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Application of Luminescence and Absorption Spectroscopy and X-ray Methods to Studies of Ln^{+3} Ions Interaction with Aminoacids

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The Nd^{+3}, Ho^{+3} and Eu^{+3} compounds with glycine, alanine and glutamic acid were synthesized and obtained as monocrystals.

Absorption spectra in the range 8000–35500 cm^{-1} were measured along the crystallographic axes at room temperature on a Cary 14 spectrophotometer.

Luminescence spectra were recorded at the same temperature in the range 9000–16600 cm^{-1}.

Intensities of the f–f transitions were analyzed on the basis of the Judd theory, taking the dependence of intensity on the crystallographic axis position into account.

Considerable differences in hypersensitive transitions in crystals with alanine, glycine and glutamic acid, whose symmetry changed from triclinic to monoclinic, were explained in terms of differences in the Me–O distances.

Introduction

The lanthanides are often used as spectroscopic probes in systems of biological importance [1, 2]. Since Ln^{+3} ions can substitute the Ca^{+2} ion, the explanation of the bonding mode of lanthanide ions with aminoacids seemed reasonable. Studies in solution [3–10] have shown that aminoacids connect the lanthanide ions through the oxygen atoms of carboxyl groups, and the bonding *via* nitrogen of the amino group in the pH range 1.5–5.6 seems unlikely [3, 9].

From our investigations it follows that the dimeric or polynuclear form may also occur in those solutions [9]. The possibility to create such a form in pH over 5.6 has been reported [3, 7]. Spectroscopic and crystallographic studies of lanthanide compounds with aminoacids in solid state were up to now limited to the Nd compounds with glycine. Poray-Koshits [11] has reported the initial crystallographic data for $NdCl_3(Gly)_3 \cdot 3H_2O$; we have published the spectroscopic and crystallographic data for $Nd(Gly)_3(ClO_4)_3 \cdot 4.5H_2O$ crystals [12]. For this reason we have extended our studies to crystals of lanthanide compounds with aminoacids, to elucidate their structure and spectroscopic properties. Luminescence and absorption spectroscopy, as well as X-ray methods, were applied.

Experimental

The Nd^{+3}, Ho^{+3} and Eu^{+3} complexes with glycine, alanine and glutamic acid were synthesized and obtained as monocrystals from aqueous solutions at the pH 1.5–3.5. The concentration of Ln^{+3} ions always exceeded the aminoacid concentration. Density of the obtained crystals was measured by the flotation method in a mixture of chloroform and ethylene bromide. The concentrations of Ln^{+3} ions in crystals determined by the EDTA titration are as follows: $Nd(Gly)_3(ClO_4)_3 \cdot 4.5H_2O$, 2.799 *M*; $Nd(Ala)_2(ClO_4)_3 \cdot 5H_2O$, 2.950 *M*; $NdGlu(ClO_4)_2 \cdot 7H_2O$, 3.4185 *M*; $Ho(Gly)_3(ClO_4)_3 \cdot 5H_2O$, 2.8212 *M*; $Ho(Ala)_2(ClO_4)_3 \cdot 5H_2O$, 2.8781 *M*; $HoGlu(ClO_4)_2 \cdot 7H_2O$, 3.5882 *M*.

Complexes with glycine and alanine crystallized in the triclinic system with the crystal data for $Nd(Gly)_3(ClO_4)_3 \cdot 4.5H_2O$: $a = 11.554$ Å, $b = 14.108$ Å, $c = 15.660$ Å, $\alpha = 97.14$, $\beta = 102.82$, $\gamma = 105.28$, $V = 2355.25$ Å, M.w. = 747.7, $D_c = 2.129(3)$ g cm^{-3}, $D_M = 2.103(1)$ g cm^{-3}, space group $P\bar{1}$; $Z = 4$; and for $Eu(Ala)_2(ClO_4)_3 \cdot 5H_2O$ [13]: $a = 11.071$ Å, $b = 11.338$ Å, $c = 11.990$ Å, $\alpha = 123.43$, $\beta = 100.94$, $\gamma = 101.59$, space group $P\bar{1}$.

The crystals seem to be isomorphic with the other lanthanide complexes. Monocrystals of Ho(Glu)-

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$(ClO_4)_2 \cdot 7H_2O$ exhibit a monoclinic symmetry and are isomorphic with Eu^{+3} and Nd^{+3} complexes. Preliminary crystal data are as follows: $a = 11.26$ Å, $b = 16.27$ Å, $c = 21.05$ Å, $\beta = 102.38$, space group $P2_1$. Absorption spectra of monocrystals polished along the crystallographic axes were recorded at room temperature, in the range 8000–35 000 cm^{-1} on a Cary 14 spectrophotometer. The areas of the absorption bands were calculated numerically by the graphical integration method and expressed in terms of the oscillator strength.

The fluorescence spectra were excited with an HBO 200 lamp with UG-1 and UG-11 glass filters and recorded on a GDM 1000 grating monochromator coupled with a cooled photomultiplier M10 FD9 (Carl Zeiss, Jena).

The relative intensities of the ${}^5D_0 \rightarrow {}^7F_J$ and ${}^5D_0 \rightarrow {}^7F_4$ $(J = 0, 1, 2)$ transitions for Eu^{+3} complexes were measured planimetrically, because the response of the monochromator in the measured range is almost constant.

Results and Discussion

The absorption spectra of Nd^{+3} complexes with glycine measured along the crystallographic axes are shown in Fig. 1. In Fig. 2 are presented the spectra of holmium with glycine, alanine and glutamic acid compounds. In Fig. 3 are shown the spectra for 3 orientations of the crystal for the Nd complex with glutamic acid, in the region particularly sensitive to the orientation changes.

The absorption spectra are complex, and are different along the three crystallographic axes. $4f^N$ transitions in the absorption spectra of Ln^{+3} ions usually correspond to the transition from the ground state $\psi_y \rightarrow \psi_{y'}$.

The band intensities correspond mainly to the contribution of the electric dipole transitions and, for particular bands, also to a contribution of the magnetic dipole transitions. The measured oscillator strengths can be expressed by the relation:

$$P_{exp} = \frac{2303\, mc^2}{N\pi e^2} \int_{\sigma_1}^{\sigma_2} \epsilon_{(\sigma)}\, d\sigma \qquad (1)$$

where $\epsilon_{(\sigma)}$ is the molar extinction of the band at the wavenumber σ (cm^{-1}); other symbols have their usual meaning.

These values were determined for all bands in the measured spectral range and are tabulated in Tables I and II. Among the f–f transitions in lanthanide ions, some satisfying the selection rule $|\Delta J| \leqslant 2$ manifest some extraordinary sensitivity to the variation of ion environment. These transitions are termed the hypersensitive ones. Figure 4 shows the hypersensitive transitions ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$, ${}^2G_{7/2}$ for Nd^{+3} ion compounds with alanine, glycine and glutamic acid. Smaller changes are seen in the shape of the

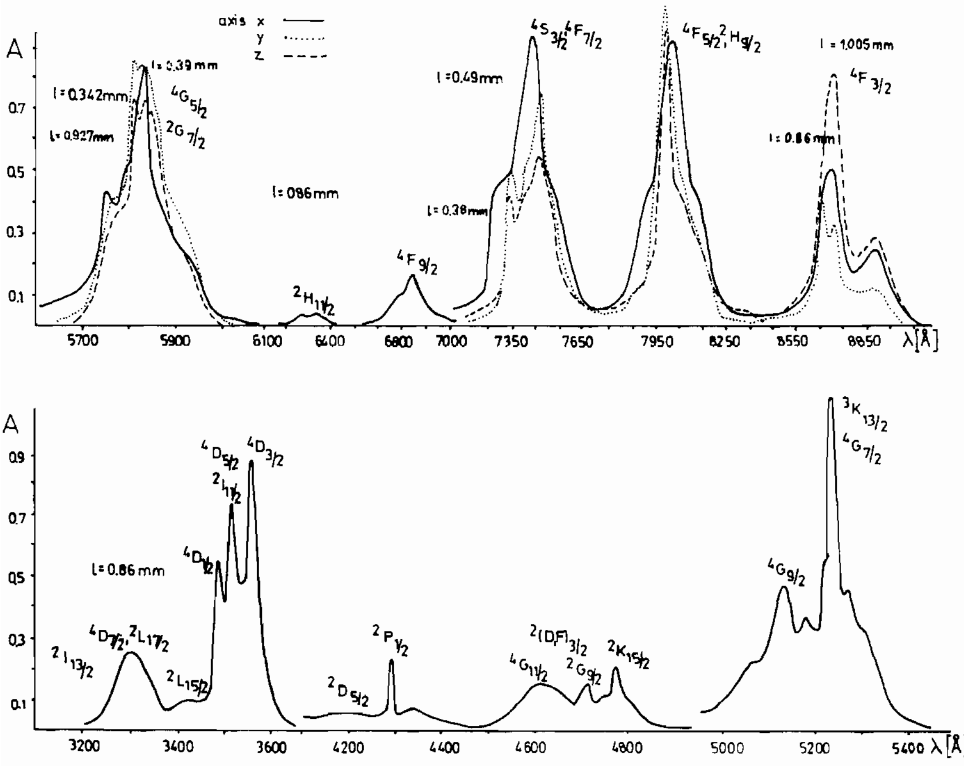

Fig. 1. Absorption spectrum along the crystallographic axes of $Nd(Gly)_3(ClO_4)_3 \cdot 4.5H_2O$ crystal.

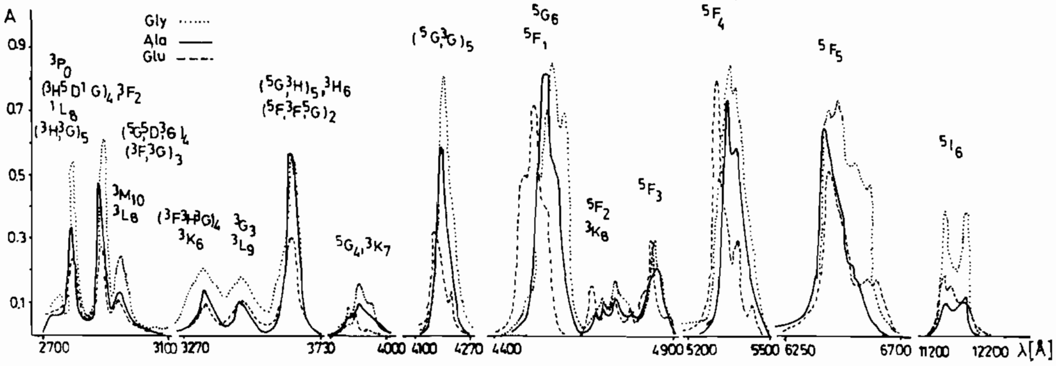

Fig. 2. Absorption spectra of holmium compounds with glycine, alanine and glutamic acid.

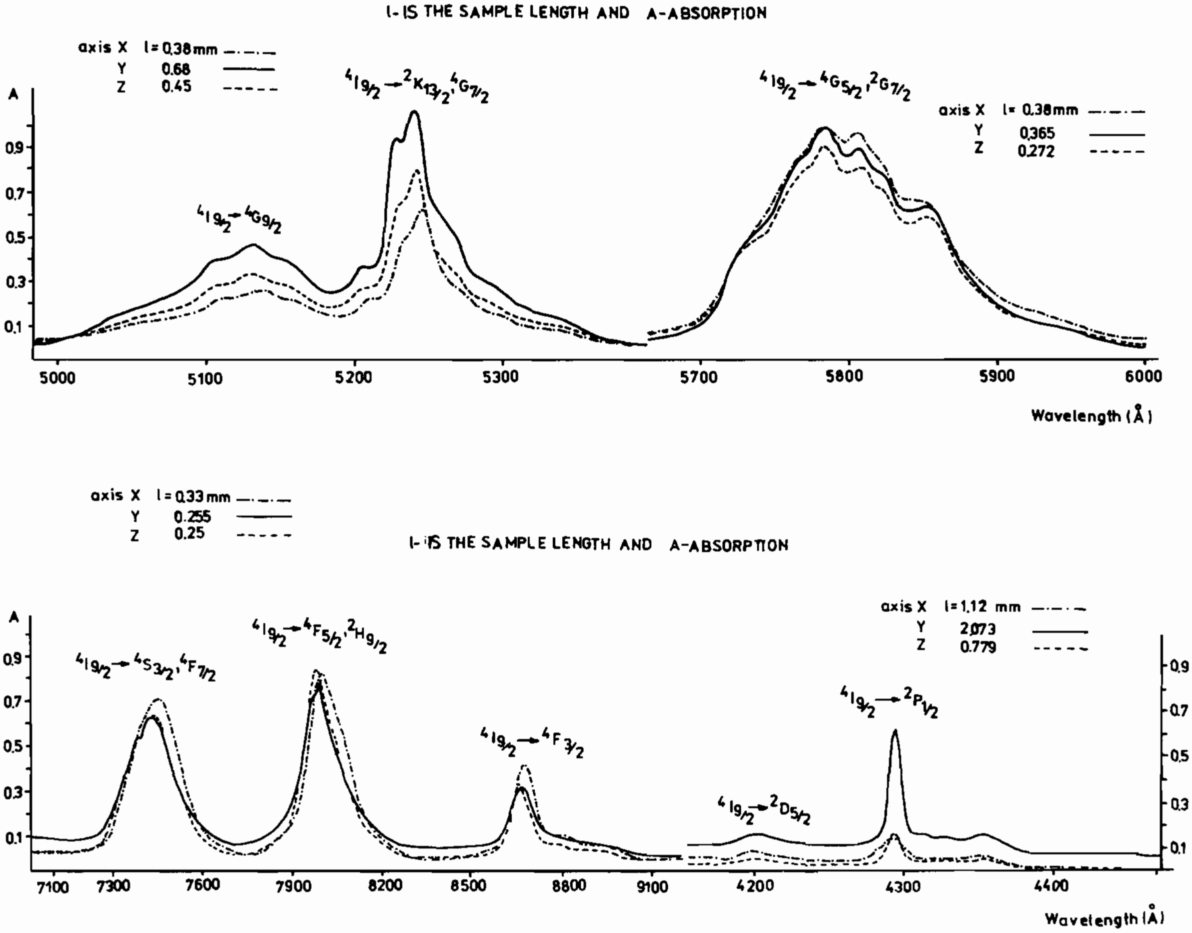

Fig. 3. Absorption spectrum along the XYZ crystallographic axes of $Nd(Glu)(ClO_4)_2 \cdot 7H_2O$ crystal.

spectra for glutamic acid complex, depending on orientation, than for complexes with glycine.

Hypersensitive transitions differ considerably in intensity decay for different orientations of the crystal (see Tables I and II). There also appear differences in the character of this transition for the Nd^{+3} and Ho^{+3} complexes with glycine, alanine and glutamic acid (see Figs. 2, 4). Examination of the luminescence spectra of Eu^{+3} crystals with glycine, alanine and glutamic acid, as well as absorption

TABLE 1. Oscillator Strength Values of f–f Transitions for Nd^{+3} Ion Complexes with Glycine, Alanine and 1-Glutamic Acid.

Spectral region S'L'J'	P × 10^8											
	$[Nd(Gly)_3](ClO_4)_3 \cdot 4.5H_2O$						$[Nd(Ala)_2](ClO_4)_3 \cdot 5H_2O$		$[Nd(Glu)](ClO_4)_2 \cdot 7H_2O$			
	Expt-X	Calc	Expt-Y	Calc	Expt-Z	Calc	Expt	Calc	Expt-X	Expt-Y	Expt-Z	Calc
8300–9090 $^4F_{3/2}$	203.01	214.86	314.1	216.9	294.9	227.8	266.9	242.7	329.1	332.3	296.0	230.2
7700–8330 $^4F_{5/2}$, $^2H_{9/2}$	862.90	900.11	863.7	862.4	905.9	855.8	1051.8	1009.4	1083.9	846.9	932.5	979.2
7200–7700 $^4S_{3/2}$, $^4F_{7/2}$	1004.00	1048.99	926.3	981.8	848.2	958.4	1005.8	1168.7	1156.4	963.5	1079.2	1140.1
6580–7040 $^4F_{9/2}$	75.77	77.78	62.0	73.4	77.2	71.9	74.02	86.41	70.85	77.0	99.8	84.1
6170–6410 $^2H_{11/2}$	18.0	21.3	8.8	20.1	14.5	19.9	18.07	23.77	22.43	21.3	17.8	23.1
5500–6024 $^4G_{5/2}$, $^2G_{7/2}$	1282.20	1303.5	1228.8	1242.9	1035.1	1054.5	1237.7	1246.93	1506.6	1350.7	1215.2	1367.9
4950–5376 $^2K_{13/21}$, $^4G_{7/2}$, $^4G_{9/2}$	832.23	555.38	729.3	538.9	799.2	534.5	725.8	603.3	792.3	759.1	687.1	590.5
4460–4950 $^2K_{15/2}$, $^2G_{9/2}$	257.5	140.68	238.5	136.5	274.6	138.4	219.5	156.9	237.3	230.2	230.8	149.9
4130–4330 $^2P_{1/2}$, $^2D_{5/2}$	47.0	52.6	52.0	53.8	74.8	57.9	46.8	59.08	47.6	54.8	42.8	54.8
3360–3620 $^4D_{9/2}$, $^2I_{11/2}$, $^4D_{1/2}$, $^2L_{15/2}$	918.3	977.2	934.4	998.4	975.8	1063.6	1053.1	1094.7	968.7	926.98	1089.1	1024.5
3190–3360 $^2I_{13/2}$, $^4D_{7/2}$, $^2L_{17/2}$	304.5		291.8		292.8		277.7		263.1	195.50		
RMS deviation	$1.15 \cdot 10^{-7}$		$0.94 \cdot 10^{7}$		$1.28 \cdot 10^{-7}$		$0.62 \cdot 10^{-7}$		$1.31 \cdot 10^{-7}$			

Compound		$\tau_2 \cdot 10^9$	$\tau_4 \cdot 10^9$	$\tau_6 \cdot 10^9$
$[Nd(Gly)_3](ClO_4)_3 \cdot 4.5H_2O$	X	3.65 ± 0.85	5.48 ± 0.78	11.49 ± 1.10
	Y	3.25 ± 0.68	5.67 ± 0.63	10.7 ± 0.88
	Z	1.83 ± 0.93	6.17 ± 0.86	10.4 ± 1.20
	mean	2.83 ± 0.76	5.92 ± 0.71	10.8 ± 0.99
$[Nd(Ala)_2](ClO_4)_3 \cdot 5H_2O$		2.81 ± 0.45	6.16 ± 0.42	12.77 ± 0.58
$[Nd(Glu)](ClO_4)_2 \cdot 7H_2O$	mean	3.86 ± 0.58	5.68 ± 0.53	12.4 ± 0.74

TABLE II. Oscillator Strengths of f–f Transitions for Ho^{+3} Crystals.

Spectral region (Å)	S'L'J'	[Ho(Gly)$_3$](ClO$_4$)$_3$·5H$_2$O X	[Ho(Ala)$_2$](ClO$_4$)$_3$·5H$_2$O X	[HoGlu](ClO$_4$)$_2$·7H$_2$O
12500–11111	$^5I_6$	110.29	36.31	32.50
9259–8771	$^5I_5$	33.72	137.22	135.67
7692–7407	$^5I_4$	~0	~0	~0
6666–6250	$^5F_5$	343.82	458.87	425.55
5555–5208	$^5S_2$, $^5F_4$	534.16	669.05	555.29
4975–4784	$^5F_3$	173.46	245.03	235.85
4784–4629	$^5F_2$, $^3K_3$	132.58	176.81	157.09
4629–4310	$^5G_6$, $^5F_1$	1024.58	1012.41	1137.61
4273–4065	$(^5G, {}^3G)_5$	302.53	385.57	386.11
4000–3787	$^5G_4$, $^3K_7$	79.60	108.14	104.03
3676–3508	$(^5G, {}^3H)_5$, $(^5F, {}^3F, {}^5G)_2$, $^3H_6$	492.50	450.44	493.20
3508–3378	$^5G_3$, $^3L_9$	132.12	133.82	106.46
3378–3278	$(^3F, {}^3H, {}^3G)_4$, $^3K_6$	88.53	90.70	80.97
3278–3164	$^5G_2$			
3039–3012	$^3D_3$, $^3P_1$	~0	~0	~0
2976–2890	$^3M_{10}$, $^3L_8$	130.68	142.22	96.65
2890–2816	$(^5G, {}^5D, {}^3G)_4$, $(^3F, {}^3G)_3$	287.60	341.32	291.94
2840–2690	$^3P_0$, $(^3H, {}^5D, {}^1G)_4$, $^3F_2$, $^1L_8$, $(^3H, {}^3G)_5$	312.8	487.95	243.76

The τ_λ parameters values

Compound	$\tau_2 \cdot 10^9$	$\tau_4 \cdot 10^9$	$\tau_6 \cdot 10^9$
Ho(Gly)$_3$(ClO$_4$)$_3$·5H$_2$O	2.69 ± 0.46	4.18 ± 0.59	4.08 ± 0.52
Ho(Ala)$_2$(ClO$_4$)$_3$·5H$_2$O	2.09 ± 0.24	4.85 ± 0.32	5.19 ± 0.26
HoGlu(ClO$_4$)$_2$·7H$_2$O	3.07 ± 0.45	4.39 ± 0.56	4.48 ± 0.50

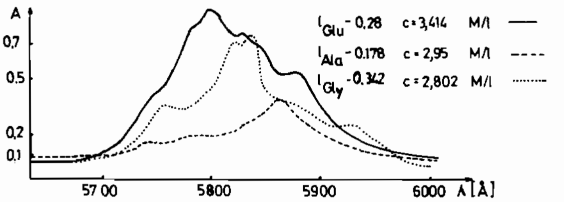

Fig. 4. Behaviour of hypersensitive band $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ for Nd^{+3} ion complexes with glycine, alanine and glutamic acid.

spectra for neodymium and holmium complexes, revealed quite remarkable differences in the Ln^{+3} ion environment which may result either from the different coordination mode of glutamic acid, alanine and glycine, or symmetry changes (see Figs. 1, 2, 3 and 5). Tables I and II give oscillator strengths for Nd^{+3} and Ho^{+3} compounds. A relation was set up between the intensities of f–f transitions and the position of crystallographic axes.

Based on the Judd theory, the intensities of f–f transitions were analyzed, taking into account their dependence on the directions of axes in the crystal.

From the Judd equation

$$P = \sum_{\lambda=2,4,6} \tau_\lambda \sigma (f^N \psi J \| U^\lambda \| f^N \psi' J')^2 / 2J + 1 \qquad (2)$$

where: $(f^N \psi J \| U^\lambda \| f^N \psi' J')$—the reduced matrix element of the unit tensor operator; τ_λ—phenomenological parameters estimated from experimental data; σ—the wavenumber in cm^{-1}; the τ_λ parameters were evaluated using the least squares method (JCH 30 programme). One can determine $\Omega_\lambda = (1.085 \cdot 10^{11} \chi)^{-1} \cdot \tau_\lambda$ where: $\chi = (n^2 + 2)^2 / 9n$, whose values are frequently discussed in the literature. Since the Judd-Ofelt eqn. (2) has no polarization or angular details the total integrated absorbances (over direction) are required to fit the theory. For optical isotropic materials (cubic crystals and glasses) this presents no difficulty. For the case of other crystals the absorption spectrum is somewhat different in structure, when measured along the three crystallographic directions.

The oscillator strengths (band for band) stay about the same (within 5%), but for others change more. In Figs. 1 and 2 and in Tables I and II one can notice such a change for hypersensitive transitions, and transitions $^4I_{9/2} \rightarrow {}^4F_{3/2}$ for Nd^{+3} and $^5I_8 \rightarrow (^5G, {}^3H)_5$, $(^5F, {}^3F, {}^5G)_2$, $^3H_6$; $^5I_8 \rightarrow {}^5G_3$, $^3L_9$ for Ho^{+3}. The best procedure is to average the oscillator strengths of each band over the three directions.

In Tables I and II are presented the oscillator strength values for three orientations of a crystal of neodymium compound with glutamic acid; similar data were obtained for Nd^{+3} complex with glycine

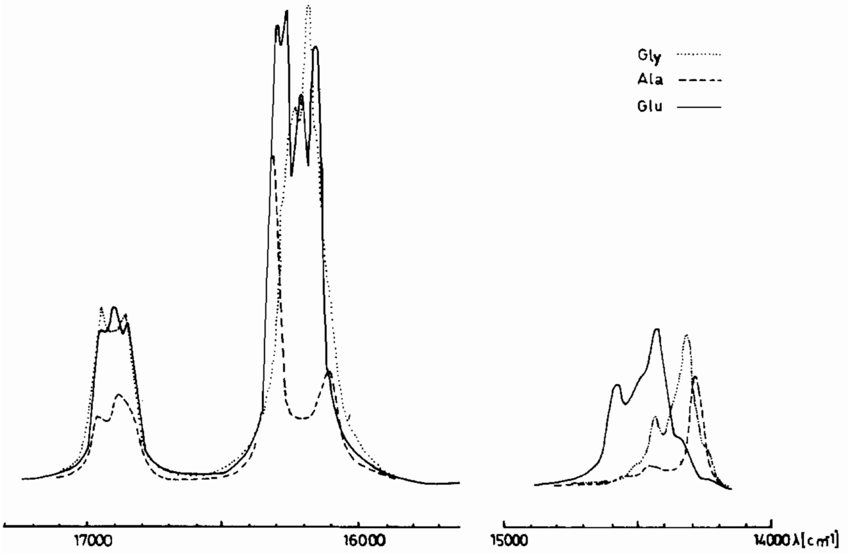

Fig. 5. Behaviour of fluorescence transition $^5D_0 \rightarrow {}^7F_J$ for Eu^{+3} ion complexes with glycine, alanine and glutamic acid.

[12]. For the other crystals we report the oscillator strength value for only one orientation of a crystal.

Dimensions of crystals of holmium complexes with aminoacids and those of Nd^{+3} with alanine prevent their polishing in the direction of axes Y and Z. For those reasons the Judd parameters for Nd complexes with glycine [12] and glutamic acid were calculated from the averaged oscillator strength values; for the other ones the data for an axis were used.

It should be noted that the intensity of hypersensitive transition $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ for Nd^{+3} ion and $^5I_8 \rightarrow {}^5G_6$, $^7F_1$ for Ho^{+3} ion is not so high as could be expected for such a low symmetry. The oscillator strength values of those transitions for complexes with glutamic acid exceed those for complexes with glycine and alanine, although the latter ones have lower symmetry.

The values of τ_λ are gathered in Tables I and II. For three distinct orientations of the crystal, the significant differences were observed in the τ_2 parameters. The change of the τ_2 parameters towards glutamic acid-alanine-glycine was observed. The τ_2 values exceeded those found for aquo ions and tetraphosphates. The trend of the τ_2 parameters and of oscillator strength values of hypersensitive transition changes in studied compounds seems to point out that the intensities of hypersensitive transitions are influenced not only by the symmetry of Ln ion, but propably also by the metal–oxygen distances.

Similar changes as in the absorption spectra are observed in the luminescence spectra. Calculated relative intensities of

$$\frac{I^5D_0 \rightarrow {}^7F_2}{I^5D_0 \rightarrow {}^7F_4} \quad \text{and} \quad \frac{I^5D_0 \rightarrow {}^7F_1}{I^5D_0 \rightarrow {}^7F_4}$$

transitions for Eu^{+3} ion compounds are presented in Table III. The change of the relative intensity of hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition in luminescence spectra is greater for the Eu complex with glutamic acid than for the complex with alanine and glycine.

TABLE III. Fluorescent ratios of Integral Intensities from the $^5D_0$ Level into the ^7F_J Levels.

	$\frac{I^5D_0 \rightarrow {}^7F_2}{I^5D_0 \rightarrow {}^7F_4}$	$\frac{I^5D_0 \rightarrow {}^7F_{1,0}}{I^5D_0 \rightarrow {}^7F_4}$
$[Eu(Glu)](ClO_4)_2 \cdot D_2O$	4.15	1.36
$[Eu(Gly)_3](ClO_4)_3 \cdot D_2O$	3.84	1.44
$[Eu(Ala)_2](ClO_4)_3 \cdot D_2O$	3.57	1.36

Since the europium compounds are isomorphic with Nd and Ho compounds the results obtained from the luminescence spectra seem to support the hypothesis that the intensity of hypersensitive transitions is not influenced solely by symmetry changes.

On the other hand, it follows from crystallographic investigations of the glycine complex [12] and of calcium complexes with glycine and glutamic acid [14, 15] that there could be considerable differences in the bonding mode of the functional groups of aminoacids. The Me–L bonding distances can also vary. The influence of the latter ones can thus be considered after the complete structures of the compounds under study are solved.

Conclusions

1) The relation between the f–f transition intensity and the position of crystallographic axis of a crystal has been stated.

2) On the basis of absorption and luminescence studies the differences in structure of three types of complexes of Ln^{+3} ion with glycine, alanine and glutamic acid have been shown.

3) It was found and confirmed that symmetry does not have the sole influence on intensity changes of hypersensitive transitions in the examined compounds.

References

1 E. Nieboer, *Structure and Bonding*, (1975).
2 R. B. Martin and F. S. Richardson, *Quart. Rev., Biophys., 12*, 181 (1979).
3 R. Prados, L. G. Stadtherr, H. Donato, Jr and R. B. Martin, *J. Inorg. Nucl. Chem., 36*, 689 (1974).
4 H. B. Brittain, F. S. Richardson and R. B. Martin, *J. Am. Chem. Soc., 98*, 8255–8260 (1976).
5 W. De W. Horrocks, Jr and D. R. Sudnick, *J. Am. Chem. Soc., 101*, 334–340 (1979).
6 W. De W. Horrocks, Jr and W. E. Collier, *J. Am. Chem. Soc., 103*, 2856–2862 (1981).
7 H. G. Brittain, *Inorg. Chem., 18*, 7, 1740 (1979).
8 H. G. Brittain, *Coord. Chem. Rev.*, in press.
9 J. Legendziewicz, E. Huskowska, H. Kozłowski and B. Jeżowska-Trzebiatowska, *Inorg. Nucl. Chem. Letters, 15*, 349–353 (1979); *ibid., A*, 57–61 (1981); *ibid., 14*, 400–414 (1978).
10 J. Legendziewicz, E. Huskowska and W. Stręk, *J. of Luminescence, 24/25*, 819–824 (1981).
11 K. F. Belayeva, M. A. Poray-Koshits, T. J. Malinowski and N. D. Mitrofanova, *Tezisy Dokl. 12-th vses. Chugaevskoe Soveshch. Khim kompleks, Sojedin., 2*, 246 (1975).
12 J. Legendziewicz, E. Huskowska, A. Waśkowska and Gy. Argay, *Inorg. Chim. Acta, 94*, 89 (1984).
13 J. Legendziewicz, E. Huskowska and T. Głowiak, Abstracts of Papers XXII ICCC Th P12 541 (1982).
14 S. Natarajan and J. K. Mohana Rao, *J. Inorg. Nucl. Chem., 43*, 1693–1699 (1981).
15 H. Einspahr, G. L. Garthand and H. E. Bugg, *Acta Cryst., B33*, 3385–3390 (1977); *ibid., B30*, 1037 (1974).