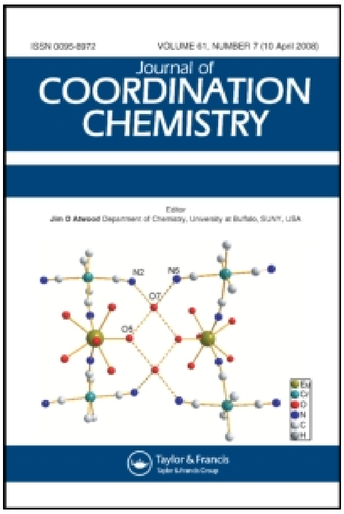

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

TRENDS IN THE OPTICAL ROTATORY DISPERSION SPECTRA OF R-(-)-1,2-PROPYLENEDIAMINETETRAACETATO COMPLEXES OF GROUPS IIA,IIB,IIIA,IIIB,IVB AND SOME HEAVY METALS

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To cite this Article Pearson, Karl H. , Palma Sr., R. J. and Baker, Joyce R.(1978) 'TRENDS IN THE OPTICAL ROTATORY DISPERSION SPECTRA OF R-(-)-1,2-PROPYLENEDIAMINETETRAACETATO COMPLEXES OF GROUPS IIA,IIB,IIIA,IIIB,IVB AND SOME HEAVY METALS', Journal of Coordination Chemistry, 7: 4, 203 — 212
To link to this Article: DOI: 10.1080/00958977808079912
URL: http://dx.doi.org/10.1080/00958977808079912

J. Coord. Chem.
1978, Vol. 7, pp. 203–212

TRENDS IN THE OPTICAL ROTATORY DISPERSION SPECTRA OF R-(-)-1,2-PROPYLENEDIAMINETETRAACETATO COMPLEXES OF GROUPS IIA,IIB,IIIA,IIIB,IVB AND SOME HEAVY METALS

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(Received August 25, 1975; in final form April 1, 1977)

A general periodic trend was observed in the optical rotatory dispersion spectra of the R-(–)-1,2-propylenediaminetetraacetato (R(–)PDTA) complexes of Group IIA metals: magnesium(II), calcium(II), strontium(II), and barium(II); Group IIIB metals: scandium(III), yttrium(III), and lanthanum(III); Group IVB metals: titanium(IV), zirconium(IV), and thorium(IV); Group IIB metals: zinc(II), cadmium(II), and mercury(II); Group IIIA metals: aluminum(III), indium(III), and thallium(III); and the heavy metals: mercury(II), thallium(III), lead(II), and bismuth(III). The periodic trend was related to the ionic potential of the metals within each group, in that as the ionic potential increases within a group, the molecular rotations decrease from a positive to a negative value at any given wavelength outside of a region of anomalous optical rotatory dispersion. Comparing the heavy metal, mercury(II), lead(II), thallium(III), and bismuth(III), complexes of R(–)PDTA, outside of the region of anomalous rotatory dispersion, the metal with the same charge but smaller ionic potential has the greater positive molecular rotation at any given wavelength.

INTRODUCTION

R-(–)-1,2-Propylenediaminetetraacetic acid, R(–)-PDTA, is a potential sexadentate coordinating ligand which, in general, has greater stability constants than EDTA for most metals. Figure 1 shows the three possible rotamers of R(–)PDTA. Rotamer I is the *anti* configuration which is geometrically unsuitable for chelation to either a proton or metal ions. Rotamers II and III for R(–)PDTA are both in the *gauche* configuration with the methyl group axial on rotamer II and equatorial in rotamer III. Molecular models show that the methyl group is sterically hindered in forming one configuration of the metal complexes, regardless of whether the ligand is attached to four (nonplanar), 5, or 6 positions of the inner coordinate sphere. Figure 2 shows the stereospecificity of the rotamers II and III when complexed to metal ions. Rotamer III corresponds to the Δ isomer (structure I) and rotamer II corresponds to the Λ isomer (structure II). From rotamer III and structure I (Δ) the reason for the stereospecificity of R(–)PDTA becomes readily apparent, since the methyl group is equatorial and points away from the other atoms having little steric effects. In rotamer II and structure II the methyl group is in the axial position and interacts very strongly with the atoms associated with the nonplanar acetate bridge chelated from the ethylene coordinated nitrogen in the methyl substituted ethylenedinitrilo chain (indicated by the dotted line in structure II). The free energy differences due to this methyl-acetate interaction in the Λ isomer (structure II) compared to the Δ isomer (structure I) has been estimated to be 3 kcal/mole, thus giving a minimum of 99.9% stereospecificity to R(–)PDTA.[1]

From Table I the molecular rotation of R(–)PDTA

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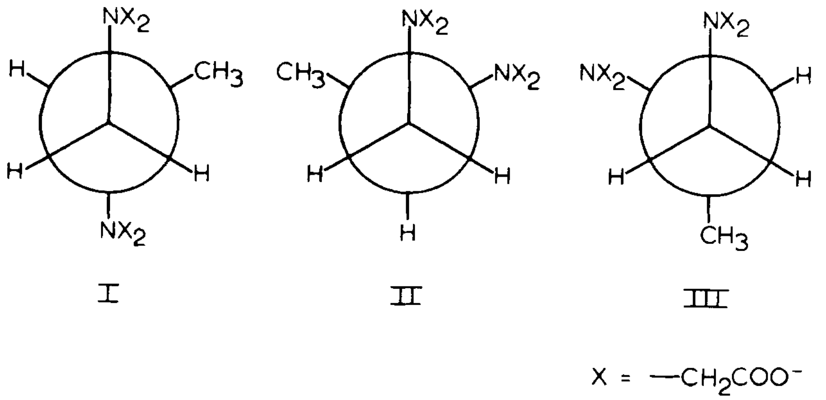

FIGURE 1 Rotamers of R(−)PDTA.

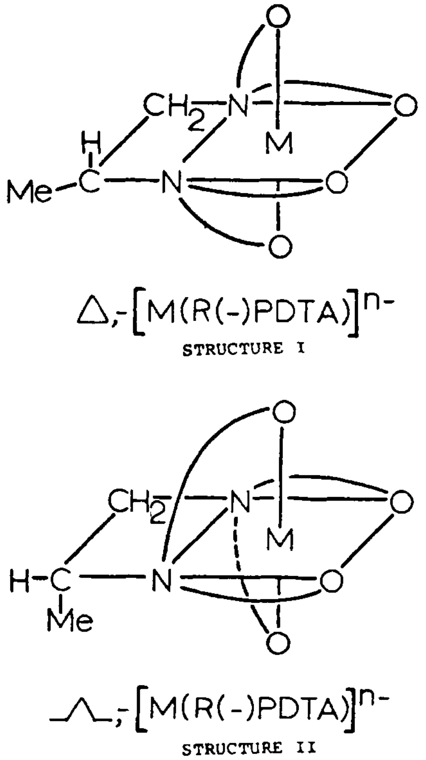

FIGURE 2 Stereospecificity of R(−)PDTA.

are given at various pH's. From the pKa's (pK_1 = 2.60, pK_2 = 3.03, pK_3 = 6.20, pK_4 = 10.84)[2] it can be seen that at pH 2 approximately 80% of the R(−)PDTA is in the $H_4R(-)PDTA$ species and approximately 20% in the $H_3R(-)PDTA^-$ species. Both species would be in the *anti* configuration (rotamer I) and the combined molecular rotation of these species is greater than at pH 5 where the predominant species is the $H_2R(-)PDTA^{2-}$ with the preferred configuration of rotamer I. Thus, both species, $H_4R(-)PDTA$ and $H_3R(-)PDTA^-$, have larger negative molecular rotations than $H_2R(-)PDTA^{2-}$, with the tetra-protonated R(−)PDTA having the largest negative molecular rotation of these species.

At a pH of approximately 8 where approximately 98% of the R(−)PDTA is in the $HR(-)PDTA^{3-}$ form, there is a minimum in the negative molecular rotation. At this pH the R(−)PDTA can exist in all three rotamer configurations, and with rotamer III being in the "proton chelate" structure.[3] From pH 8 through pH 12, the solution has an increasingly larger negative molecular rotation as the concentration of the completely deprotonated R(−)PDTA increases. Thus, the $R(-)PDTA^{4-}$ species has a much larger negative molecular rotation than any of the other deprotonated species.

A trend in the optical rotatory dispersion spectra of R(−)PDTA complexes of the lanthanide elements has been reported.[4] This research was undertaken to determine from the optical rotatory dispersion spectra of the many metal complexes of R(−)PDTA if relationships or trends existed among the ORD spectra of metal complexes of the same family or of the same charge.

EXPERIMENTAL

Reagents and Solutions

All solutions were prepared using demineralized water and were stored in polyethylene bottles. All chemicals used were reagent grade or better. R-(−)-1,2-Propylenediaminetetraacetic acid monohydrate was prepared by the method of Dwyer and Garvan[5] with certain modifications to increase the overall yield.[6] A 0.5%

TABLE I
Molecular rotations of metal R(−)PDTA complexes and R(−)PDTA at selected wavelengths

Metal	Ionic radius	Ionic Potential (ion charge /ion radius)	Molecular rotation (deg ml dm^{-1} mole^{-1})							pH
			589 nm	546 nm	436 nm	365 nm	300 nm	275 nm	250 nm	
					Group IIA					
Mg^{2+}	0.65	3.08	−146	−173	−284	−424	−684	−858	−1130	9.8
Ca^{2+}	0.99	2.02	− 61	− 71	−103	−125	− 96	− 3	+316	9.8
Sr^{2+}	1.13	1.77	+ 12	+ 14	+ 41	+102	+316	+560	+1160	9.8
Ba^{2+}	1.35	1.48	+ 39	+ 48	+100	+197	+482	+784	+1480	9.8
					Group IIIB					
Sc^{3+}	0.81	3.71	−414	−486	−830	−1330	−2430	−3360	−5040	5.0
Y^{3+}	0.93	3.23	−300	−352	−604	−968	−1760	−2410	−3610	5.0
La^{3+}	1.15	2.61	+210	+260	+395	+715	+1160	+1640	+2480	5.0
					Group IVB					
Ti^{4+}	0.68	5.88	−275	−282	−112	+1680	+6060			1.1
Zr^{4+}	0.80	5.00	−427	−509	−850	−1310	−2190	−2660	−2310	3.0
Th^{4+}	0.95	4.21	+425	+580	+1090	+1730	+3120	+4320	+6430	3.0
					Group IIB					
Zn^{2+}	0.74	2.70	−466	−534	−918	−1500	−2790	−3960	−6480	5.0
Cd^{2+}	0.97	2.06	+426	+524	+935	+1550	+3060	+4430	+7410	5.0
Hg^{2+}	1.10	1.82	+796	+952	+1720	+2950	+6490			5.0
					Group IIIA					
Al^{3+}	0.50	6.00	−310	−388	−672	−1090	−2010	−2800	−4260	5.0
In^{3+}	0.81	3.71	+503	+605	+1060	+1740	+3360	+4790	+7620	3.0
Tl^{3+}	0.95	3.16	+884	+1090	+2040	+3710	+9510			3.0
					Heavy Metals					
Hg^{2+}	1.10	1.82	+796	+952	+1720	+2950	+6490			5.0
Tl^{3+}	0.95	3.16	+884	+1090	+2040	+3710	+9510			3.0
Pb^{2+}	1.20	1.67	+1450	+1820	+3420	+6030	+13600	+23400	+50000	5.0
Bi^{3+}	1.20	2.50	+1150	+1400	+2640	+4820	+14500	+21100	+3960	1.1
	Ligand									
	R(−)PDTA		−159	−186	−305	−455				2.0
	R(−)PDTA		−120	−142	−236	−362	−655	−848	−1240	3.0
	R(−)PDTA		−117	−138	−230	−354				5.1
	R(−)PDTA		−183	−215	−355	−534				10.0

aqueous solution gave $[\alpha]_{589} = -47.2°$, comparing favorably with the literature value of $-47.0°$.[5] Solutions of R(−)PDTA were prepared by reacting one equivalent of the free acid monohydrate with two equivalents of aqueous sodium hydroxide, and the resulting colorless solution was filtered through a fine sintered glass filter. The R(−)PDTA solutions were standardized against standard lead nitrate solutions at pH 5; 10% hexamethylenetetramine was used to adjust the pH and xylenol orange was the indicator.[7] Standard Na_2H_2EDTA solutions were prepared from dried primary standard disodium dihydrogen ethylenediaminetetraacetate dihydrate and checked for purity.

Aluminium(III),[8] indium(III),[9] thallium(III),[10] zirconium(IV) and thorium(IV),[11] zinc(II) and cadmium(II),[12] magnesium(II)[13] and barium(II)[14] ion solutions were prepared from their respective perchlorate salts and standardized by EDTA titrimetry. Scandium(III) and yttrium(III),[12] lead(II) and mercury(II),[11] bismuth(III),[15] lanthanum(III),[10] and strontium(II)[14] ion solutions were prepared from either their respective nitrate salts or oxides, dissolved in nitric acid and fumed, and standardized by EDTA titrimetry. Calcium(II) ion solution was prepared from primary standard calcium carbonate and hydrochloric acid.

Titanium(IV) solution was prepared from titanium tetrachloride and hydrochloric acid and standardized gravimetrically as TiO_2.

The 0.0100 M metal-R(−)PDTA complexes were prepared for optical rotatory dispersion studies by mixing 1:1 stoichiometric amounts of the standardized metal ion solutions with the standard Na_2H_2-R(−)-PDTA and adding the appropriate buffer. The pH 9.8 buffer was prepared from ammonium chloride and aqueous ammonia. The pH 5.0 and pH 3.0 buffers were prepared from sodium acetate and glacial acetic acid. Concentrated nitric acid was used to buffer solutions at pH 1.1.

Instruments

Preliminary optical rotations were obtained using a 1-dm polarimeter cell in a Perkin-Elmer Model 141 polarimeter. Optical rotatory dispersion spectra (600–250 nm) were obtained on a Cary Model 60 recording spectropolarimeter using appropriate Cary cylindrical quartz cells (1 dm–0.1 mm). An Orion Model 801 digital pH meter with a Sargent combination glass electrode was used for all pH measurements except the perchlorate solutions where a double junction reference electrode was used.

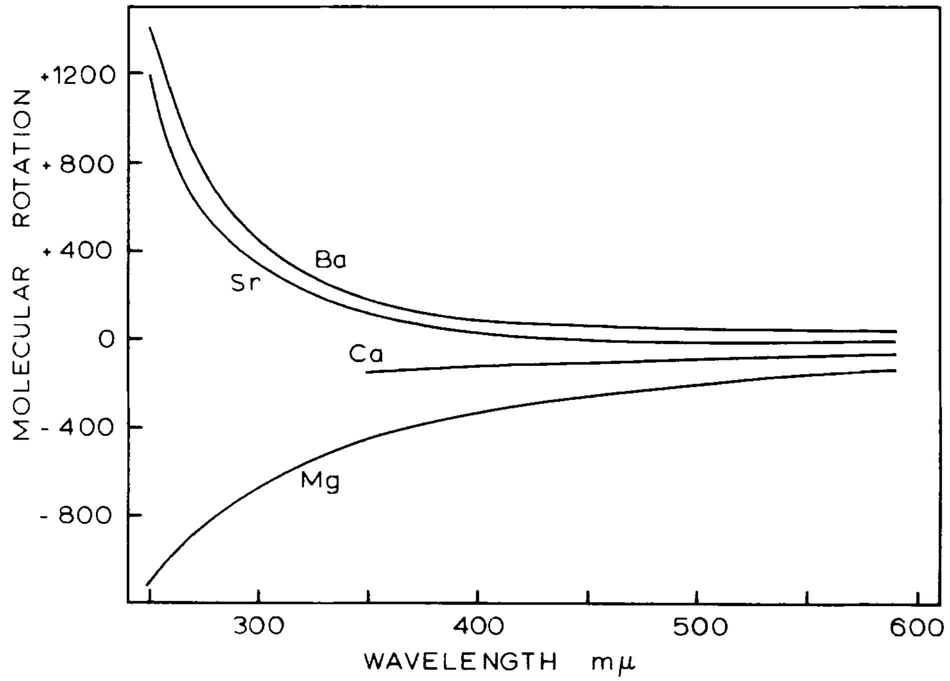

FIGURE 3 Optical rotatory dispersion spectra of Group IIA metal complexes of R(−)PDTA.

RESULTS AND DISCUSSION

Figure 3 shows the optical rotatory dispersion spectra of the Group IIA metal complexes of R(−)PDTA. The first two members of the Group IIA family, magnesium(II) and calcium(II) ions, have inert gas ion configurations with no underlying d-electrons and both of these ions have essentially negative molecular rotations throughout their spectra. The other two members of the Group IIA family, strontium(II) and barium(II) ions, have inert gas configurations, however, they do have underlying d-electrons, and both have plain positive ORD spectra over the range from 600 to 250 nm. The molecular rotations of the Group IIA metal complexes of R(−)PDTA increase in a positive manner from magnesium(II) regularly through barium(II). Thus this periodicity of the Group IIA metals can be correlated with the ionic radius and ionic potentials (ion charge/ion radius) of these ions as shown in Table I. As the ionic potential decreases within this family, there is increasing positive rotation, as can be seen from the molecular rotations at the various selected wavelengths. This periodic trend of increasing positive rotation with the corresponding decrease of ionic potential has been previously noted for the optically active lanthanide-R(−)PDTA complexes.[4] As can be seen in Table I, the plain negative ORD curve of magnesium(II) does not increase in magnitude as fast as plain positive ORD curve of barium(II).

Figure 4 shows the ORD spectra of the Group IIIB metal complexes of R(−)PDTA. In this family both scandium(III) and yttrium(III)-R(−)PDTA complexes have plain negative ORD spectra throughout the region studied with the scandium(III)-R(−)PDTA having a greater negative molecular rotation in the 600–250 nm region than the yttrium(III)-R(−)PDTA complex. Scandium(III) has an inert gas electronic configuration with no underlying d-electrons, whereas both yttrium(III) and lanthanum(III) have inert gas electronic configurations but have underlying d-electrons. The periodic trend that has been found for the lanthanide and Group IIA metal complexes of R(−)PDTA holds for the Group IIIB metal complexes; that is, as the ionic potential decreases the molecular rotations increase in a positive direction. From Table I it can be seen that the molecular rotations at any of the selected wavelengths is much greater for the Group IIIB metal complexes of R(−)PDTA than the Group IIA metals complexes of the same period. Likewise the molecular rotations of any of the Group IIIB-R(−)PDTA complexes increase much more rapidly with decreasing wavelength than the Group IIA-R(−)PDTA complexes. Of the two metals that have similar ionic potential, yttrium(III) and magnesium(II), it can be seen that the molecular rotation of the species with the larger ionic radius and larger charge, yttrium(III), has a much greater negative molecular rotation at any selected wavelength. Thus, the perturbations that occur to cause the optical rotations in these dissymmetric complexes are not only a function of the ionic potential; however, the ionic charge on the central metal atom has a greater effect on the molecular

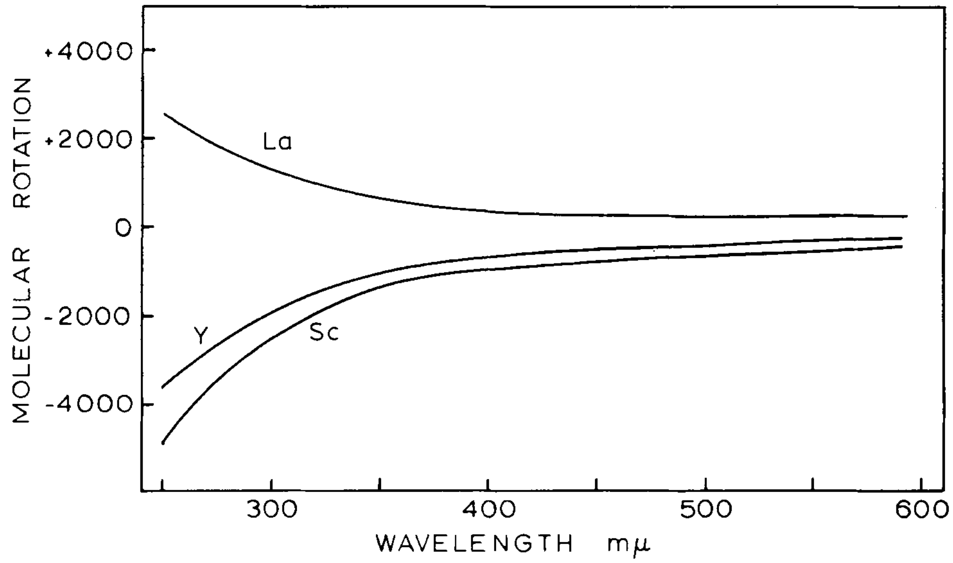

FIGURE 4 Optical rotatory dispersion spectra of Group IIIB metal complexes of R(−)PDTA.

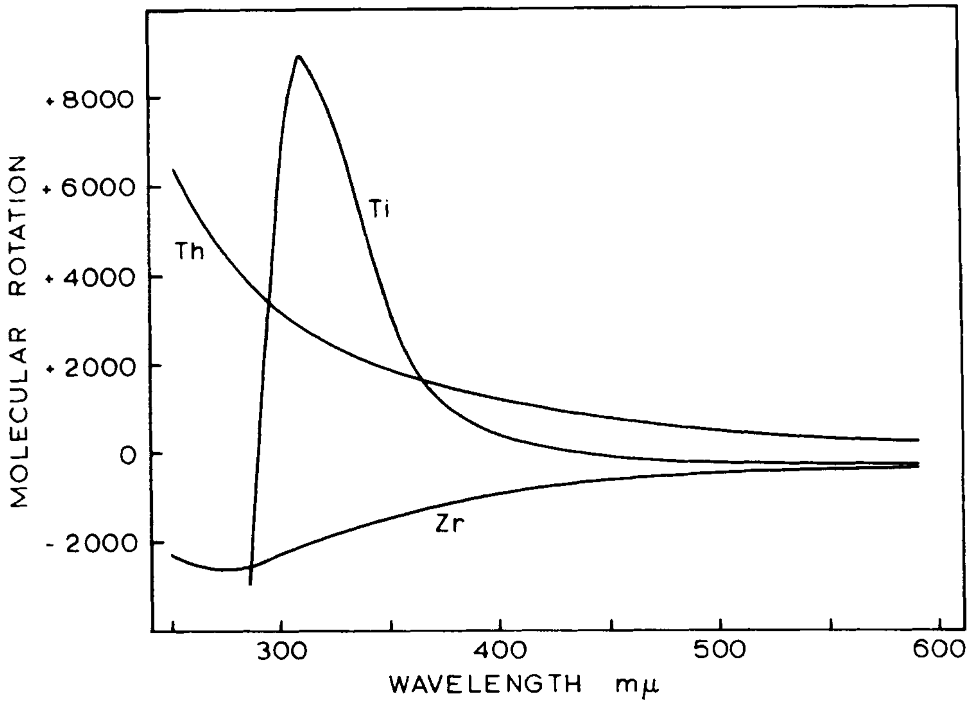

FIGURE 5 Optical rotatory dispersion spectra of Group IVB metal complexes of R(–)PDTA.

rotation than the ionic radius for metal ions with similar ionic potentials.

Figure 5 shows the optical rotatory dispersion spectra of the Group IVB metal complexes of R(–)PDTA. Titanium(IV) ion has the inert gas structure of argon as did scandium(III) and calcium(II); however, the titanium(IV)-R(–)PDTA complex shows anomalous rotatory behavior. The ORD spectra of titanium(IV)-R(–)PDTA is dominated by the Cotton Effect which has a peak at 314 nm, $[M]_{314} = 9{,}220$, with the zero crossover in the region of 290 nm. The positive Cotton Effect in the high ultraviolet region affects the molecular rotations very strongly in the region of 400–600 nm. Thus, the predicted very large negative molecular rotations in the 500–600 nm regions are completely overshadowed by the very large positive Cotton Effect. The first crossover from negative molecular rotations to positive molecular rotations occurs around 420 nm. Zirconium(IV) ion has the inert gas configuration of krypton with the completely filled underlying 3d-electrons. Zirconium(IV)-R(–)PDTA shows a similar anomalous optical rotatory dispersion curve to titanium(IV)-R(–)PDTA as the spectra starts out with a high negative molecular rotation at 589 nm going to increasingly more negative molecular rotations in the range of 275 nm. Below 275 nm the molecular rotations become less negative and approach a Cotton Effect like the titantium(IV)-R(–)PDTA spectra. However, the Cotton Effect spectra for zirconium(IV)-R(–)PDTA lies much lower in the ultraviolet than the anomalous rotatory dispersion spectra for titanium(IV)-R(–)PDTA. Thorium(IV)-R(–)PDTA has essentially a plain positive optical rotatory dispersion spectra throughout the 600–250 nm region. Thus, when one compares the electronic configuration of thorium(IV), zirconium(IV), and titanium(IV), one can see essentially the same periodic trend; that is; as the ionic potential decreases the molecular rotations outside of a Cotton Effect region increase in a positive direction. This comparison is not as easily seen as in the other Group IIA- and Group IIIB-R(–)PDTA complexes due to the optically active transitions in the ultraviolet region.

Figure 6 gives the optical rotatory dispersion spectra of the Group IIB metal complexes of R(–)PDTA. The general trend that the molecular rotations within a given family removed from an optically active transition changes in a positive manner with decreasing ionic potential holds for the Group IIB metal complexes. Calculation of the wavelength of the "effective center" of the

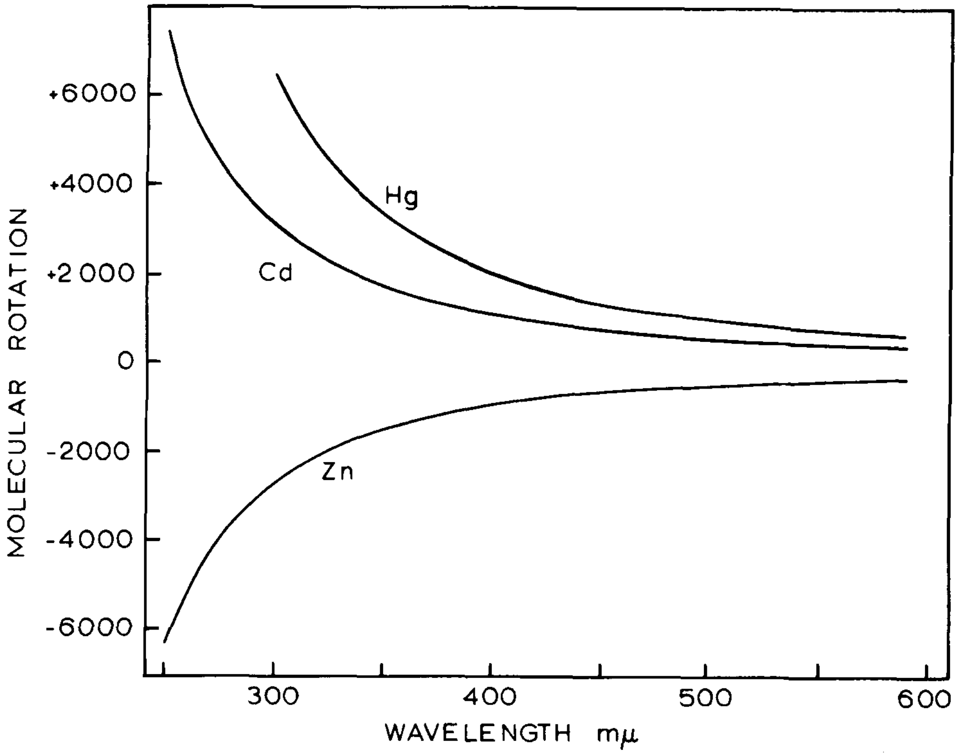

FIGURE 6 Optical rotatory dispersion spectra of Group IIB metal complexes of R(−)PDTA.

predominately optical active band[4] using the selected wavelengths 589 and 300 nm shows that the calculated wavelengths for zinc(II), cadmium(II), and mercury(II) complexes are 196, 220, and 232 nm, respectively. Thus, the calculated "effective center" has a bathochromic shift of approximately 35 nm from the zinc(II) to mercury(II)-R(−)PDTA complexes. In comparing the optical rotatory dispersion spectra of the Group IIA and IIB complexes of R(−)PDTA it is noted that the molecular rotations of the inert gas structure in absolute magnitude are much less than the molecular rotations of the psuedo-inert gas structures. Thus, comparing calcium(II) and zinc(II), which are in the fourth period, calcium(II)-R(−)PDTA has a much smaller negative molecular rotation from 400–600 nm than does zinc(II)-R(−)PDTA. Likewise, if the comparison of the Group IIA and IIB molecular rotations are compared for ions with approximately the same radius, calcium(II) and cadmium(II), and strontium(II) and mercury(II), it can again be seen that the absolute magnitudes of the molecular rotations are much smaller for the inert gas structure complexes than for the psuedo-inert gas structure complexes. Thus, where calcium(II)-R(−)PADTA has a very small negative molecular rotation throughout the range, cadmium(II)-R(−)PDTA has a fairly large positive molecular rotation. Likewise, comparing strontium(II) and mercury(II), which have approximately the same ionic radius, strontium(II)-R(−)-PDTA has small positive molecular rotations throughout the wavelengths studied; whereas, mercury(II)-R(−)PDTA has very large positive molecular rotations in the same wavelength region. Thus, the psuedo-inert gas ion structures have a much greater effect on the overall perturbations of the optically active transitions.

Figure 7 shows the optical rotatory dispersion spectra of the Group IIIA metal complexes of R(−)PDTA. Aluminium(III) which has an inert gas electronic configuration shows a plain negative ORD curve throughout the 600–250 nm wavelength range. The two psuedo-inert gas ions which are shown in Figure 7, indium(III) and thallium(III), both show positive ORD curves in the 600 to 300 nm wavelength range. The calculated "effective centers" on the optically active band using the selected wavelengths 589 and 300 nm show that the calculated

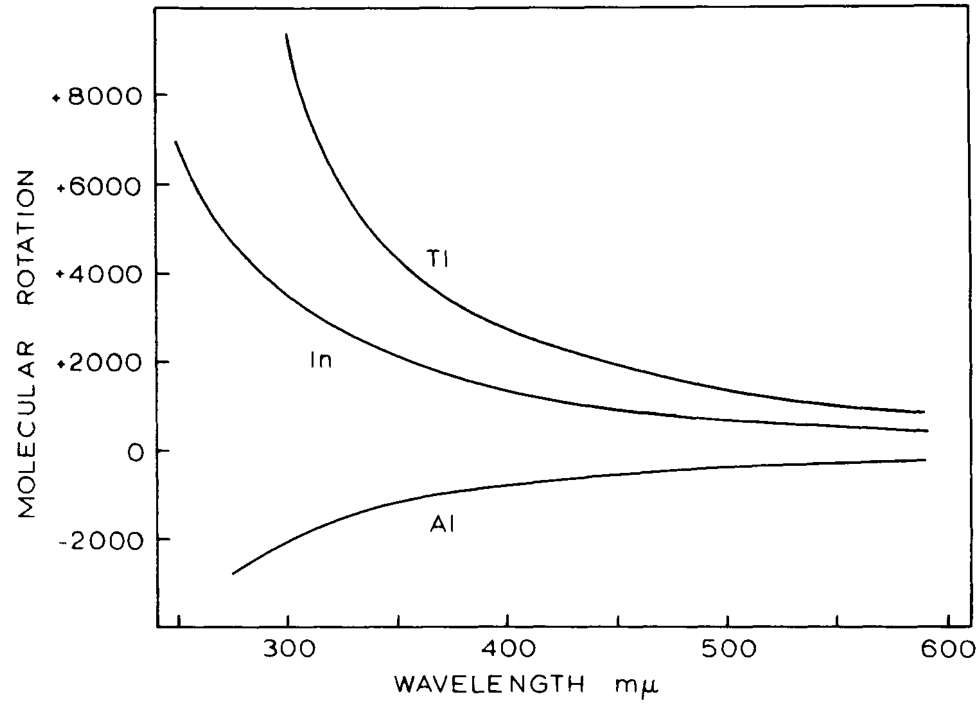

FIGURE 7 Optical rotatory dispersion spectra of Group IIIA metal complexes of R(–)PDTA.

wavelength for aluminium(III), indium(III), and thallium(III) complexes are 207, 217, and 252 nm, respectively. Thus, the calculated "effective center" has a bathochromic shift of approximately 45 nm from aluminium(III) to thallium(III)-R(–)PDTA. In comparing the optical rotatory dispersion spectra of the Group IIIA and IIIB complexes of R(–)PDTA, it is again noted that the molecular rotations of the inert gas structure ions are much less in absolute magnitude than the molecular rotations of the psuedo-inert gas ion structure. Thus, comparing yttrium(III) and indium(III), which are in the fifth period, yttrium(III)-R(–)PDTA has moderately negative molecular rotations throughout the wavelength range; whereas, indium(III)-R(–)PDTA has molecular rotations almost twice as large as the yttrium(III) complex. Thus, one can see the large effect of having a psuedo-inert gas structure on the optical rotatory dispersion spectra, since indium(III) has a smaller ionic radius and a larger ionic potential than does the yttrium(III). For lanthanum(III) and thallium(III), again both in the same period, the relationship holds in that the lanthanum(III)-R(–)PDTA has relatively small positive rotations throughout the 600–300 nm wavelength range; whereas, thallium(III)-R(–)PDTA has very large positive molecular rotations ranging from about four times larger at 589 nm to about eight times larger at 300 nm. A very striking difference between the inert gas ion complexes and psuedo-inert gas ion complexes is shown by the correlation of scandium(III) and indium(III). Both scandium(III) and indium(III) have the same ionic radius and ionic potential and have essentially the same absolute values of molecular rotations, however scandium(III) has negative molecular rotations throughout the total wavelength range whereas indium(III) has positive molecular rotations. Although aluminum(III) has a much greater ionic potential than scandium(III), and both have inert gas structures, scandium(III)-R(–)PDTA has larger negative molecular rotations from 600 to 250 nm than does aluminum(III)-R(–)PDTA. This can be attributed to very small ionic radius of the aluminium(III) and the strains involved in chelation of the R(–)PDTA around this small ionic size.

Figure 8 shows the optical rotatory dispersion spectra of the heavy metals mercury(II), thallium(III), lead(II), and bismuth(III) complexes of R(–)PDTA. As can be seen from Figure 8 and Table I, the positive molecular rotations of these complexes are extremely high and all have increasingly greater positive rotations with decreasing wavelength until the anomalous optical rotatory dispersion region. Comparing the mercury(II) and lead(II)-R(–)PDTA

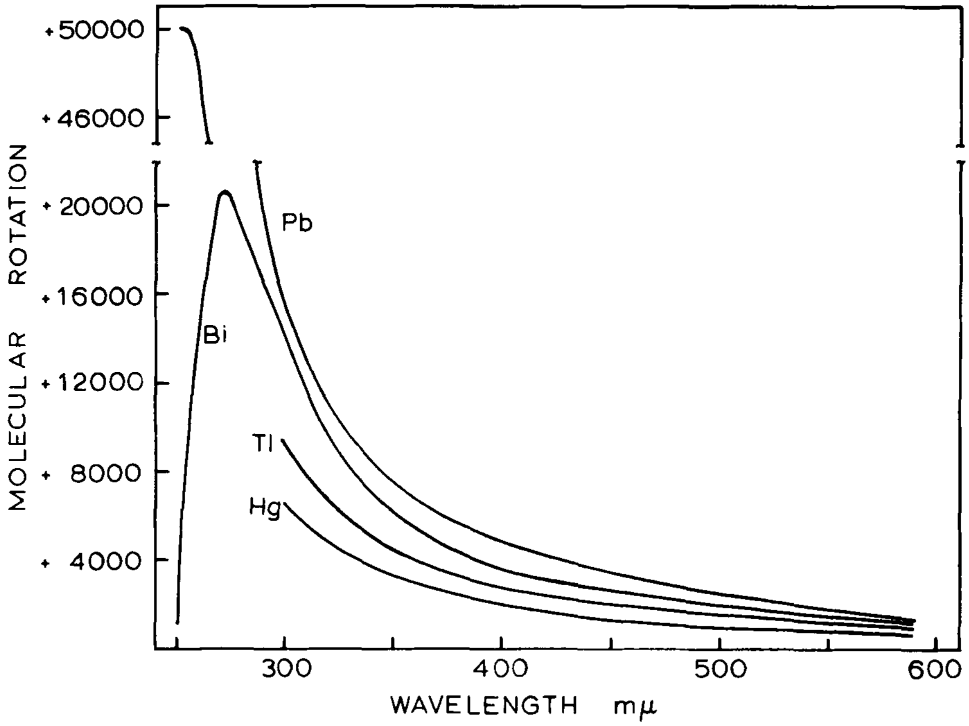

FIGURE 8 Optical rotatory dispersion spectra of Hg^{2+}, Tl^{3+}, Pb^{2+}, and Bi^{3+} complexes of R(−)PDTA.

molecular rotations, it can be seen that the lead(II)-R(−)PDTA complex has much greater positive molecular rotations throughout the complete spectra than does the mercury(II)-R(−)PDTA complex. Mercury(II) has a psuedo-inert gas ion structure; whereas, lead(II) has a psuedo-inert +2 ion structure. Likewise, comparing thallium(III) and bismuth(III)-R(−)PDTA complexes, bismuth(III), the ion with the psuedo-inert +2 ion structure, has much greater positive molecular rotations for its R(−)PDTA complex until the Cotton Effect region than does the thallium-R(−)PDTA complex where thallium(III) has a pseudo-inert gas ion structure. The greater molecular rotations of the lead(II) and bismuth(III) complexes compared to the mercury(II) and thallium(III) complexes are probably due to the greater deformation that the lead(II) and bismuth(III) ions undergo upon complexation. However, comparing the ionic potential of the ions with the same charge among these heavy metals; that is, lead(II) and mercury(II), and bismuth(III) and thallium(III), respectively, it is seen that as the ionic potential decreases, the molecular rotations increase positively outside the anomalous optical rotatory dispersion region. Thus, these heavy metals follow the same characteristic trend as has been seen with the previously described metal complexes.

CONCLUSIONS

The strong unambigous periodic trend of the molecular rotations in the optical rotatory dispersion spectra of the lanthanide-R(−)PDTA complexes has also been shown to exist in the metal ions under study in this paper. Thus, in these complexes of octahedral geometry where the ligand, R(−)PDTA, is completely stereospecific, the general periodic trend remains valid in that as the ionic potential decreases, the molecular rotations at a given wavelength outside of an optically active transition have a greater positive value. Although the perturbing forces that give rise to the optical rotatory dispersion spectra are a function of the ionic potential, it is clearly evident that more than simple electrostatic interactions between a ligand and the metal ion are involved; since ions that have a greater tendency toward deformation on complexation; for example lead(II) and bismuth(III), have the largest positive molecular rotations at a given wavelength.

The observed optical rotations are a summation of all the optically active transitions for a given metal complex, including the n–π* carboxylate transition at 205–210 nm, which has a molar absorptivity, ε, of approximately 50, and a pH dependent π–π* transition in the far UV. The plain ORD curves for R(–)PDTA show that the π–π* transition, possessing an extremely large rotational strength, dominates the plain negative curves, and has been calculated to have an "effective center" at 163.4 ± 0.6 nm.[4]

For the metal ions that have optically active charge transfer bands with high rotational strengths in the UV, the observed anomalous optical rotation is dominated by these optically active CT bands over a large range of wavelengths, (e.g., Ti). This effect is similar to the d–d transitions of the first row transition metals which lead to their anomalous ORD curves. Optically active transitions that have small rotational strengths, (i.e., f–f transitions) only effect the observed ORD spectrum over a very narrow wavelength range.[4]

Spectra on a circular dichroism instrument that is modified for far UV measurements, would be useful in determining the transition type and the rotational strengths of the contributing optically active transitions.

The CD spectra would further elucidate the effects of the different metal ions, as well as their ionic potentials, on the ORD spectra of these optically active complexes.

ACKNOWLEDGEMENTS

The authors wish to acknowledge The Robert A. Welch Foundation, Fellowship Grant No. A-262 (K.H.P.) and a C.S.U. Faculty Research Grant (K.H.P.) for partial support of this research. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research PRF-9041-B3-C (R.J.P.) and PRF-2623-G3 (J.R.B.). Part of this study was conducted at Texas A&M University.

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