the facilitating mechanism. There seems no difficulty, therefore, in extending this interpretation to the monocarboxylic acid systems and to the parallel spectral and CD changes which characterize what we have labeled as the neutral complexes.

Whereas among the acid complexes, the sign of the CD pattern correlates with the configuration at the α-carbon, the CD sign for the neutral complexes of the hydroxy acids which have the same configuration at the α-carbon may be different. D-Gluconic and D-galactonic acids are epimeric isomers (Figure 1). Their configurations are the same at the β-carbon, as well as at the α position, and are opposite only at the γ-carbon. Their neutral-complex CD spectra are essentially mirror images through the base line (Figure 8). This suggests strongly that chelation is through the γ-hydroxyl, to give a seven-membered ring. It is well known that the lactones of the sugar acids generally form through the γ-hydroxyl, though δ-lactones also occur in equilibrium, and it has been demonstrated that the sign of rotation is correlated with the configuration at the γ-carbon,[7] positive rotation going with D configuration at this point. In the case of our neutral Pr(III) complexes with the sugar acids, the T-type spectrum at the $^3P_0$ band correlates with positive lactone rotation, and the anti-T spectrum, with the negative rotation. The intercalated metal ion apparently is exposed to the equivalent field influences as is the carboxyl chromophore in the lactone.

Lactic acid, which has only an α-hydroxyl, does not form a chelate which can keep it in solution in the neutral or alkaline pH region. Pantoic acid, which has a CH_2OH terminal group, can make a γ chelate which is probably the analog of the other acid complexes and which is stable at least to pH 7. At higher environmental pH, there is a slow reaction to give a soluble product, whose CD pattern does not generally fit with those of the other hydroxy acids discussed. There is an indication that at relatively low ligand concentration, when there may be only one ligand group in the coordination sphere of the Pr(III), alkaline conditions may produce a species with a CD pattern rather like that of the amino acid complexes of praseodymium,[5] but it is not determined that this is an equilibrium species. The first observation agrees with intuition that deprotonation of the terminal hydroxyl is much more difficult than deprotonation of the hydroxyl on a secondary carbon and that the fields producing the CD pattern are different. An uncertain factor is the higher pH needed to produce the complex. The other observation implies that under some conditions it may be possible to form a five-membered chelate ring with the α-hydroxyl but that this probably occurs only in the absence of competition.

Erythronic acid represents another instance where the γ-hydroxyl is a terminal one. However, a β-hydroxyl is also present, and from the chemical behavior and CD pattern it may be assumed that this is the one forming the neutral complex chelate. As the tartaric and malic acid complexes show, a six-membered ring formed by β chelation is quite stable. The fact that γ chelation occurs generally with the sugar acids must be correlated with the strong tendency of these acids to form γ-lactones—*i.e.*, we must be concerned with an intrinsic property of the γ-hydroxyl rather than with a steric demand of the metal ion.

The formation of the alkaline tartrate and saccharate complexes seems clearly to involve a second deprotonation process. This does not define whether it is a deprotonation of the organic ligand or of one of the coordinated water groups. The failure to produce such a complex, as judged by the CD patterns, in the case of malic acid, which contains a single hydroxyl group, may be taken as presumptive support for the verdict that it is the ligand which is deprotonated. This would also be consistent with the relative difficulty of producing stable alkaline complexes with the monocarboxylic ligands, which might not be expected if the metal-coordinated water groups were being deprotonated, and with the variable nature of the alkaline CD patterns, which would then rest on the variety of steric influences and even mixtures of species, which would be possible with doubly deprotonated species.

(9) N. K. Davidenko, *Redkozem. Elementy Akad. Nauk SSSR, Inst. Geokhim. Analit. Khim.*, 149 (1963); *Chem. Abstr.*, **61**, 5011 (1964).

(10) O. E. Zvyagintsev and B. P. Tikhonov, *Zh. Neorgan. Khim.*, **9**, 1588 (1964).

The kinetics of formation of the alkaline tartrate complex, with its apparent dependence on free tartrate, together with the reversion of the alkaline complex to a different neutral complex than the starting one, suggests that the formation process is not a simple deprotonation. Linkage with a dimerization reaction is one possibility.

The nonprecipitation of praeseodymium malate in the acid region, in which both tartaric and saccharic acids precipitate strongly, suggests either that the intermolecular hydrogen-bonding capabilities of the extra hydroxyl groups are determinative for the precipitation or that the possible intramolecular coordination of more than one ligand hydroxyl frees a carboxyl for intermolecular interaction. The first explanation would imply the intermolecular hydrogen bonding is effected through carboxylate–hydroxyl interaction, as the monocarboxylic acids do not precipitate either. The second implies that the free carboxyl by itself is determinative in the precipitation, since tartrate only has two hydroxyls.

In summary of the spectral findings, formation of a chelate complex definitely produces splittings both in the $^3H_4$ ground state and in the upper states of Pr(III). With the optically active ligands, there is a CD component for each absorption component, and the former components are not uniform in sign. The $^3P_0$ band is a uniquely useful one in Pr(III) for following effects on the ground state relatively independently of the upper state (possible vibrational interactions representing the limitation). Similarly, differences in the $^3P_2$ and $^3P_1$ bands reflect differences in the splittings of these upper levels. The pairing of strong CD components of opposite sign seen here, as well as in many other places in the rare earth CD spectra which have been looked at in this laboratory (see also ref 11), represents both a challenge to theoretical explanation and a criterion which any detailed spectral analysis must satisfy. The vibrational interactions alluded to might, for example, be a mechanism which could be invoked to account for the CD sign phenomenon.

On the chemical side, coordination of the optically active ligand induces a CD of the central metal ion absorption. For the acid-region complexes, the correlation of the sign of the CD with the configuration at the carbon α to the carboxyl group verifies the expectation that the negatively charged carboxylate of the ligand is presented to the cation for coordination. It would not have been a compelling prediction that the CD sign should be correlated with the configuration at this position, however. The data do not define whether this is a monodentate or chelate coordination, but the author favors the latter, with the coordinated hydroxyl, however, not being the α-hydroxyl. Comparison of the weakness of this CD with the strength and structure of that for the amino acids,[5] where the amino group lone pair is coordinated instead of the hydroxyl lone pair, suggests that the strength of the acid–base interaction between ligand and metal ion is a significant factor. Certainly the hydroxylate chelation in the neutral-region complexes of the hydroxy acids is stronger, with a stronger CD.

The correlation of the sign of the $^3P_0$ CD with the configuration at the γ-carbon is a result of chemical significance which could not have come from the absorption spectral alterations alone, and in fact the dramatic alteration generally seen in the CD on going from the acid to the neutral complex is itself more definitive than the absorption spectral alterations. A similar situation exists for the alkaline complexes. There are indications in some of the detailed data that perhaps internal information on the site of the chelation exists in the CD spectra—*e.g.*, the amino acid type of CD occasionally seen in a hydroxy acid system.

(11) S. Kida, T. Isobe, and S. Misumi, *Bull. Chem. Soc. Japan*, **39**, 2786 (1966).