

Trends in the Optical Rotatory Dispersion Spectra of D-(−)-1,2-Propylenediaminetetraacetato Complexes with Metal Ions. I. The Lanthanides

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Abstract: A general periodic trend was observed in the optical rotatory dispersion spectra of the lanthanide-D-(−)-1,2-propylenediaminetetraacetato complexes. This strong unambiguous periodic trend of the molecular rotations and the optical rotatory dispersion spectra has not previously been reported for any optically active complexes. The periodic trend was related to the ionic potential of the lanthanide(III) ions, in that as the ionic potential increases across the series, the molecular rotations decrease from a positive to a negative value at any given wavelength. An explanation for this general trend, based upon the effect of the ionic potential upon far-ultraviolet CT bands, has been proposed. For the neodymium-D-(−)-PDTA complex, the rotational strengths of the f-f transitions and the d-f transitions were calculated from the circular dichroic data.

Classically the coordination chemistry of the lanthanide ions was of great interest only as it pertained to separation techniques. Recently, increased interest in the chemistry of the lanthanides has led to extensive investigations of their coordination behavior and associated solution and solid-state spectra. Besides the hydrated cations, the only appreciably stable lanthanide complexes are those obtained through complexation with very strongly coordinating chelating ligands. These ligands contain the highly electronegative donor atoms, oxygen and nitrogen, and the stabilities of the complexes generally increase with increasing numbers of chelate rings.

Moeller² has stated that the electron configurations of the trivalent rare earth ions are not very favorable for the formation of strong covalent bonds. Seaborg³ has proposed that since the 4f orbitals are buried inside the 5s and 5p shells, they are not likely to be very useful in covalent bonding. Therefore, if strong covalent bonding does occur, it would involve the higher energy orbitals such as 5d, 6s, 6p, etc. It has been stated that the trivalent rare earth ions form predominantly ionic bonds, as evidenced from the infrared spectra of rare earth EDTA complexes.^{4,5} However, Shulman and Wyluda⁶ have offered evidence that covalent bonding does occur, at least to some extent, for the aquo complexes of the lanthanide ions. By nmr studies of the Gd³⁺ ion in water enriched with ¹⁷O, a diamagnetic shift was observed which Orgel⁷ accounts for by a proposed transfer of charge from the lone pair of electrons of the oxygen in water to the empty orbitals on the Gd³⁺ ion. Holleck and coworkers^{8,9} have offered as evidence for covalent bonding the decrease in magnetic susceptibility of the amino-

polyacetato complexes of Nd³⁺ and Er³⁺. Krumholz¹⁰ believes that the observed effects of the paramagnetic susceptibility are the result of covalent bonding which disturbs the quantum situation of the 4f electrons. Jørgensen,¹¹ comparing the absorption bands of the aquo ions to those of the rare earth complexes, attributes the bathochromic shift in these absorption bands mainly to a decrease in term differences which can arise from the shielding of the central field by electrons donated from the ligands and/or from an expansion of the electron cloud of the rare earth ions (nephelauxetic effect). Vickery¹² states that dsp hybrid bonding in the rare earth chelates is a major factor responsible for the perturbations of the 4f levels, and this perturbation is of such an extent that the 4f electrons might become involved in bond formation. Moeller³ proposes that such perturbations are caused chiefly from the imposition of strong electrostatic fields and that the 4f electrons are not directly involved in bond formation.

The lanthanide ions and EDTA react in solution to give a 1:1 stoichiometry; the absorption spectra of the lanthanide-EDTA complexes are distinctly changed from the absorption spectra of the lanthanide-aquo complexes. These changes are of three types: (a) bathochromic and hypsochromic shifts, (b) changes in intensities, and (c) band splitting.¹³⁻¹⁵ The absorption spectra of the rare earth complexes with D-(−)-1,2-propylenediaminetetraacetic acid also show these changes and have a very strong band below 250 nm.

Although six potential donor groups are available in both the EDTA and PDTA structures, there is controversy as to whether these ligands coordinate as sexadentate or pentadentate groups. The formation of a [Ln(edta)]⁻ or a [Ln(edta)(H₂O)]⁻ group should be dissymmetric in an octahedral geometry, and thus potentially capable of resolution, providing the bonding

(1) Author to whom all correspondence should be addressed.

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is sufficiently covalent in character. Attempted resolutions of the EDTA complexes of the lanthanide ions have been unsuccessful, even though the low equilibrium concentrations for the Ln^{3+} ions in these complexes tend to suggest that there is a certain amount of covalency present.

Thus, the study of optically active complexes of the rare earth metal ions with a stereospecific ligand for octahedral complexes was conducted in order to obtain the optical rotatory dispersion spectra of the complexes and the ligand and to determine if any relationships or trends exist in the ORD spectra of the lanthanide complexes.

Experimental Section

Reagents and Solutions. All solutions were prepared using demineralized water and were stored in polyethylene bottles. D-(−)-PDTA was prepared by a modification of the method of Dwyer and Garvan.¹⁶ Modifications consisted of techniques that increased the overall yield.¹⁷ A 0.5% aqueous solution gave $[\alpha]_{589}^{20} -47.2^\circ$, comparing favorably with the literature value of $[\alpha]_{589}^{20} -47.0^\circ$.¹⁶ The $\text{Na}_2\text{H}_2\text{D}(-)$ -PDTA solution was prepared by dissolving 195 g of D-(−)-PDTA and 48 g of analytical reagent grade NaOH pellets in hot demineralized water, filtering through a sintered glass filter, and diluting to 1 l. This solution was standardized by the procedure of Fritz, *et al.*¹⁸ Standard EDTA solutions were prepared from G. F. Smith Co. dried primary standard disodium dihydrogen ethylenediaminetetraacetate dihydrate and checked for purity.¹⁸ The solutions of the perchlorates of lanthanum(III), neodymium(III), samarium(III), europium(III), gadolinium(III), and ytterbium(III) were prepared by dissolving Matheson Coleman and Bell 99.9% Ln_2O_3 in hot perchloric acid. After appropriate treatment and dilution, these solutions were standardized with EDTA, using xylenol orange as the indicator.¹⁹ The praseodymium(III) perchlorate solution was prepared and standardized as above, except that 99.9% Pr_6O_{11} was used as the oxide. The terbium(III) nitrate solution was prepared from Matheson Coleman and Bell 99.9% Tb_4O_7 in hot concentrated nitric acid and was standardized by spectropolarimetric titration using $\text{Na}_2\text{H}_2\text{D}(-)$ -PDTA.²⁰ A pH 5.0 buffer was prepared from reagent grade glacial acetic acid and sodium acetate. The metal-D-(−)-PDTA complexes (0.0100 M) for optical rotatory dispersion and circular dichroism studies were prepared by mixing 1:1 stoichiometric amounts of the standardized metal solutions with the standard $\text{Na}_2\text{H}_2\text{D}(-)$ -PDTA solution and buffered at pH 5.0 with the acetic acid-sodium acetate buffer.

Instruments. Preliminary optical rotations were obtained using a 1-dm polarimeter cell in a Perkin-Elmer Model 141 polarimeter. Optical rotatory dispersion and circular dichroism spectra (600–200 nm) were obtained on a Cary Model 60 CD recording spectropolarimeter using appropriate Cary cylindrical quartz cells (1 dm–0.1 mm). Spectra of the neodymium and praseodymium complexes were also obtained on a Durrum-Jasco J-20 spectropolarimeter from 800 to 200 nm. An Orion Model 801 digital pH meter with a Sargent combination glass electrode was used for all pH measurements.

Results and Discussion

Figure 1 and Table I give the complete optical rotatory dispersion and circular dichroism spectra along with the analysis of the circular dichroism data for the neodymium-D-(−)-PDTA complex. The optical rotatory dispersion spectrum shows the superimposed f–f transitions on a curve that has an overall shape similar to a plain positive ORD curve. Unlike the

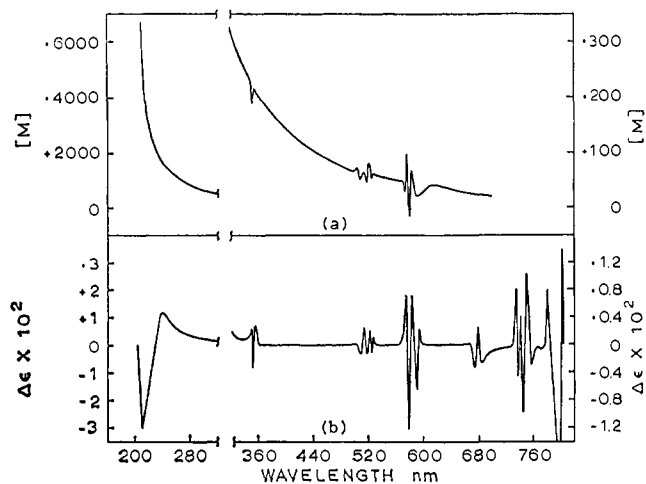


Figure 1. Optical rotatory dispersion spectrum (a) and circular dichroism spectrum (b) of neodymium(II)-D-(−)-PDTA at pH 5.0.

Table I. Circular Dichroism Data for the Neodymium-D-(−)-PDTA Complex

λ_{max} , nm	ν_{max} , cm^{-1}	$\Delta\epsilon \times 10^2$	$\Delta\nu^{1/2}$, cm^{-1}	$R \times 10^{43}$, cgs units
800.8	12488	+2.30	37	+1.67
796.0	12563	-3.09	114	-6.87
782.0	12788	+0.76	82	+1.19
756.0	13228	-0.30	70	-0.39
749.2	13348	+0.99	78	+1.42
744.8	13426	-0.97	50	-0.89
741.0	13495	+0.36	41	+0.27
738.0	13550	-0.47	44	-0.37
733.2	13639	+0.82	74	+1.09
685.8	14582	-0.25	93	-0.39
680.0	14706	+0.23	61	+0.23
675.2	14810	-0.32	101	-0.54
595.0	16807	+0.22	101	+0.32
588.8	16984	-0.63	144	-1.31
583.0	17153	+0.70	77	+0.77
579.0	17271	-1.24	96	-1.69
574.4	17409	+0.72	134	+1.36
531.0	18832	-0.06	89	-0.07
527.5	18957	+0.11	7	+0.01
524.0	19084	-0.09	54	-0.06
522.0	19157	+0.20	74	+0.19
518.0	19305	-0.11	149	-0.21
512.0	19531	+0.24	76	+0.23
509.0	19646	-0.12	77	-0.12
504.0	19841	+0.16	236	+0.47
474.0	21097	-0.12	178	-0.25
470.0	21277	+0.10	227	+0.26
435.0	22989	-0.06	105	-0.07
429.0	23310	+0.14	108	+0.16
356.0	28090	+0.25	158	+0.35
353.0	28329	-0.29	160	-0.40
349.0	28653	+0.38	247	+0.80
241.0	41494	+12.1	2735	+195
212.0	47170	-30.3	1975	-311

d–d transitions of the transition metals, where the Cotton effects are very large and affect the overall shape of the ORD spectra, the f–f transitions are approximately 10^3 times weaker and affect only the curve in the very narrow optically active absorption regions. Thus, from Figure 1a, the three groups of weak f–f transitions can be seen clearly to be superimposed on the general spectrum, with the group around 580 nm showing the greatest effect on the optical rotatory dispersion spectrum. These f–f transitions,

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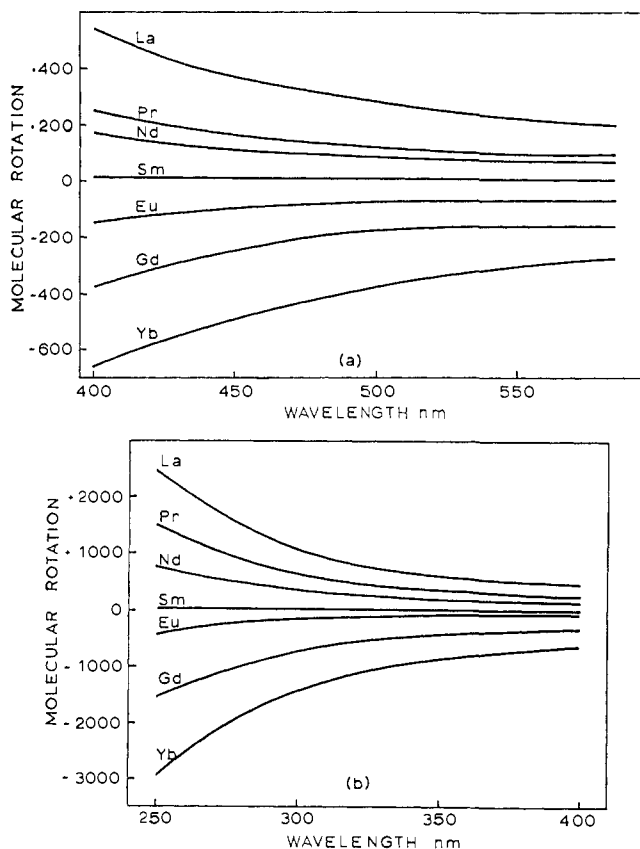


Figure 2. "Smoothed" optical rotatory dispersion spectra of lanthanide(III)-D(-)-PDTA complexes at pH 5.0: (a) 600-400 nm, (b) 400-250 nm.

although very weak and sharp, can change the sign of the rotation over very narrow wavelengths, *e.g.*, at 581 nm the molecular rotation is -15.0 . However, their overall effect on the ORD spectrum outside the narrow optically active absorption regions is very small. Thus, the predominant optically active transitions, those responsible for the overall spectrum, are clearly seen to be in the far-ultraviolet. These optically active transitions in the ultraviolet which produce the general characteristics of the overall ORD curve have rotatory strengths of approximately 10^2 - 10^3 times the rotatory strengths of the strongest f-f transitions. Because of the sharpness of the f-f transitions in the visible region and the possible large errors owing to wavelength inaccuracies and poor resolution of visible polarimeters, the optical rotatory dispersion curves are of much greater significance in categorizing the rare earth complexes than are the molecular rotations at a single wavelength.

In Figure 1b the f-f transitions in the 800-350-nm region in the circular dichroism spectrum are much more distinct than those in the optical rotatory dispersion spectrum. The intensities and sharpness of the circular dichroism bands compared to the optical rotatory dispersion bands show the much greater resolution that is possible for the f-f transitions in circular dichroism. Likewise, the very strong bands in the 240-200-nm region can be distinguished as first showing a large positive Cotton effect at 241 nm and then a very strong negative Cotton effect at 212 nm. These two optically active bands could not be resolved in the optical rotatory dispersion spectrum.

Rotational strengths can be calculated from the equation

$$R_{ba} = \frac{3hc \times 10^3 \ln 10}{32 \pi^3 N} \int \frac{(\epsilon_l - \epsilon_r)}{\nu} d\nu \quad (1)$$

for gaussian CD bands; this general relationship between the rotational strength and the area under the CD curve has been derived by Moffitt and Moscovitz.²¹ In the case of a gaussian CD band with a maximum at ν and half-width $\Delta\nu_{1/2}$, integration and insertion of the proper constants into eq 1 yield

$$R_{ba} = (2.45 \times 10^{-39}) \frac{(\epsilon_l - \epsilon_r) \Delta\nu_{1/2}}{\nu_{\max}} \quad (2)$$

Equation 2 was used exclusively in calculating the rotational strengths of the neodymium-D(-)-PDTA complex.

The average rotational strength of the transitions between 800 and 350 nm, excluding those values of R_{ba} greater than 1×10^{-43} cgs unit, is 0.33×10^{-43} cgs unit. There are eight transitions that have R_{ba} greater than 1×10^{-43} cgs unit. For the transition at 801 nm, the large rotational strength is mainly due to the large value of $\Delta\epsilon$, the circular dichroic absorption ($\epsilon_l - \epsilon_r$), since $\Delta\nu_{1/2}$ is very narrow. The transition at 796 nm has a very large rotational strength since both $\Delta\epsilon$ and $\Delta\nu_{1/2}$ are large compared to those of other f-f transitions. The bands at 749 and 579 nm have moderately large $\Delta\epsilon$ values and medium values of $\Delta\nu_{1/2}$. The two bands at 588 and 574 nm have only moderate values of $\Delta\epsilon$ and their high comparable rotational strengths are chiefly the result of the large values of $\Delta\nu_{1/2}$. The two other bands that have rotational strengths greater than 1×10^{-43} cgs unit, the 782- and 733-nm bands, have slightly larger than average values for both $\Delta\epsilon$ and $\Delta\nu_{1/2}$. These above-mentioned bands have rotational strengths greater than those of the other f-f transitions in the 800-350-nm range by factors of 3-20. The two very strong bands at 241 and 212 nm, having rotational strengths of approximately $2-3 \times 10^{-41}$ cgs unit, arise from 4f-5d transitions. These 4f-5d transitions for the tripositive rare earth ions have been determined by spectroscopic studies to occur in this ultraviolet region. Mason has estimated that the rotational strengths of the d-f transitions are no more than *ca.* 2×10^{-41} cgs unit.²² The value obtained from the CD data of the neodymium-D(-)-PDTA complex is very close to this value.

Figures 2a and 2b show the "smoothed" optical rotatory dispersion curves (*i.e.*, the plain ORD curves excluding the sharp, weak f-f transitions) for several of the lanthanide complexes of D(-)-PDTA. D(-)-PDTA is stereospecific in octahedral complexes, whether it is coordinated to four (nonplanar), five, or six positions in the octahedral structure. However, because the lanthanides can have larger coordination numbers than six, the stereospecificity of this ligand with the lanthanides is uncertain.

The negative plain ORD curve for D(-)-PDTA is drastically altered upon complexation with the lanthanide(III) ions. Lanthanum, praseodymium, and neodymium complexes give smoothed ORD curves

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Table II. Molecular Rotation of Lanthanide-D(-)-PDTA Complexes at Selected Wavelengths

Metal	Ionic radius, Å	Ionic potential	Molecular rotation, deg ml dm ⁻¹ mol ⁻¹						
			589 nm	546 nm	500 nm	400 nm	300 nm	275 nm	250 nm
La ³⁺	1.061	2.83	+210	+260	+310	+540	+1160	+1640	+2480
Pr ³⁺	1.013	2.96	+87	+105	+130	+250	+700	+1020	+1320
Nd ³⁺	0.995	3.02	+65	+80	+97	+165	+390	+540	+820
Sm ³⁺	0.964	3.11	+6	+6	+6	+8	+18	+35	+54
Eu ³⁺	0.950	3.16	-65	-74	-90	-130	-230	-260	-340
Gd ³⁺	0.938	3.20	-145	-170	-214	-370	-790	-1060	-1520
Tb ³⁺	0.923	3.25	-161	-189	-234	-385			
Yb ³⁺	0.858	3.50	-275	-320	-390	-660	-1480	-2000	-2960

that have fairly large positive rotations. The samarium complex, on the other hand, would appear optically inactive if the rotation is taken at 589 nm only. However, if a complete ORD spectrum is obtained, a slightly positive overall plain curve is clearly evident. Although the smoothed ORD spectrum for the europium-D(-)-PDTA complex shows a general curve similar to a plain negative ORD spectrum, the molecular rotations at any given wavelength are less negative than the molecular rotations of the ligand itself. The complexes with gadolinium, terbium, and ytterbium have overall smoothed ORD spectra that are similar to the plain spectra of D(-)-PDTA, but the molecular rotations are increasingly much more negative with increasing atomic number than that of the ligand itself. From Table II and Figure 2 it can be seen that a general trend in the molecular rotations of the lanthanides with the same charge shows that the molecular rotations at any wavelength on the smoothed curves become progressively more positive with increasing ionic radii of the lanthanide ions. The smoothed curves have the overall shape of plain ORD spectra. This trend in the optical rotations of the lanthanide complexes is very similar to the trends observed for other metal-D(-)-PDTA complexes.²³ If a comparison is made of the molecular rotation *vs.* ionic potential, the fundamental relationship of molecular rotation becoming progressively more positive with decreasing ionic potential in any series of similarly structured complexes is valid. The molecular rotations of the lanthanide-D(-)-PDTA complexes at selected wavelengths in Table II were used to calculate the "effective centers" of the predominant optically active bands, Table III, that are responsible for

Table III. Calculated Wavelength of the "Effective Center" of the Predominant Optically Active Band

Metal	Wavelength, nm
La ³⁺	184.1 ± 4.7
Nd ³⁺	193.4 ± 1.4
Gd ³⁺	180.4 ± 1.1
Yb ³⁺	181.5 ± 1.9
D(-)-PDTA	163.4 ± 0.6

the general shape of the ORD curves in Figure 2. The calculated wavelengths in Table III were obtained from a modification of eq 3, where R_{ba} is the rotational

$$[M] = \frac{96\pi N n^2 + 2}{hc} \sum_b \frac{R_{ba}\nu^2}{\nu_{ba}^2 - \nu^2} \quad (3)$$

strength, ν_{ba} is the frequency at the transition, ν is

(23) D. L. Caldwell, R. J. Palma, P. E. Reinbold, and K. H. Pearson, unpublished work.

the measured frequency, n is the refractive index, and the other constants have their usual meanings. Assuming a constant value of 1.4 for the index of refraction, which is a representative value for these aqueous solutions, eq 3 simplifies to the more convenient form

$$[M] = 1.21 \times 10^{42} \frac{R_{ba}\lambda_0^2}{\lambda^2 - \lambda_0^2} \quad (4)$$

where λ_0 is the wavelength of the effective center of the optically active transitions and λ is the wavelength at which $[M]$ was determined. The value of R_{ba} was assumed to be a constant for the calculation of each separate complex; this is valid because the value of R_{ba} is for the same effective center of the predominant optically active absorption bands in that complex. Equation 4 was equated, assuming constant R_{ba} , giving eq 5, from which λ_0 can be easily obtained by sub-

$$[M]_{\lambda_1}(\lambda_1^2 - \lambda_0^2) = [M]_{\lambda_2}(\lambda_2^2 - \lambda_0^2) \quad (5)$$

stituting in various values of $[M]$ at the corresponding values of λ from Table II. The λ_0 for praseodymium gave erroneous results due to the strong 4f-5d transition with a slight bathochromic shift that has been also observed in the spectroscopic studies of the praseodymium(III) perchlorates.²⁴ The λ_0 values were not calculated for samarium and europium because the small magnitude of the molecular rotations gave large errors. The λ_0 value for the terbium complex was not calculated because the nitrate solution had very high absorbance in the ultraviolet and therefore the molecular rotations could not be obtained accurately in this region. From the spectrum of neodymium in Figure 1 it can be seen that there is some 4f-5d contribution, but because of instrumental limitations and high absorbance it was not possible to go below 200 nm to see the contribution of any CT band. Likewise, for lanthanum, gadolinium, and ytterbium, which have similar calculated predominant optically active bands, information could not be obtained below 200 nm. The average λ_0 value for the four calculated effective centered optically active bands was 184.9 nm. The calculated λ_0 of the predominant optically active band of D(-)-PDTA showed excellent agreement with the literature value of 163.0 nm.²⁵ However, there is a significant difference (*ca.* 22 nm) between the calculated λ_0 values for the complexes and the λ_0 value for the ligand D(-)-PDTA.

In order to explain the general trend of the smoothed optical rotatory dispersion curves from strongly positive to strongly negative with increasing ionic potential

(24) C. K. Jørgensen and J. S. Prinen, *Mol. Phys.*, 6, 629 (1963).

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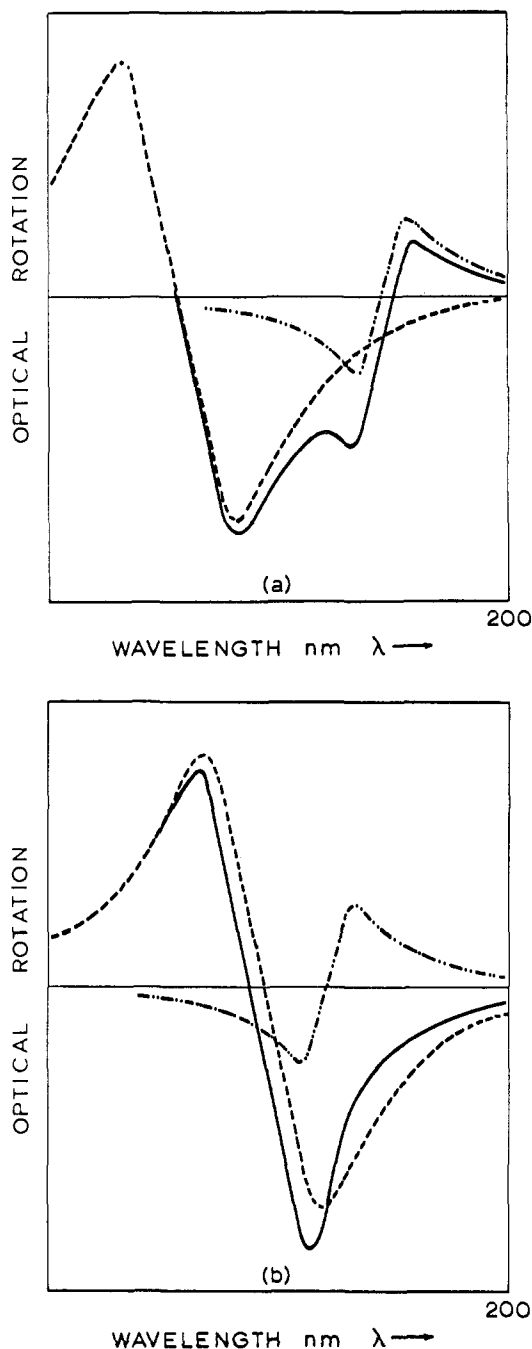


Figure 3. Idealized two-band optical rotatory dispersion curves giving (a) plain positive resultant spectrum and (b) plain negative resultant spectrum at wavelengths greater than 200 nm: negative, ---; positive, - · - · -; resultant, —, spectra.

of the trivalent lanthanide ions, it is proposed that the effective band center λ_0 mentioned above is not a single isolated band, but is rather a combination of two bands: (a) a positive circular dichroic band that is essentially constant in intensity and wavelength and (b) a large negative CT circular dichroic band the wavelength of which is a function of the ionic potential of the central metal ion. Thus, the observed rotations on the smoothed curves are the results of the contributions of the overlapping far-ultraviolet circular dichroic bands, as expressed in the following empirical equation

$$\alpha_{\text{obsd}} = \alpha_{1(+)} + \frac{Ze}{r} \alpha_{2(-)} \quad (6)$$

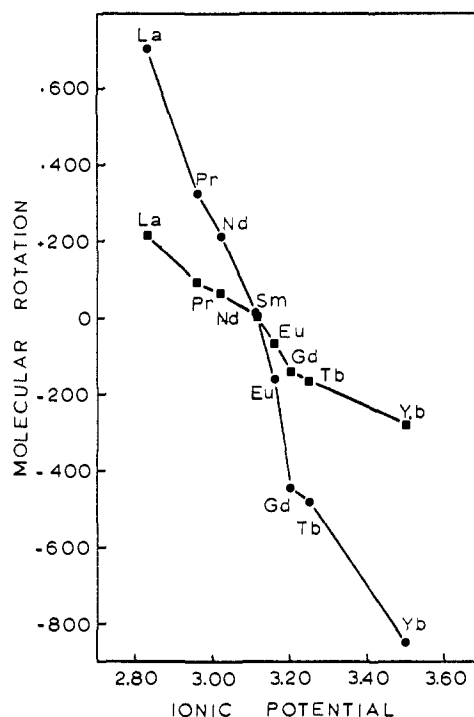


Figure 4. Molecular rotations of the lanthanide(III)-D(-)-PDTA complexes *vs.* ionic potential at pH 5.0: ●, 365 nm; ■, 589 nm.

As the ionic potential of the central metal ion increases, there is a bathochromic shift in the wavelength of the CT band associated with α_2 .

Idealized optical rotatory dispersion curves associated with the above-mentioned far-ultraviolet circular dichroic bands are shown in Figures 3a and 3b, along with the resulting complex spectra. In Figure 3a, the smaller positive band at longer wavelength causes the resulting smoothed spectrum to be positive at all wavelengths greater than 200 nm. If the larger negative CT band shifts to longer wavelength as is shown in Figure 3b, the resulting complex optical rotatory dispersion spectrum is negative and would appear as a plain negative curve at all wavelengths greater than 200 nm. As the ionic potential on the central lanthanide ion increases, the electrostatic field associated with the central metal ion will increase, causing greater perturbation and resulting in the bathochromic shift. Thus, progressively more of the negative band affects the smoothed plain curves as the ionic potential increases, resulting in increasingly more negative smoothed plain optical rotatory dispersion curves.

Figure 4 shows plots of the molecular rotations *vs.* the ionic potential of the data from Table II. These plots show deviations from a straight line plot which are similar to plots of $\log K_{\text{stability}}$ *vs.* the reciprocal of the ionic radii for the lanthanide-EDTA complexes.²⁶ Although the molecular rotations at a given wavelength decrease from lanthanum to praseodymium to neodymium, etc., there seem to be two breaks in the plots of the molecular rotation *vs.* ionic potential. The first segment would contain lanthanum, praseodymium, neodymium, and samarium; the second segment would contain samarium, europium, and gadolinium; and the third segment would contain gado-

(26) G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, 37, 937 (1954).

linium, terbium, and ytterbium. A single break has been observed when plotting the $\log K_{\text{stability}}$ vs. the reciprocal of the ionic radius for the lanthanide-EDTA complexes, which is often called the "gadolinium break."²⁶ Likewise, the molecular rotations show this gadolinium break with the possibility that there are two breaks instead of one in these rare earth complexes.

Conclusions

This strong unambiguous periodic trend of the molecular rotations and the optical rotatory dispersion spectra has not previously been reported for any optically active complexes. An explanation based on a bathochromic shift of a large negative circular dichroic CT band is proposed to explain the observed trends for the lanthanide-D(-)-PDTA complexes. The same strong unambiguous periodic trends of the molecular rotations have been observed for complexes of octahedral geometry where the ligand is completely stereospecific.²³ Although the perturbing forces that give rise to the ORD spectra are a function of the ionic

potential, it is clearly evident that more than simple electrostatic interactions between the ligand and the metal ions are involved, and a greater degree of covalency seems apparent than has been previously proposed for the lanthanide-amino-polyacetato complexes.

The ligand field splitting of the J levels shows a greater degree of resolution in the circular dichroism spectra than in optical rotatory dispersion spectra or plain absorption spectra. Further research using circular dichroism and magnetic circular dichroism in the study of the optical phenomena of optically active lanthanide complexes may be of great help in assigning the exact $f-f$ transitions in solution chemistry.

Acknowledgment. The many helpful suggestions of Henry Eyring are gratefully acknowledged. This research was supported by The Robert A. Welch Foundation, Fellowship Grant No. A-262. Appreciation is expressed to the Dow Chemical Company for its grant of a leave of absence for the summer of 1968 to D. L. C. This study was presented in part at the 158th National Meeting of the American Chemical Society on Sept 10, 1969, at New York, N. Y.

Chelation of Uranyl Ions by Adenine Nucleotides. III. Further Nuclear Magnetic Resonance Investigation of the Uranyl Nitrate-Adenosine 5'-Monophosphate System at Basic pH¹ (7.5-11.4)

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Abstract: Nmr spectra, both proton (¹H, 100 MHz) and phosphorus (³¹P, 40 MHz), were obtained for mixtures of uranyl nitrate and adenosine 5'-monophosphate (AMP) at various stoichiometries and alkalinities. The spectra indicate that in an equimolar mixture (0.1 and 0.05 M) the strong chelate with 1:1 stoichiometry (whose structure was previously given² as a 2:2 sandwich-type dimer), which is exclusively present above pD 10.9, disproportionates below this pD to uncomplexed AMP, sandwich-type chelates (two forms) with 2:1 (U:AMP) stoichiometry, and nonsandwich-type complex(es). Only the latter type of complex is present at pD 7.5 in 0.05 M equimolar mixture. The extent of disproportionation and the ligand exchange rate both increase with decrease in pH, probably owing mainly to the competition between uranyl ions and protons for the ribose hydroxyl-oxygen sites. Structures for the 2:1 chelates and also 3:1 chelates, compatible with the spectra, are given. A series of equilibria is suggested to describe the U-AMP system from pH 2 to 11.5.

From an earlier proton magnetic resonance study² we concluded that the predominant solute species in an equimolar mixture of uranyl nitrate and adenosine 5'-monophosphate (U-AMP) at high pD is a chelate with 1:1 stoichiometry in which the uranium is bound to the phosphate group and to both of the ribose hydroxyl-oxygen atoms. At high pD the uranyl

ion does not bind to the adenine group, although it does so at pH below 4.5.³ A *dimeric sandwich-type* (ST) chelate, similar to structure 1, was postulated for this high-pD species.⁴ It became necessary in our investigation of metal-ion-catalysis of ATP hydrolysis⁵ to elucidate the U-AMP system over as wide a pD

(3) I. Feldman, J. Jones, and R. Cross, *ibid.*, **89**, 49 (1967).

(1) (a) This paper is based on work performed under contract with the U. S. Atomic Energy Commission at the University of Rochester Atomic Energy Project, and has been assigned Report No. UR-49-1123. (b) Part of this paper was presented at the Second Rochester Conference on Toxicity, Rochester, N. Y., June 1969.

(2) R. P. Agarwal and I. Feldman, *J. Amer. Chem. Soc.*, **90**, 6635 (1968); **91**, 2411 (1969).

(4) The only difference between the ST chelate postulated previously² and structure 1 of this paper is that in 1 we have taken cognizance of the fact that the titration curve of an equimolar U-AMP mixture shows that this chelate is doubly hydroxylated. This point is explained in the Results section.

(5) K. E. Rich, R. P. Agarwal, and I. Feldman, submitted for publication.