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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

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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 1-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)	Ligand	Αq	uo		L – Alanine			L-Serine			L - Lysine				
(ground state)	P	_,mμ	.Β ε	_λ,mμ	<u>ε</u> 4Β	_λ,mμ	α×10⁴	λ,mμ	ΑΒ <i>ι</i> ε	ζ,mμ	D ∝x10⁴	λ, m/	AB <u>∠ €</u> _	CD , mμ	a × 10⁴
		443 (³P₂)	9.7	446	8.5	442 446	- 0.9 + 2.5	446	8.0	441 445 450	- 0.3 + 0.5 - 0.4	445	10.0	442 446 450	- 1.5 + 6.3 - 1.2
Pr (³H₄)		468 (³P,)	4.1	472	3.7	467 472 477	- 1.4 + 5.9 - 1.6	472	4.0			472	4.0	466 472	- 4.8 + 9.0
		481 (³₽₀)	3.5	484	3.9	483 486	- 5.1 + 3.3	485	2.7	485 489	- 1.3 + 0.3	484	4.5	483 487	-10.9 + 6.4
		589 ('D₂)	1.8	592	1.8	587 595 599	- 22 + 7.8 - 7.2	591	1.8	591 602	+ 1.7 - 1.1	591	1.8	586 592 600 606	- 6.1 +22.2 - 7.2 - 3.9
Nd (*I _{9/2})	2.5 × 10 ⁷	353 (²I _{11/2})	0.92					356	0.3	355 358	- 6.3 +12.3	355	0.7	356	-27.1
	0.8× 10 ⁻¹⁰	475 (⁴ G _{9/2})	0.64	476 478	0.52 0.44	479	-29.7					478	0.5	480	-18.0
	0.3 × 10 [°]	512 ·(²G _{9/2})	1.81	513	1.93	511 514	-43.4 + 5.1	512	1.8	512	+ 9.2	514	2.0	511 514	- 12.0 + 4.5
	0.4 × 10 [°]	522 (*G _{7/2})	4.29	524 527	3.81 2.24	521 524 528	+ 4.0 -20.6 -12.8	525	4.6	522 525	- 1.6 + 2.3	525	4.8	525 529	- 4.0 + 1.3
				530 534	1.07 0.45	532 537	+20.2			530	- 1.2				
	0.5 × 10 [°]	680 (*F _{9/2})	0.46			541	+21.0					681	0.5	672 681 686	+16.0 -22.0 +40.0
Sm { [•] H _{5/2})		357 (⁴H _{7/2})	0.03	356	0.06	355 356 357	-150.0 -66.7 -136.7	357	0.05	357	+100.0	356	0.05	355 358	-260.0 +180.0
	0.9×10 [°]	450 452 (⁴F₅₂)	0.05 0.03	449	0.05	449	+324.0	452	0.05	452	+120.0	451	0.05	448 454	+660.0 - 1 60.0
	1.2 × 10 [°]	499 (*G _{7/2})	0.05	499	0.06	500	+153.3					499	0.05	498	+360.0
	0.7×10 ⁻⁸	560 (⁴G₅₂)	0.02	561	0.05	557 562	-230.0 +60.0	562	0.05	557 562	+80.0 -140.0	562	0.05	556 567	-480.0 +180.0
Dy {(*H _{15/2})		300 (⁴H _{i3/2})	0.19					300	0.23	300 302	-57.0 +22.6				
		389 (*I _{\3/2})	0.80	388	0.90	388 392	-17.2 -13.6	389	1.17	388 389 391	- 2.0 + 2.8 - 6.8	390	0.9	388 391 395	- . - 2.2 + 8.9
	2.1×107	450 452 (*I:4/2)	0.29 0.26	448 450 452	0.25 0.26 0.28	448 452 458	+256.0 -288.6 +46.4	453	0.23	448 453 456	+71.3 -244.8 +71.3	450	0.3	448 452 458	+ 166.7 -230.0 +33.0
	0.6 × 10"	294 (³ L ₈)	0.40					295	0.25	293	+ 10.8				
Ho (^s Is)	0.4×10 [°]	383 (³K,)	0.08	383	0.10	382 384	+88.0 - 164.0	384	0.12	384 385	- 16.4 + 14.3	384	0.15	384	- 46.7
	0.7 × 10 ⁷	468 (³K ₈)	0.58	467	0.40	466 468 470	-70.0 +140.0 -80.0	468	0.61	466 468 470	-42.7 + 5.6 -22.6	468	0.7	466 468 470	-32.9 +32.9 +35.7
Er (⁴ I _{15/2})	0.4×10 ⁻⁷	358 361 (²K _{15/2})	0.81 0.10	362	0.04	361 363	-680.0 +720.0	358 361	0.92 0.08	358 359 362	- 1.2 + 0.4 -26.9	358 361	0.92 0.12	358 359 363	-45.8 -51.7 +273.3
Tm /3u	1.5×10 [°]	288 ('Is)	0.035	290	0.09	289 290	-91.4 -194.3	290	0.07	290	-36.0				
("H ₆)		660 (³ F ₂)	0.16	660	0.14	660	-341.8					660	0.21	659	-271.0

L – Threonine				L – Arginine					L-Asp	artic acid	L-EDDS			
Ω ,mμ	ε	λ, mμ	CD ∝×IO⁴	λ,mμ	ΑΒ ε	<u>λ,m</u>	CD ∠ αxi0 ⁴	λ,mμ	AB ε	CD ,mµ ∝ x10⁴	λ,mμ	ΑΒ 4 ε	СD 入,mµ ∝×10⁴	
446	9.1	440 445 449	- 0.4 + 1.5 + 0.4	446 449	7.4 8.8	444 447	- 1.6 + 1.7	446	7.90	447 - 1.1	445 448	6.76 6.65	445 - 9.6 450 + 3.2	
472	4.4	469 474	+ 2.0 - 2.5	474	3.6	470 473 477	- 1.1 + 4.4 - 1.7	472	4.08	473 + 1.8	472	3.94	471 - 3.2 475 + 2.4 480 - 2.4	
485	2.8	484	- 3.6	486	3.3	486 488	+ 1.8 - 4.5	485	2.48	487 + 3.7	485	2.39	484 +18.5 488 - 9.0	
592	2.1	584 596 602	- 1.4 + 4.3 - 1.9	594	1.8	584 592 596 605	- 3.3 + 1.7 - 2.8 + 4.4	593	1.64	585 + 1.5 590 - 1.8 600 + 2.4	592 600	1.82 0.84	592 - 1.5 601 + 4.9	
356	0.7	356	-1 4.3	357	0.4	355 359	+25.0 -25.0	356	0.38	355 +12.5 357 +22.5	352	0.25	352 +46.0 350 -124.4	
				479	0.8	479	- 7.5							
513	2.8	512 515	- 2.9 + 1.4	515 518	2.1 2.2	513 518	+ 4.3 - 3.2	515	2.23	512 + 2.9 514 + 0.3				
524	7.1	523 526	- 1.4 + 2.8	527	5.0	524 528	- 1.8 + 2.8	526	5.24	522 + 2.4 526 - 0.7				
				687	0.6	683	+25.0							
357	0.1	356 358	-90.0 +60.0	358	0.05	356	+280.0	355	0.03	355 -318.0 359 +208.7				
452	0.05	452 454	+80.0 -40.0	452	0.05	449 453	-100.0 +100.0	450	0.03	449 -102.7 451 -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	561 569	+140.0 -140.0	560	0.03	557 -201.7 564 +119.7	563	0.05	564 -160.0	
300	0.4	300 301	- 8.0 +10.0	300	0.3	299	-300							
390	1.2	388 391	- 6:7 +10.0	389	I.O	386 391	- 6.0 + 7.0	390	1.25	388 - 3.5 390 + 9.2 392 - 7.3	389	1.2	390 +50.0 392 -26.7	
452	0.3	447 450 452 456 459	-33.0 -60.0 +100.0 -130.0 +20.0	450	0.3	450 453	-100.0 +46.7	451 454	0.31 0.32	448 +132.3 453 -208.1 458 +13.5	452	0.3	448 - 293.3 453 +440.0 457 -106.7	
384	0.2	382 383	-15.0 +10.0	386	0.1	385	- 60.0	382	0.11	383 +96.0	382	0.2	383 +240.0	
468	0.75	466 470	-29.3 -18.7	469	0.75	467 469	+20.0 -37.3	466	0.37	463 +19.4 465 -52.9 467 +51.8	467	0.4	465 +150.0 468 +270.0	
				358 362	1.2 0.1	357 359 361	+ 6.7 -11.7 +210.0	360	0.05	360 - 420.0	357 360	1.0 0.1	357 +56.0 359 +800.0 362 -1080.0	
				291	0.05	290 292	~80.0 +60.0	290	0.09	290 -268.0	289	0.12	289 -420.0 292 +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 theory³) *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 method⁴) from 1,2-dibromoethane and L-aspartic acid.

Found: C, 32.95; H, 6.80; N, 7.42%. Calcd for $C_{10}H_{24}N_2O_{13}$: 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



(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).

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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 method⁵) using eigen vectors of the secular equations for the intermediate coupling scheme.⁶⁻⁹

- 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).

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 m μ in the spectra of some Tm(III) complexes, where α shows a large value $(100-200 \times 10^{-4})$ for P=0. This can not be explained at present.

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W. F. Krupke and J. B. Gruber, Phys. Rev., 139, 2008 (1965).