BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3433—3438 (1969)

The " Circular Dichroism-sensitive Band " in the Optical Absorption of the Lanthanide(III) Complexes with Some Optically Active Ligands

Seizo MISUMI, Sigeo KIDA, Toshiyuki ISOBE, Yuzo NISHIDA and Haruko FURUTA

Inorganic Chemistry Laboratory, Faculty of Science, Kyushu University, Hakozaki, Fukuoka

(Received June 30, 1969)

The circular dichroism and absorption spectra of Pr(III), Nd(III), Sm(III), Dy(III), Ho(III), Er(III) and Tm(III) complexes with some natural amino acids and L-EDDS have been measured at room temperature. The "circular dichroism-sensitive bands" have been observed on the J-bands where magnetic dipole transitions are allowed to some extent. The experimental results are in accordance with the theory proposed previously. The theory can be applied at least for lanthanide(III) complexes.

In previous papers,[1,2] we reported the circular dichroism (CD) and absorption spectra of f-f transitions of l-PDTA(propylenediaminetetraacetic acid) complexes of Pr(III), Nd(III), Sm(III), Ho(III), Dy(III) and Er(III) in aqueous solutions, and compared the relative intensities of CD and absorption bands. In most of the J-bands, CD intensities were found to be parallel to the corresponding absorption intensities. However, some CD bands were observed to be exceptionally strong in comparison to the corresponding absorption bands. Those J-bands were named "CD-sensitive bands". The CD intensity of the "CD-sensitive

1) S. Kida, T. Isobe and S. Misumi, This Bulletin, **39**, 2786 (1966).

2) S. Misumi, S. Kida and T. Isobe, *Spectrochim. Acta*, **24A**, 291 (1968).

Ln(III) (ground state)	Ligand P	Aquo AB λ, mμ	Aquo AB ε	L-Alanine AB λ, mμ	L-Alanine AB ε	L-Alanine CD λ, mμ	L-Alanine CD α x10⁴	L-Serine AB λ, mμ	L-Serine AB ε	L-Serine CD λ, mμ	L-Serine CD α x10⁴	L-Lysine AB λ, mμ	L-Lysine AB ε	L-Lysine CD λ, mμ	L-Lysine CD α x10⁴
		443	9.7	446	8.5	442	− 0.9	446	8.0	441	− 0.3	445	10.0	442	− 1.5
		($^3P_2$)				446	+ 2.5			445	+ 0.5			446	+ 6.3
										450	− 0.4			450	− 1.2
Pr		468	4.1	472	3.7	467	− 1.4	472	4.0			472	4.0	466	− 4.8
($^3H_4$)		($^3P_1$)				472	+ 5.9							472	+ 9.0
						477	− 1.6								
		481	3.5	484	3.9	483	− 5.1	485	2.7	485	− 1.3	484	4.5	483	−10.9
		($^3P_0$)				486	+ 3.3			489	+ 0.3			487	+ 6.4
		589	1.8	592	1.8	587	− 2.2	591	1.8	591	+ 1.7	591	1.8	586	− 6.1
		($^1D_2$)				595	+ 7.8			602	− 1.1			592	+22.2
						599	− 7.2							600	− 7.2
														606	− 3.9
	2.5×10^{-7}	353	0.92					356	0.3	355	− 6.3	355	0.7	356	−27.1
		($^3I_{11/2}$)								358	+12.3				
	0.8×10^{-10}	475	0.64	476	0.52	479	−29.7					478	0.5	480	−18.0
		($^4G_{9/2}$)		478	0.44										
Nd	0.3×10^{-9}	512	1.81	513	1.93	511	−43.4	512	1.8	512	+ 9.2	514	2.0	511	−12.0
($^4I_{9/2}$)		($^2G_{9/2}$)				514	+ 5.1							514	+ 4.5
	0.4×10^{-8}	522	4.29	524	3.81	521	+ 4.0	525	4.6	522	− 1.6	525	4.8	525	− 4.0
		($^4G_{7/2}$)				524	−20.6							529	+ 1.3
				527	2.24	528	−12.8			525	+ 2.3				
				530	1.07	532	+20.2								
				534	0.45	537	−43.6			530	− 1.2				
						541	+21.8								
	0.5×10^{-8}	680	0.46									681	0.5	672	+16.0
		($^4F_{9/2}$)												681	−22.0
														686	+40.0
		357	0.03	356	0.06	355	−150.0								
		($^4H_{7/2}$)				356	−66.7	357	0.05	357	+100.0	356	0.05	355	−260.0
						357	−136.7							358	+180.0
	0.9×10^{-8}	450	0.05												
Sm		452	0.03	449	0.05	449	+324.0	452	0.05	452	+120.0	451	0.05	448	+660.0
($^6H_{5/2}$)		($^4F_{5/2}$)												454	−160.0
	1.2×10^{-8}	499	0.05	499	0.06	500	+153.3					499	0.05	498	+360.0
		($^4G_{7/2}$)													
	0.7×10^{-8}	560	0.02	561	0.05	557	−230.0	562	0.05	557	+80.0	562	0.05	556	−480.0
		($^4G_{5/2}$)				562	+60.0			562	−140.0			567	+180.0
		300	0.19					300	0.23	300	−57.0				
		($^4H_{13/2}$)								302	+22.6				
		389	0.80	388	0.90	388	−17.2	389	1.17	388	− 2.0	390	0.9	388	−11.1
Dy		($^4I_{13/2}$)				392	−13.6			389	+ 2.8			391	−12.2
($^6H_{15/2}$)										391	− 6.8			395	+ 8.9
	2.1×10^{-7}	450	0.29	448	0.25	448	+256.0	453	0.23	448	+71.3	450	0.3	448	+166.7
		452	0.26	450	0.26	452	−288.6			453	−244.8			452	−230.0
		($^4I_{15/2}$)		452	0.28	458	+46.4			456	+71.3			458	+33.0
	0.6×10^{-9}	294	0.40					295	0.25	293	+10.8				
		($^3L_8$)													
Ho	0.4×10^{-9}	383	0.08	383	0.10	382	+88.0	384	0.12	384	− 16.4	384	0.15	384	−46.7
($^5I_8$)		($^3K_7$)				384	−164.0			385	+ 14.3				
	0.7×10^{-7}	468	0.58	467	0.40	466	−70.0	468	0.61	466	−42.7	468	0.7	466	−32.9
		($^3K_8$)				468	+140.0			468	+ 5.6			468	+32.9
						470	−80.0			470	−22.6			470	+35.7
Er	0.4×10^{-7}	358	0.81	362	0.04	361	−680.0	358	0.92	358	− 1.2	358	0.92	358	−45.8
		361	0.10			363	+720.0	361	0.08	359	+ 0.4			359	−51.7
($^4I_{15/2}$)		($^2K_{15/2}$)								362	−26.9	361	0.12	363	+273.3
	1.5×10^{-8}	288	0.035	290	0.09	289	−91.4	290	0.07	290	−36.0				
Tm		($^1I_6$)				290	−194.3								
($^3H_6$)															
		660	0.16	660	0.14	660	−341.8					660	0.21	659	−271.0
		($^3F_2$)													

L-Threonine				L-Arginine				L-Aspartic acid				L-EDDS			
AB		CD		AB		CD		AB		CD		AB		CD	
λ,mμ	ε	λ,mμ	α×10⁴	λ,mμ	ε	λ,mμ	α×10⁴	λ,mμ	ε	λ,mμ	α×10⁴	λ,mμ	ε	λ,mμ	α×10⁴
446	9.1	440	− 0.4	446	7.4	444	− 1.6	446	7.90	447	− 1.1	445	6.76	445	− 9.6
		445	+ 1.5	449	8.8	447	+ 1.7					448	6.65	450	+ 3.2
		449	+ 0.4												
472	4.4	469	+ 2.0	474	3.6	470	− 1.1	472	4.08	473	+ 1.8	472	3.94	471	− 3.2
		474	− 2.5			473	+ 4.4							475	+ 2.4
						477	− 1.7							480	− 2.4
485	2.8	484	− 3.6	486	3.3	486	+ 1.8	485	2.48	487	+3.7	485	2.39	484	+18.5
						488	− 4.5							488	− 9.0
592	2.1	584	− 1.4	594	1.8	584	− 3.3	593	1.64	585	+ 1.5	592	1.82	592	− 1.5
		596	+ 4.3			592	+ 1.7			590	− 1.8	600	0.84	601	+ 4.9
		602	− 1.9			596	− 2.8			600	+2.4				
						605	+ 4.4								
356	0.7	356	−14.3	357	0.4	355	+25.0	356	0.38	355	+12.5	352	0.25	352	+46.0
						359	−25.0			357	+22.5			350	−124.4
				479	0.8	479	− 7.5								
513	2.8	512	− 2.9	515	2.1	513	+ 4.3	515	2.23	512	+ 2.9				
		515	+ 1.4	518	2.2	518	− 3.2			514	+ 0.3				
524	7.1	523	− 1.4	527	5.0	524	− 1.8	526	5.24	522	+ 2.4				
		526	+ 2.8			528	+ 2.8			526	− 0.7				
				687	0.6	683	+25.0								
357	0.1	356	−90.0	358	0.05	356	+280.0	355	0.03	355	−318.0				
		358	+60.0							359	+208.7				
452	0.05	452	+80.0	452	0.05	449	−100.0	450	0.03	449	−102.7				
		454	−40.0			453	+100.0			451	−171.0				
				500	0.08			498	0.05	500	+28.8	500	0.07	500	−114.3
560	0.05	560	−160.0	563	0.05	561	+140.0	560	0.03	557	−201.7	563	0.05	564	−160.0
						569	−140.0			564	+119.7				
300	0.4	300	− 8.0	300	0.3	299	−30.0								
		301	+10.0												
390	1.2	388	− 6.7	389	1.0	386	− 6.0	390	1.25	388	− 3.5	389	1.2	390	+50.0
		391	+10.0			391	+ 7.0			390	+ 9.2			392	−26.7
										392	− 7.3				
452	0.3	447	−33.0	450	0.3	450	−100.0	451	0.31	448	+132.3	452	0.3	448	−293.3
		450	−60.0			453	+46.7	454	0.32	453	−208.1			453	+440.0
		452	+100.0							458	+13.5			457	−106.7
		456	−130.0												
		459	+20.0												
384	0.2	382	−15.0	386	0.1	385	−60.0	382	0.11	383	+96.0	382	0.2	383	+240.0
		383	+10.0												
468	0.75	466	−29.3	469	0.75	467	+20.0	466	0.37	463	+19.4	467	0.4	465	+150.0
		470	−18.7			469	−37.3			465	−52.9			468	+270.0
										467	+51.8				
				358	1.2	357	+ 6.7	360	0.05	360	−420.0	357	1.0	357	+56.0
						359	−11.7					360	0.1	359	+800.0
				362	0.1	361	+210.0							362	−1080.0
				291	0.05	290	−80.0	290	0.09	290	−268.0	289	0.12	289	−420.0
						292	+60.0							292	+136.0
				659	0.2	660	+50.0	659	0.20	658	−170.9	658	0.16	660	+212.3
														662	+118.5
														664	+212.3

bands" was well elucidated on the basis of Condon's theory[3] *i.e.*, the CD intensity is proportional to the imaginary part of the scalar product of the magnetic and the electric dipole moments associated with the electronic transitions.

CD and absorption spectra of Pr(III), Nd(III), Sm(III), Dy(III), Ho(III), Er(III) and Tm(III) complexes of six natural amino acids and L-EDDS (ethylenediaminedisuccinic acid) have been measured. The relative intensities of CD and absorption bands with regard to the calculated oscillator strengths of magnetic dipole transitions of the J-bands have been discussed in order to verify the general validity of the theory which was previously proposed for the elucidation of the "CD-sensitive bands".

Experimental

Materials. The natural amino acids, L-alanine, L-serine, L-threonine, L-aspartic acid, L-arginine and L-lysine were commercial products and were of GR grade. L-Ethylenediaminedisuccinic acid (EDDS) was prepared by Neal's method[4] from 1,2-dibromoethane and L-aspartic acid.

Found: C, 32.95; H, 6.80; N, 7.42%. Calcd for $C_{10}H_{24}N_2O_{12}$: C, 32.97; H, 6.59; N, 7.69%.

Lanthanide perchlorate was obtained by dissolving commercial lanthanide oxide of 99.9% purity. The concentration of lanthanide(III) ions were determined by means of volumemetric EDTA titration.

Measurements. Absorption and CD spectra were measured by a JASCO-ORD/UV-5 optical rotatory dispersion recorder with a CD attachment.

The solutions used for the measurements were prepared by dissolving lanthanide(III) perchlorate and the ligand in water in about 1 : 5 mole-ratio (except for EDDS complexes where metal to ligand ratio is 1 : 1), and were made alkaline with aqueous ammonia.

Results and Discussion

CD and absorption spectra of 51 complexes were measured. A few examples of these results are shown in Fig. 1. As was observed in PDTA

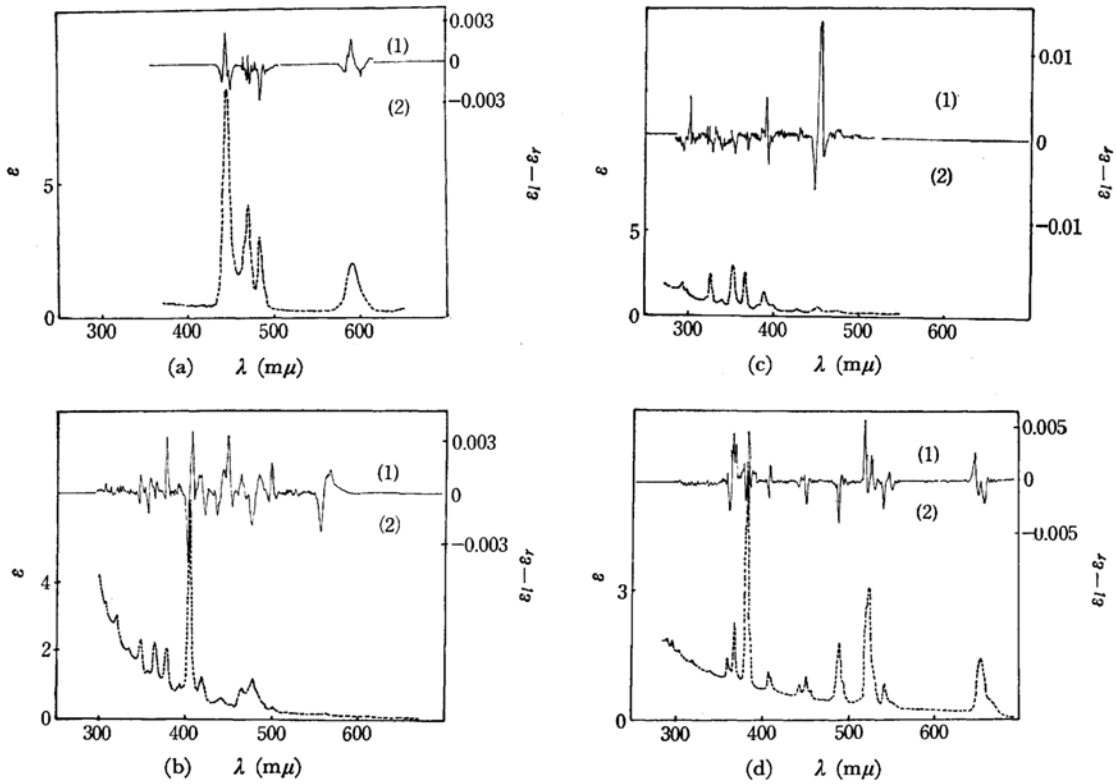

Fig. 1. Examples of CD and absorption spectra of lanthanide(III) complexes in aqueous solutions. (1 cm cell)
(1) CD spectrum; (2) absorption spectrum
(a) Pr - L-serine complex (1 : 5), pH=9.6, 26°C
(b) Sm - L-lysine complex (1 : 10), pH=9.9, 26°C
(c) Dy - EDDS complex (1 : 1.5), pH=9.0, 26°C
(d) Er - L-alanine complex (1 : 6), pH=8.5, 26°C

3) E. U. Condon, *Rev. Mod. Phys.*, **9**, 432 (1937).

4) T. A. Neal and N. T. Rose, *Inorg. Chem.*, **7**, 2405 (1968).

complexes,[2] a group of sharp CD bands was observed in the region of each absorption region.

The intensities of CD bands are parallel to those of corresponding absorption bands in most of the J-bands. However, as expected, unusually strong CD bands in comparison to the absorption bands were observed in the regions where the "CD-sensitive bands" were observed in the PDTA complexes.

In order to make clear the relation between the CD intensity and the magnetic dipole transition, we have calculated the oscillator strength, P, of magnetic dipole transition of J-bands by means of Pasternack's method[5] using eigen vectors of the secular equations for the intermediate coupling scheme.[6-9]

The results are summarized in Table 1, where $\alpha(=(\varepsilon_l-\varepsilon_r)/\varepsilon)$ was used as a parameter for representing relative intensities of CD and absorption bands. As seen in Table 1, when $P=0$, α remains only in the order of 10^{-5}—10^{-4}. However, when P exceeds the value $\sim 10^{-7}$, α becomes the order of 10^{-4}—10^{-3}, and the "CD-sensitive bands" were observed distinctly. Agreement between theory and experiment is satisfactory as is seen from Table 1. Thus we may conclude that our theory for the "CD-sensitive bands" is on the whole valid. However, one exception was the band at 660 mμ in the spectra of some Tm(III) complexes, where α shows a large value (100—200×10^{-4}) for $P=0$. This can not be explained at present.

5) S. Pasternack, *Astrophys. J.*, **92**, 129 (1940).
6) B. G. Wybourne, *J. Chem. Phys.*, **36**, 2301 (1962).
7) S. Hüfner, *Z. Phys.*, **164**, 456 (1961).
8) B. G. Wybourne, *J. Chem. Phys.*, **34**, 279 (1961).
9) W. F. Krupke and J. B. Gruber, *Phys. Rev.*, **139**, 2008 (1965).