Crystal Structure, Absorption and Fluorescence Spectra of Lanthanoid Glutamate Perchlorate Nonahydrates, $Ln_2(C_5H_8NO_4)_2(ClO_4)_4 \cdot 9H_2O$

Ingeborg Csöregh,[a] Mátyás Czugler,[a] Peder Kierkegaard,[a] Janina Legendziewicz[b] and Ewa Huskowska[b]

[a]Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden and [b]Institute of Chemistry, University of Wrocław, Joliot-Curie 14, PL-50383 Wrocław, Poland

Csöregh, I., Czugler, M., Kierkegaard, P., Legendziewicz, J. and Huskowska, E., 1989. Crystal Structure, Absorption and Fluorescence Spectra of Lanthanoid Glutamate Perchlorate Nonahydrates, $Ln_2(C_5H_8NO_4)_2(ClO_4)_4 \cdot 9H_2O$. – Acta Chem. Scand. 43: 735–747.

Crystals with the composition $Ln_2(L\text{-}Glu)_2(ClO_4)_4 \cdot 9H_2O$ (Ln = Nd^{3+}, Eu^{3+}, Dy^{3+} and Ho^{3+}) have been studied. The structures of the complexes with Ho^{3+} and Dy^{3+}, respectively, have been determined by X-ray diffraction. The unit cell dimensions of the monoclinic crystals were a = 10.863(3), b = 16.587(7), c = 19.741(5) Å and β = 102.93(3)° measured at 140 K for the holmium compound, and a = 11.015(1), b = 16.560(2), c = 19.939(3) Å and β = 103.16(1)°, determined at room temperature for the dysprosium complex. These two structures are isomorphous ($P2_1$, Z = 4). The two lanthanoid ions in each complex are bridged by four carboxylate groups so that two of the oxygens are coordinated to both cations. The coordination is completed by four water oxygens around each cation, making the coordination number equal to nine. The L-glutamic acid residues link together the lanthanoid ion pairs into infinite layers. In the voids of this matrix are located the perchlorate groups, exhibiting rotational disorder. The structural models have been refined to linear R values of 0.0515 (for 8974 reflections collected at 140 K for the holmium compound) and 0.0507 (for 7518 reflections measured at room temperature for the dysprosium complex). The absolute configuration of the glutamic acid residues are also confirmed by statistical tests. An absorption spectrum along the crystallographic c axis of a single crystal of the dysprosium complex was recorded at room temperature, and the probabilities of the f-f transitions have been analyzed on the basis of the Judd-Ofelt theory. Solid-state fluorescence spectra of the Nd^{3+}, Eu^{3+} and Dy^{3+} compounds have been recorded at 77 K; the results are discussed and Stark components are determined. The decay time for the dysprosium-containing crystal was measured and the fluorescence quenching mechanism is briefly discussed.

Calcium ions are essential in living systems, but there is no physical technique suitable for detecting Ca^{2+}. Therefore the substitution of lanthanoids for calcium in biologically interesting probes has proved to be a useful tool for deepening the understanding of the role of Ca^{2+}.[1-3] In biological systems Ca^{2+} often occurs bonded to proteins via aspartate or glutamate residues. Since the characteristic features of lanthanoid coordination chemistry are quite similar to those of Ca^{2+} (size, preference for oxygen donors, variability in coordination number, lack of strong directionality)[1], the study of Ln^{3+}-amino acid complexes can be helpful in understanding the bonding of calcium in more complicated bioorganic systems.

The crystal structure of a praseodymium L-glutamate perchlorate complex was recently published by us.[4] We now present an X-ray diffraction, absorption and fluorescence spectroscopic study of related rare earth glutamate perchlorates. These investigations are part of a research programme for structural and spectroscopic studies of interactions between trivalent lanthanoid cations and amino acids in the solid state.

Experimental

Sample preparation. The complexes were prepared by dissolving $Ln(ClO_4)_3 \cdot 6H_2O$ (synthesized from the appropriate lanthanoid oxide [Merck] as described earlier[5]) in a half-neutralized aqueous solution of L-glutamic acid (Reanal, Hungary). The crystals were grown at room temperature by slow evaporation of the aqueous solutions at pH ~ 3.5. Single crystals suitable for spectroscopic measurements were grown from saturated solutions stirred mechanically in a thermostat (298 K, 40 rpm.).

Titration with EDTA (ethylenediaminetetraacetic acid), using xylenol orange as indicator, was used for the determination of the Ln^{3+} concentration in the crystals. The densities, measured by the flotation method in a mixture of

bromoform and dibromoethane, were found to be 2.12 (Nd^{3+}), 2.16 (Eu^{3+}), 2.22 (Dy^{3+}) and 2.27 g cm^{-3} (Ho^{3+}).

X-Ray data collection and reduction. A selected light-yellow single crystal of the Ho complex with approximate dimensions 0.26×0.27×0.54 mm, and a colourless crystal of the Dy compound, about 0.22×0.45×0.08 mm, were sealed in epoxy glue for X-ray diffraction measurements. Intensity data were collected from both crystals using a computer-controlled Siemens/AED2 diffractometer at room temperature (293 K), with graphite-monochromated Mo*K*α radiation (λ = 0.71069 Å, θ_{max} = 30°). The net intensities of a total of 11 074 reflections for the Ho complex and 11 103 reflections for the Dy compound were corrected for Lorentz and polarization effects as well as for absorption.

The unit cell parameters were refined by the least-squares method using accurately measured angular diffractometer settings for 46 (Ho) and 53 (Dy) strong well-centered reflections within the 2θ range 20–40°.

The crystal structures could not be exhaustively determined from the room-temperature diffraction data sets; the positions of twenty-two chlorate oxygens and two non-coordinated water O atoms (out of the 102 crystallographically independent non-hydrogen atoms) remained indeterminate. Therefore the intensity data collection was repeated at 140(±3) K (liquid N_2) using a second crystal of the holmium complex of approximate size 0.40×0.35×0.15 mm, mounted in a glass capillary. The results concerning the holmium compound that are presented in the following were obtained from this low-temperature data set. The new low-temperature unit cell dimensions were refined using the angular settings for 37 well-centered, accurately measured reflections in the interval 20° < 2θ < 38°. The corrections for the absorption effects were carried out by the numerical absorption correction programme of the SHELX system.[6] The transmission factors varied between 0.5034 and 0.1685 (Ho, low temp.), and 0.7124 and 0.2993 (Dy).

Solution and refinement of the structures. The first of the four crystallographically independent metal positions was derived from a Patterson synthesis. The remaining three lanthanoid ions were located by subsequent difference electron density calculations. Solving the structure from this starting point was not straightforward, although about fifty reliable atomic positions could be derived from difference Fourier maps. The structure was finally solved with the program DIRDIF,[7] which gave an initial structural model comprising seventy-eight atoms. Nevertheless, this model could be completed when the low-temperature data set for the holmium complex became available.

The structural models were refined with the SHELX 76 program system.[6] Because of the large number of variables (cf. Table 1) the "blocked full-matrix" refinement technique (with two blocks) had to be used. The number of atoms which can be treated in this program is limited to $2N_{aniso} + N_{iso} < 160$. Thus, only fifty-eight non-hydrogen atoms (4Ho + 8Cl + 46O) could be assigned anisotropic vibrations in the final structural models. The remaining forty-four non-hydrogen atomic positions (the atoms of the glutamic acid residues + four water oxygens) were refined in the isotropic mode. No hydrogen positions were taken into account in the structure factor calculations. In all these refinements only reflections with $F/\sigma(F) > 10$ were used. An empirical extinction correction factor[6] was also included in the last stage of the refinements.

It is seen from the difference electron density maps, and also from the results of the refinement using room-temper-

Table 1. Selected crystal data and some details of the refinement of the different structural models. The e.s.d.'s, where given, are in parentheses.

Compound	Holmium complex		Dysprosium complex	
Formula unit	$C_{10}H_{34}N_2O_{33}Cl_4Ho_2$		$C_{10}H_{34}N_2O_{33}Cl_4Dy_2$	
Formula weight	1182.04		1177.18	
Space group symmetry	Monoclinic ($P2_1$)		Monoclinic ($P2_1$)	
Unit cell dimensions measured at	Room temp.	Low temp.	Room temp.	
a/Å	11.011(1)	10.863(3)	11.015(1)	
b/Å	16.532(1)	16.587(7)	16.560(2)	
c/Å	19.907(2)	19.741(5)	19.939(3)	
β/°	103.18(1)	102.93(3)	103.16(1)	
V_c/Å^3	3528	3467	3542	
Z	4	4	4	
D_c/g·cm^{-3}	2.225	2.265	2.208	
$\mu_{MoK\alpha}$/cm^{-1}	49.22	50.09	46.41	
No. of reflections used in the refinements		8974	7518	
Total no. of variables		700	688	
Final agreement factors and absolute conf. of the glutamate residues	L	D	L	D
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.0515	0.0540	0.0507	0.0520
$R_w = \Sigma\sqrt{w}\|\Delta F\|/\Sigma\sqrt{w}\|F_o\|$	0.0588	0.0611	0.0586	0.0599
$R_G = [\Sigma w\cdot\|\Delta F\|^2/\Sigma w\cdot\|F_o\|^2]^{\frac{1}{2}}$	0.0796	0.0814	0.0804	0.0814

ature data, that the perchlorate groups are partially disordered. This is clearly the reason why several of these atomic positions could not be determined from room-temperature data. No disorder sites were, however, included in the calculations because of the limitation of the least-squares programme employed and our difficulties arising from the relatively large size of the structure (discussed above). Moreover, the refinement of the structure of the dysprosium complex converged satisfactorily only when the four oxygen positions of the most disordered perchlorate group containing Cl(2) were held fixed.

Atomic scattering factors for C, O, N and Cl were taken from Cromer and Mann,[8] for the Ho^{3+} and Dy^{3+} ions from Cromer and Waber,[9] and anomalous dispersion correction factors for the non-hydrogen atoms from Cromer and Liberman.[10]

Structural models of the Ho and Dy complexes were refined both with L and D configuration assumed for the glutamic acid residues. The structure factors were weighted according to $w = k/\sigma^2(F) + g \cdot F^2)$,[6] with $\sigma(F)$ derived from counting statistics and g estimated to be 0.00041 (Ho, L config.), 0.00026 (Ho, D), 0.004055 (Dy, L) and 0.003766 (Dy, D) in these refinements. The resulting final agreement factors are listed in Table 1. Statistical tests[11,12] on the $R_G(L)/R_G(D)$ ratios confirmed at a significance level of 0.001 that the glutamic acid residues have the L configuration in both structures, as expected. Table 2 lists the refined atomic coordinates of the correct enantiomers.

Spectroscopic measurements. A polished single crystal of $Dy_2(L\text{-}Glu)_2(ClO_4)_4 \cdot 9H_2O$ with the approximate dimensions 0.40×0.40×0.06 cm was used for absorption measurements along the crystallographic c axis. The spectrum was recorded at room temperature on a Cary 14 spectrophotometer. The oscillator strengths of the *f-f* transitions were estimated with the standard integrating program ICH 30.[13]

Fluorescence spectra of the single crystals of the glutamate perchlorate hydrate complexes of Eu^{3+}, Nd^{3+} and Dy^{3+} were recorded at 77 K with a spectrophotometer designed in the laboratory of the Institute for Low Temperature and Structure Research (Wrocław, Poland). The instrument has a GDM 1000 grating monochromator (Carl Zeiss, Jena) with a cooled M 10FD29 photomultiplier tube (Carl Zeiss, Jena). An ILA 120 argon laser (Carl Zeiss, Jena) was used as excitation source. Fluorescence was excited with the 458 nm line for Eu^{3+} and Dy^{3+}, and the 488 and 514 nm lines for Nd^{3+}. The resolution of the instrument is 2 cm^{-1}. The decay time was measured by sampling the photomultiplier current decay curve and accumulating up to 100 runs in a multi-channel analyser.

Crystallographic description and discussion of the structures. Since the holmium and dysprosium compounds crystallize with isomorphous structures, only one of them, the holmium complex, is shown in the figures and Table 3 lists only the geometric data of the coordination polyhedra around the holmium ions. The same data concerning the dysprosium complex are included in the supplementary material.

Fig. 1 is a perspective view of the crystallographic asymmetric unit, showing also the numbering of the atoms. The structures of the perchlorate hydrates of the holmium and dysprosium glutamates are similar and can be compared with that of the corresponding praseodymium salt.[4] In all these three complexes the unit cell contains four formula units, but whereas the Pr complex show orthorhombic ($P2_12_12_1$) symmetry, the related Ho and Dy compounds crystallize with monoclinic ($P2_1$) space group symmetries and have twice as large asymmetric units. Each lanthanoid ion coordinates nine ligand oxygens in all these complexes, but the coordination polyhedron for Pr differs from those of the two other ions. The praseodymium compound provides an example of an inner-sphere perchlorate anion. The coordination polyhedra of the pair of Pr^{3+} ions have been described as strongly distorted mono-capped square antiprisms (CSAP). The coordination of the Ho and Dy ions, however, cannot be approximated either by a capped square antiprism (CSAP) or by a tricapped trigonal prism (TCTP). Furthermore, there are no perchlorate groups in direct contact with the Ho^{3+} or Dy^{3+} ions. Indeed, in the latter structures all the perchlorate anions seem to be completely shielded from the Ln^{3+} cations. Consequently, these less firmly bound groups are statistically disordered in the crystals (see below). The observed Me-O distances vary between 2.30 and 2.62 Å in the Ho complex (cf. Table 3), and 2.29 and 2.61 Å in the Dy complex (cf. Table 3a in the supplementary material). The mean Me-O distances, viz. 2.41[7] for Ho^{3+} and 2.42[6] Å for Dy^{3+}, are somewhat shorter than the average Pr-O distance, i.e. 2.52[9] Å, owing to the lanthanoid contraction (the r.m.s.d.'s are given in angular brackets). Perspective views of the coordination around the Ho (or Dy) ion pairs are shown in Fig. 2. The bond distances and bond angles within the glutamic acid residues conform to the expected values. Characteristic bond lengths (with r.m.s.d.'s in angular brackets) are: $C_{(sp^3)}$-$C_{(sp^3)}$ 1.53[3] and 1.53[3], $C_{(sp^2)}$-O 1.26[3] and 1.26[4], and $C_{(sp^3)}$-$N_{(sp^3)}$ 1.49[2] and 1.50[3] Å for the holmium and dysprosium complex, respectively.

Rotation of the perchlorate groups causes partial disorder in these crystal structures. In the case of the praseodymium compound, this disorder could be partly resolved to a few major disorder sites.[4] The rotation of the perchlorate groups in the holmium complex was considerably reduced by cooling the crystal to 140 K during the data collection. Thus, the observed Cl-O distances range between 1.39 and 1.52 Å, with a mean value of 1.45[3] Å. Since the perchlorate oxygens are more mobile at room temperature, as indicated by the differences in the thermal motion parameters between the Ho and Dy complexes, the observed Cl-O distance values are more widely scattered in the dysprosium (room-temperature data) than in the holmium complex (low-temperature data). In the Dy complex they range from 1.35 to 1.82 Å, and the mean value,

Table 2. Fractional atomic coordinates and equivalent isotropic[a]/isotropic temperature factors of the non-hydrogen atoms, with e.s.d.'s in parentheses. The atoms are numbered as in Fig. 1.

Atom	*x/a*	*y/b*	*z/c*	U^a_{eq}/U(Å^2)
Holmium complex				
Ho(1)	−0.16941(5)	−0.49980(0)	0.10193(3)	0.0079(1)
Ho(2)	−0.32154(4)	−0.49516(4)	−0.09661(3)	0.0073(1)
O(1W)	0.0650(9)	−0.4792(6)	0.1498(5)	0.017(3)
O(2W)	−0.1163(9)	−0.5747(7)	0.2053(6)	0.020(3)
O(3W)	−0.3446(8)	−0.4930(6)	0.1641(5)	0.015(2)
O(4W)	−0.1458(10)	−0.3885(6)	0.1789(6)	0.020(3)
O(5W)	−0.5454(9)	−0.5168(6)	−0.1327(6)	0.019(3)
O(6W)	−0.1536(8)	−0.4940(6)	−0.1596(5)	0.014(2)
O(7W)	−0.3467(10)	−0.6061(6)	−0.1756(5)	0.018(3)
O(8W)	−0.3892(9)	−0.4081(6)	−0.1985(5)	0.014(2)
O(1a)	−0.1856(8)	−0.3850(6)	−0.0634(5)	0.012(2)
O(2a)	−0.0990(8)	−0.3862(6)	0.0520(5)	0.014(2)
C(1a)	−0.1126(11)	−0.3594(8)	−0.0105(7)	0.011(2)
C(2a)	−0.0332(11)	−0.2829(8)	−0.0170(7)	0.010(2)
N(2a)	−0.0498(10)	−0.2648(7)	−0.0914(6)	0.014(2)
C(3a)	−0.0712(12)	−0.2116(8)	0.0220(7)	0.014(3)
C(4a)	0.0308(12)	−0.1515(9)	0.0463(7)	0.016(3)
C(5a)	0.0672(11)	−0.0974(8)	−0.0063(7)	0.010(2)
O(5a)	0.0362(8)	−0.1107(6)	−0.0709(5)	0.013(2)
O(6a)	0.1464(7)	−0.0374(6)	0.0128(5)	0.009(2)
O(1b)	−0.3711(9)	−0.6162(7)	−0.0445(6)	0.020(2)
O(2b)	−0.3011(8)	−0.6106(6)	0.0725(5)	0.013(2)
C(1b)	−0.3569(11)	−0.6436(8)	0.0170(6)	0.010(2)
C(2b)	−0.4148(12)	−0.7284(8)	0.0209(7)	0.014(3)
N(2b)	−0.3995(11)	−0.7480(8)	0.0962(6)	0.017(3)
C(3b)	−0.5472(12)	−0.7376(9)	−0.0206(7)	0.016(3)
C(4b)	−0.5826(13)	−0.8235(9)	−0.0510(8)	0.021(3)
C(5b)	−0.5986(11)	−0.8880(8)	0.0034(8)	0.011(2)
O(5b)	−0.5556(8)	−0.8790(6)	0.0689(5)	0.012(2)
O(6b)	−0.6571(8)	−0.9534(6)	−0.0194(5)	0.013(2)
Ho(3)	−0.8236(5)	−0.52189(4)	−0.60723(3)	0.0075(1)
Ho(4)	−0.67983(4)	−0.51230(4)	−0.40800(3)	0.0078(1)
O(1'W)	−1.0541(9)	−0.5179(7)	−0.6372(6)	0.021(3)
O(2'W)	−0.8760(9)	−0.6106(6)	−0.7071(5)	0.015(3)
O(3'W)	−0.6633(8)	−0.5020(6)	−0.6711(5)	0.015(2)
O(4'W)	−0.8943(10)	−0.4293(6)	−0.7014(5)	0.020(3)
O(5'W)	−0.4575(9)	−0.5272(7)	−0.3645(5)	0.018(3)
O(6'W)	−0.8660(9)	−0.5134(6)	−0.3565(6)	0.021(3)
O(7'W)	−0.6537(10)	−0.6242(6)	−0.3308(5)	0.018(3)
O(8'W)	−0.6350(9)	−0.4480(7)	−0.2990(5)	0.021(3)
O(1c)	−0.8841(8)	−0.4024(6)	−0.5633(5)	0.014(2)
O(2c)	−0.8246(8)	−0.4055(6)	−0.4478(5)	0.013(2)
C(1c)	−0.8890(11)	−0.3806(8)	−0.5043(7)	0.010(2)
C(2c)	−0.9820(12)	−0.3155(8)	−0.4991(7)	0.012(2)
N(2c)	−0.9872(10)	−0.3058(7)	−0.4244(6)	0.016(2)
C(3c)	−0.9442(12)	−0.2358(9)	−0.5289(7)	0.015(3)
C(4c)	−1.0540(13)	−0.1729(9)	−0.5486(8)	0.020(3)
C(5c)	−1.0846(12)	−0.1257(8)	−0.4888(7)	0.011(3)
O(5c)	−1.0616(8)	−0.1486(6)	−0.4280(5)	0.014(2)
O(6c)	−1.1460(8)	−0.0605(6)	−0.5050(5)	0.011(2)
O(1d)	−0.6216(9)	−0.6348(6)	−0.4591(5)	0.017(2)
O(2d)	−0.6843(8)	−0.6273(6)	−0.5766(5)	0.010(2)
C(1d)	−0.6265(11)	−0.6594(8)	−0.5201(7)	0.010(2)
C(2d)	−0.5449(12)	−0.7415(8)	−0.5273(7)	0.011(3)
N(2d)	−0.5458(11)	−0.7465(7)	−0.6008(6)	0.015(2)
C(3d)	−0.4410(14)	−0.7574(9)	−0.4745(8)	0.019(3)
C(4d)	−0.4245(12)	−0.8457(9)	−0.4474(7)	0.016(3)
C(5d)	−0.4040(11)	−0.9061(8)	−0.5001(7)	0.010(2)
O(5d)	−0.4370(8)	−0.8936(6)	−0.5642(5)	0.011(2)
O(6d)	−0.3527(8)	−0.9734(6)	−0.4783(5)	0.011(2)
Cl(1)	−0.3533(3)	−0.1668(2)	−0.1839(2)	0.018(1)
O(11)	−0.3909(11)	−0.1807(8)	−0.2573(6)	0.036(4)

contd

Table 2. (contd)

Atom	*x/a*	*y/b*	*z/c*	U^a_{eq}/U(Å^2)
O(12)	−0.4507(11)	−0.1240(7)	−0.1615(7)	0.030(4)
O(13)	−0.3359(11)	−0.2439(7)	−0.1454(7)	0.028(4)
O(14)	−0.2338(10)	−0.1232(8)	−0.1650(7)	0.033(4)
Cl(2)	−1.1930(4)	−0.9800(3)	−0.9530(2)	0.029(1)
O(21)	−1.1964(15)	−1.0414(10)	−0.8994(10)	0.064(7)
O(22)	−1.1882(13)	−1.0154(10)	−1.0187(7)	0.049(5)
O(23)	−1.0816(10)	−0.9307(7)	−0.9241(9)	0.044(5)
O(24)	−1.3005(11)	−0.9283(10)	−0.9554(8)	0.046(5)
Cl(3)	−0.1618(3)	−0.3450(2)	−0.2974(2)	0.014(1)
O(31)	−0.0633(9)	−0.3963(7)	−0.3103(6)	0.020(3)
O(32)	−0.1812(10)	−0.2756(7)	−0.3447(7)	0.027(4)
O(33)	−0.2822(10)	−0.3886(7)	−0.3112(6)	0.025(4)
O(34)	−0.1296(11)	−0.3163(7)	−0.2256(5)	0.026(4)
Cl(4)	−0.2652(3)	−0.7202(3)	−0.7054(2)	0.019(1)
O(41)	−0.2887(11)	−0.6350(7)	−0.7177(7)	0.031(4)
O(42)	−0.2832(11)	−0.7407(7)	−0.6387(6)	0.028(4)
O(43)	−0.1351(9)	−0.7357(8)	−0.7124(6)	0.026(4)
O(44)	−0.3498(11)	−0.7646(9)	−0.7580(6)	0.033(4)
Cl(5)	−0.3068(4)	−0.3562(2)	−0.6782(2)	0.021(1)
O(51)	−0.3518(18)	−0.2920(8)	−0.6406(8)	0.060(7)
O(52)	−0.3348(13)	−0.3386(9)	−0.7520(7)	0.039(5)
O(53)	−0.3699(15)	−0.4291(9)	−0.6686(9)	0.052(6)
O(54)	−0.1642(16)	−0.3636(9)	−0.6520(11)	0.067(8)
Cl(6)	−0.2043(3)	−0.5156(3)	−0.4666(2)	0.021(1)
O(61)	−0.2107(13)	−0.5587(8)	−0.5295(7)	0.038(5)
O(62)	−0.0913(10)	−0.4675(7)	−0.4563(6)	0.026(4)
O(63)	−0.3154(13)	−0.4645(12)	−0.4734(8)	0.057(6)
O(64)	−0.1949(13)	−0.5712(10)	−0.4096(7)	0-044(5)
Cl(7)	−0.0082(3)	−0.1875(2)	−0.7524(2)	0.019(1)
O(71)	−0.0830(15)	−0.2258(9)	−0.8159(7)	0.049(5)
O(72)	−0.0974(12)	−0.1553(10)	−0.7166(8)	0-046(5)
O(73)	0.0626(14)	−0.2450(9)	−0.7067(8)	0.044(5)
O(74)	0.0675(17)	−0.1258(10)	−0.7678(10)	0.071(7)
Cl(8)	−0.6669(4)	−0.3381(3)	−0.8219(3)	0.026(1)
O(81)	−0.6540(13)	−0.3353(9)	−0.7464(7)	0.042(5)
O(82)	−0.6053(15)	−0.4116(8)	−0.8438(9)	0.050(5)
O(83)	−0.5947(12)	−0.2688(7)	−0.8407(8)	0.034(5)
O(84)	−0.7971(13)	−0.3310(8)	−0.8559(9)	0.053(5)
O(9W)	−1.1757(11)	−0.9366(10)	−0.7818(6)	0.039(5)
O(10W)	0.3652(10)	−0.6679(7)	0.8084(7)	0.028(4)
Dysprosium complex				
Dy(1)	−0.16937(6)	−0.49980(0)	0.09960(3)	0.0173(2)
Dy(2)	−0.32204(5)	−0.49582(4)	−0.09787(3)	0.0151(2)
O(1W)	0.0579(13)	−0.4804(9)	0.1486(8)	0.049(5)
O(2W)	−0.1138(14)	−0.5727(10)	0.2035(6)	0.054(5)
O(3W)	−0.3431(11)	−0.4924(8)	0.1588(6)	0.037(3)
O(4W)	−0.1432(13)	−0.3879(8)	0.1786(7)	0.038(5)
O(5W)	−0.5429(12)	−0.5170(8)	−0.1371(9)	0.048(5)
O(6W)	−0.1579(11)	−0.4988(8)	−0.1611(6)	0.034(3)
O(7W)	−0.3514(14)	−0.6115(8)	−0.1764(8)	0.043(5)
O(8W)	−0.3878(11)	−0.4056(7)	−0.1980(6)	0.026(3)
O(1a)	−0.1868(10)	−0.3846(6)	−0.0658(5)	0.022(2)
O(2a)	−0.0972(12)	−0.3875(8)	0.0475(6)	0.033(3)
C(1a)	−0.1113(14)	−0.3603(9)	−0.0115(8)	0.021(3)
C(2a)	−0.0317(13)	−0.2847(8)	−0.0174(7)	0.016(3)
N(2a)	−0.0500(13)	−0.2653(8)	−0.0924(7)	0.025(3)
C(3a)	−0.0671(16)	−0.2125(10)	0.0228(9)	0.030(4)
C(4a)	0.0382(16)	−0.1554(10)	0.0491(9)	0.031(4)
C(5a)	0.0708(14)	−0.1016(9)	−0.0064(8)	0.022(3)
O(5a)	0.0370(10)	−0.1113(7)	−0.0684(6)	0.025(2)
O(6a)	0.1477(10)	−0.0413(6)	0.0152(6)	0.024(2)
O(1b)	−0.3792(11)	−0.6146(7)	−0.0446(6)	0.029(3)
O(2b)	−0.2990(11)	−0.6125(7)	0.0707(6)	0.029(3)

contd

Table 2. (contd)

Atom	*x/a*	*y/b*	*z/c*	U^a_{eq}/U (Å^2)
C(1b)	−0.3576(14)	−0.6421(9)	0.0155(8)	0.022(3)
C(2b)	−0.4174(16)	−0.7270(10)	0.0212(9)	0.028(3)
N(2b)	−0.4040(14)	−0.7443(9)	0.0947(8)	0.035(3)
C(3b)	−0.5455(15)	−0.7380(10)	−0.0211(9)	0.029(4)
C(4b)	−0.5795(17)	−0.8231(11)	−0.0476(9)	0.035(4)
C(5b)	−0.5959(14)	−0.8884(9)	−0.9937(8)	0.023(3)
O(5b)	−0.5592(10)	−0.8781(7)	0.0669(6)	0.026(2)
O(6b)	−0.6580(10)	−0.9522(7)	−0.0165(6)	0.024(2)
Dy(3)	−0.82406(6)	−0.52035(4)	−0.60654(3)	0.0159(2)
Dy(4)	−0.68140(5)	−0.50999(4)	−0.40840(3)	0.0157(2)
O(1'W)	−1.0549(12)	−0.5163(8)	−0.6395(8)	0.042(5)
O(2'W)	−0.8771(14)	−0.6102(7)	−0.7055(7)	0.037(5)
O(3'W)	−0.6636(11)	−0.5035(8)	−0.6710(6)	0.032(3)
O(4'W)	−0.8887(13)	−0.4220(8)	−0.6980(7)	0.038(5)
O(5'W)	−0.4595(10)	−0.5283(9)	−0.3649(7)	0.036(4)
O(6'W)	−0.8613(13)	−0.5116(8)	−0.3535(8)	0.044(5)
O(7'W)	−0.6565(13)	−0.6225(7)	−0.3324(7)	0.035(4)
O(8'W)	−0.6332(15)	−0.4388(10)	−0.3016(7)	0.048(5)
O(1c)	−0.8865(11)	−0.4036(7)	−0.5622(6)	0.027(3)
O(2c)	−0.8255(10)	−0.4037(7)	−0.4469(6)	0.024(2)
C(1c)	−0.8943(14)	−0.3806(9)	−0.5025(8)	0.020(3)
C(2c)	−0.9888(16)	−0.3154(10)	−0.5015(9)	0.027(3)
N(2c)	−0.9943(13)	−0.3060(8)	−0.4258(7)	0.029(3)
C(3c)	−0.9440(14)	−0.2330(9)	−0.5269(8)	0.024(3)
C(4c)	−1.0514(16)	−0.1722(10)	−0.5455(9)	0.030(4)
C(5c)	−1.0889(14)	−0.1280(9)	−0.4890(8)	0.022(3)
O(5c)	−1.0632(11)	−0.1466(7)	−0.4289(6)	0.027(3)
O(6c)	−1.1478(10)	−0.0597(6)	−0.5073(6)	0.023(2)
O(1d)	−0.6218(11)	−0.6329(7)	−0.4596(6)	0.030(3)
O(2d)	−0.6822(11)	−0.6262(7)	−0.5737(6)	0.028(3)
C(1d)	−0.6274(14)	−0.6590(9)	−0.5201(8)	0.021(3)
C(2d)	−0.5691(15)	−0.7398(9)	−0.5280(8)	0.024(3)
N(2d)	−0.5535(14)	−0.7472(9)	−0.6015(8)	0.032(3)
C(3d)	−0.4436(18)	−0.7546(11)	−0.4747(10)	0.034(4)
C(4d)	−0.4206(17)	−0.8411(11)	−0.4488(10)	0.034(4)
C(5d)	−0.3981(14)	−0.9027(9)	−0.5006(8)	0.022(3)
O(5d)	−0.4330(10)	−0.8907(7)	−0.5646(6)	0.025(3)
O(6d)	−0.3492(9)	−0.9706(6:	−0.4780(5)	0.018(2)
Cl(1)	−0.3463(5)	−0.1659(3)	−0.1888(3)	0.042(2)
O(11)	−0.378(3)	−0.192(2)	−0.259(1)	0.092(10)
O(12)	−0.447(2)	−0.118(2)	−0.195(3)	0.184(23)
O(13)	−0.339(2)	−0.237(1)	−0.149(1)	0.053(6)
O(14)	−0.234(2)	−0.128(1)	−0.172(1)	0.072(7)
Cl(2)	−1.1909(8)	−0.9761(8)	−0.9478(7)	0.126(6)
O(21)	−1.203(0)	−1.042(0)	−0.895(0)	0.398(31)
O(22)	−1.178(0)	−1.010(0)	−1.021(0)	0.281(34)
O(23)	−1.069(0)	−0.925(0)	−0.886(0)	0.152(17)
O(24)	−1.301(0)	−0.921(0)	−0.938(0)	0.235(27)
Cl(3)	−0.1588(5)	−0.3474(3)	−0.2965(2)	0.034(2)
O(31)	−0.060(2)	−0.399(1)	−0.312(1)	0.054(6)
O(32)	−0.178(2)	−0.276(1)	−0.342(1)	0.042(5)
O(33)	−0.282(2)	−0.389(1)	−0.309(1)	0.054(6)
O(34)	−0.125(2)	−0.319(2)	−0.225(1)	0.065(7)
Cl(4)	−0.2638(6)	−0.7235(4)	−0.7049(4)	0.058(2)
O(41)	−0.290(2)	−0.637(2)	−0.720(2)	0.104(11)
O(42)	−0.286(2)	−0.744(1)	−0.641(1)	0.082(9)
O(43)	−0.132(2)	−0.742(12)	−0.710(1)	0.087(9)
O(44)	−0.339(3)	−0.771(2)	−0.757(12)	0.141(15)
Cl(5)	−0.3105(6)	−0.3553(3)	−0.6822(3)	0.048(2)
O(51)	−0.359(3)	−0.293(2)	−0.644(12)	0.121(15)
O(52)	−0.326(2)	−0.334(2)	−0.754(1)	0.096(10)
O(53)	−0.390(4)	−0.423(2)	−0.666(3)	0.272(25)
O(54)	−0.155(4)	−0.364(2)	−0.652(2)	0.164(17)
Cl(6)	−0.2113(5)	−0.5083(4)	−0.4733(3)	0.058(2)

contd

Table 2. (contd)

Atom	*x/a*	*y/b*	*z/c*	U^a_{eq}/U(Å^2)
O(61)	−0.212(3)	−0.555(2)	−0.536(2)	0.102(12)
O(62)	−0.097(2)	−0.468(2)	−0.457(1)	0.083(8)
O(63)	−0.331(3)	−0.484(4)	−0.486(2)	0.278(31)
O(64)	−0.207(3)	−0.570(2)	−0.417(2)	0.116(13)
Cl(7)	−0.0005(5)	−0.1874(3)	−0.7515(3)	0.047(2)
O(71)	−0.062(3)	−0.227(2)	−0.814(1)	0.101(11)
O(72)	−0.084(2)	−0.148(2)	−0.718(2)	0.129(13)
O(73)	0.072(3)	−0.241(2)	−0.700(2)	0.111(13)
O(74)	0.085(4)	−0.135(2)	−0.770(1)	0.139(15)
Cl(8)	−0.6802(6)	−0.3422(4)	−0.8256(4)	0.062(3)
O(81)	−0.667(3)	−0.333(2)	−0.741(2)	0.164(20)
O(82)	−0.594(3)	−0.418(1)	−0.848(2)	0.136(13)
O(83)	−0.604(2)	−0.275(1)	−0.839(1)	0-072(8)
O(84)	−0.801(2)	−0.329(2)	−0.861(2)	0.114(12)
O(9W)	−0.154(3)	−0.796(5)	−0.844(2)	0.237(40)
O(10W)	0.348(2)	−0.662(1)	0.806(1)	0.089(8)

$^aU_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$

1.48[11] Å, is slightly greater than the commonly accepted average distance, 1.44 Å, for such bonds.[14]

The packing in the crystal structures of the Ho and Dy complexes greatly resembles, of course, that of the related praseodymium glutamate complex.[4] Each pair of lanthanoid cations coordinates four carboxyl groups: two α- and two γ-COO^- groups of four glutamic acid residues (cf. Fig. 2). The carboxyl groups, both the α and the γ, form bridges between the two rare earth cations of the pair, although in different ways: both O atoms of the α-carboxyl group coordinate only to one cation each, while one of the γ-carboxyl oxygens coordinates to both lanthanoid ions. Thus, the pairs of Ln^{3+} ions are linked together by glutamic acid residues, and infinite, polymeric layers are formed due to the bifunctionality of the glutamate moieties (Fig. 3). The layers resemble quadrangular tilings. The perchlorate anions fill up the voids in the framework built up in this way by the lanthanoid glutamate cations. Most of the hydrate molecules complete the coordination around the rare earth ions, and together with the remaining ones certainly stabilize the crystals by forming hydrogen bonds.

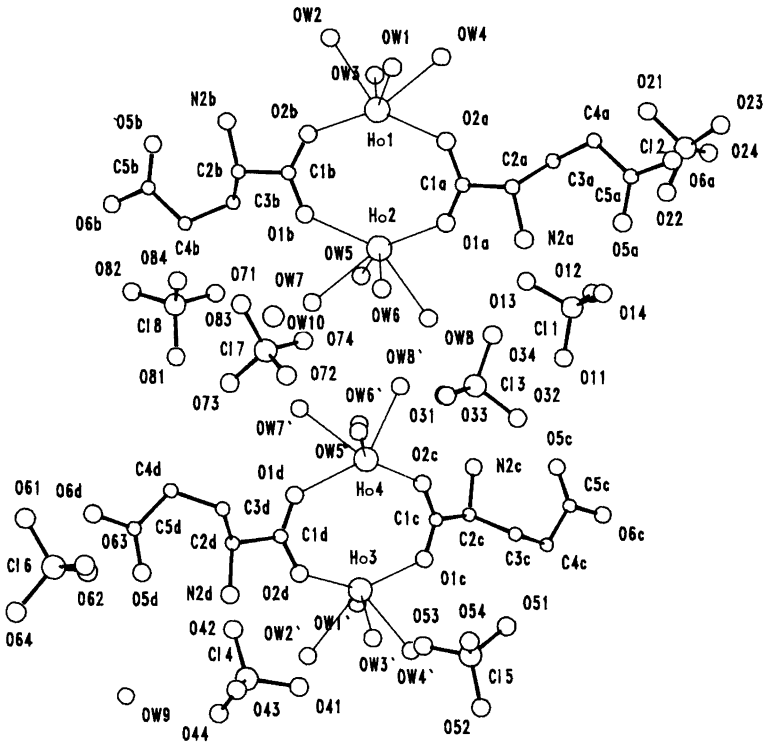

Fig. 1. Perspective view of the crystallographic asymmetric unit of Ho_2(L-Glu)$_2(ClO_4)_4 \cdot 9H_2O$ with atoms labelled as in the text.

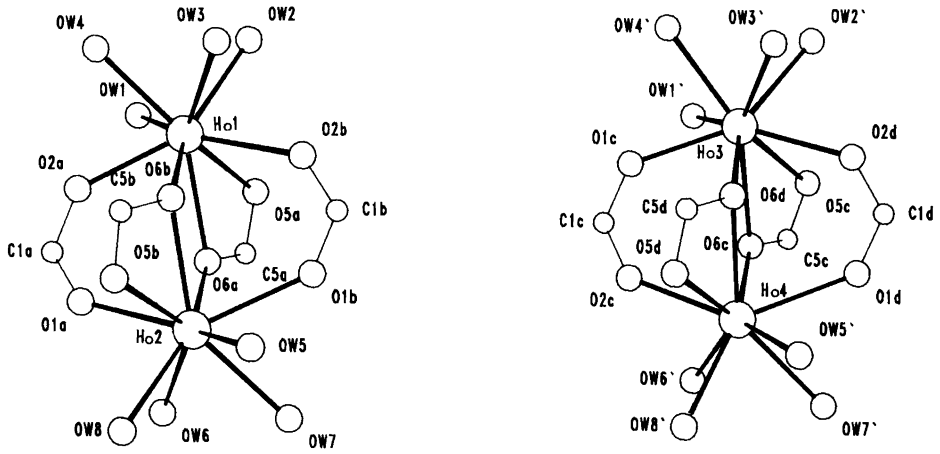

Fig. 2. Coordination figures of the two crystallographically independent pairs of Ho^{3+} ions.

Spectroscopic results and discussion. The size of the single crystal of the dysprosium complex, grown for the spectroscopic measurements, only allowed polishing perpendicular to the crystallographic *c* axis. Accordingly, the absorption spectrum was recorded only along the *c* axis. The areas of the bands that correspond to the *f-f* transitions, calculated by numerical integration, are related to the oscillator strength *P*.[15] *P* was determined for all bands in the measured spectral range (cf. Table 4). These experimentally determined oscillator strengths were then used to calculate the τ_λ and Ω_λ parameters from the Judd relation.[5,16–18] Only a few observed transitions of the trivalent lanthanoids have significant dipole character, and consequently the band intensities correspond mainly to the contribution of the electric dipole transitions. The τ_λ and Ω_λ parameters, listed in Table 4, involve the radial parts of the $4f$ wave functions, the wave functions of perturbing configurations such as $4f^{N-1}5d$ and $4f^{N-1}g$, and the interactions between the central ion and the immediate environment. The theoretically evaluated oscillator strengths, P_{calc} in Table 4, calculated by using the Ω_λ parameters, successfully reproduce the observed intensitites of the transition bands in the 5 000–30 100 cm^{-1} range.

The present absorption spectrum can be compared with those of dysprosium chloroacetate[19] and of $KDy(MoO_4)_2$ crystals.[20] The band intensities of the present spectrum and of the chloroacetate complex resemble each other, especially in the IR region. Only the hypersensitive transition $^6H_{15/2} \rightarrow {}^6F_{11/2}$, $^6H_{9/2}$ shows significantly higher oscillator strengths in the chloroacetate crystal ($P_{exp} = 740 \cdot 10^{-8}$) than in the glutamate complex. The carboxyl groups, which can coordinate in five different ways to a rare earth ion,[21] seem to coordinate in the same way to the Dy^{3+} ion in the glutamate and in the chloroacetate complex. However, the dysprosium coordination is completed by two water molecules in the chloroacetate and by four in the glutamate. This fact may influence the nature of the Dy^{3+}-ligand bonding and thus be the cause of the differences in spectroscopic properties of the Dy^{3+} ions in these crystals. The $KDy(MoO_4)_2$ crystal displays a multi-layer structure containing octacoordinated Dy^{3+} ions.[20] The absorption spectra and the band intensities of the molybdate crystal are more similar to those of the chloroacetate than those of the glutamate complex.

Laser-excited fluorescence spectra of the isomorphous single crystals of Eu, Nd and Dy glutamate perchlorate complexes, recorded at 77 K, are presented in Figs 4, 5 and 6. Attempts to record the same spectra at lower temperatures were not successful because the crystals shattered and decomposed during cooling and exposure to the laser

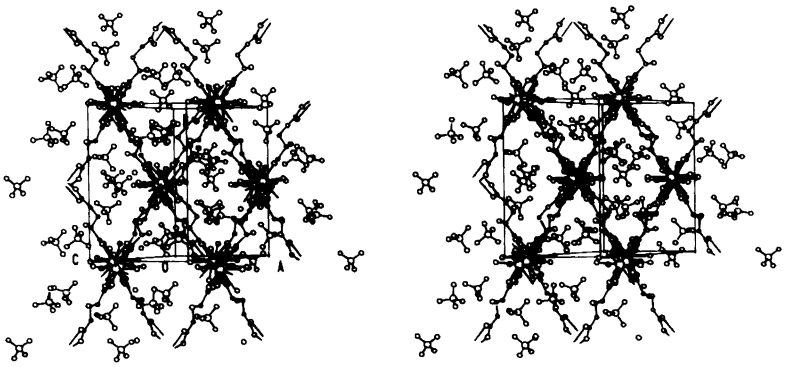

Fig. 3. Stereoscopic packing diagram of the crystal structure of the holmium glutamate perchlorate hydrate complex.

Table 3. Geometric data for the coordination around the holmium cations. List of Ho–O distances (Å) and O–Ho–O angles (°).[a]

Atoms	Distance	E.s.d.	Atoms	Distance	E.s.d.
Ho(1)–O(2b)	2.322	0.009	Ho(2)–O(6a)	2.332	0.008
–O(6b)	2.330	0.009	–O(1a)	2.349	0.009
–O(2a)	2.333	0.009	–O(1b)	2.371	0.010
–O(2W)	2.347	0.010	–O(7W)	2.387	0.010
–O(4W)	2.369	0.010	–O(5W)	2.404	0.009
–O(6a)	2.416	0.008	–O(6W)	2.427	0.008
–O(3W)	2.486	0.008	–O(8W)	2.451	0.009
–O(5a)	2.500	0.009	–O(6b)	2.452	0.009
–O(1W)	2.533	0.009	–O(5b)	2.473	0.009
Ho(3)–O(2d)	2.303	0.009	Ho(4)–O(8'W)	2.353	0.010
–O(1c)	2.317	0.009	–O(7'W)	2.378	0.010
–O(6d)	2.391	0.008	–O(2c)	2.382	0.009
–O(3'W)	2.391	0.008	–O(5'W)	2.389	0.009
–O(6c)	2.400	0.009	–O(6c)	2.390	0.008
–O(4'W)	2.402	0.010	–O(1d)	2.414	0.010
–O(2'W)	2.424	0.009	–O(6d)	2.436	0.009
–O(1'W)	2.441	0.009	–O(6'W)	2.459	0.009
–O(5c)	2.616	0.009	–O(5d)	2.471	0.009

Atoms involved	Angle	E.s.d.	Atoms involved	Angle	E.s.d.
O(1W) –Ho(1)–O(2W)	73.5	0.3	O(1W) –Ho(1)–O(3W)	128.8	0.3
O(1W) –Ho(1)–O(4W)	72.5	0.3	O(1W) –Ho(1)–O(2a)	69.6	0.3
O(1W) –Ho(1)–O(5a)	66.6	0.3	O(1W) –Ho(1)–O(6a)	94.5	0.3
O(1W) –Ho(1)–O(2b)	135.4	0.3	O(1W) –Ho(1)–O(6b)	143.6	0.3
O(2W) –Ho(1)–O(3W)	70.2	0.3	O(2W) –Ho(1)–O(4W)	83.4	0.4
O(2W) –Ho(1)–O(2a)	138.9	0.4	O(2W) –Ho(1)–O(5a)	77.3	0.3
O(2W) –Ho(1)–O(6a)	128.4	0.3	O(2W) –Ho(1)–O(2b)	79.4	0.4
O(2W) –Ho(1)–O(6b)	141.8	0.3	O(3W) –Ho(1)–O(4W)	68.5	0.3
O(3W) –Ho(1)–O(2a)	122.1	0.3	O(3W) –Ho(1)–O(5a)	134.7	0.3
O(3W) –Ho(1)–O(6a)	136.5	0.3	O(3W) –Ho(1)–O(2b)	70.3	0.3
O(3W) –Ho(1)–O(6b)	75.0	0.3	O(4W) –Ho(1)–O(2a)	69.1	0.3
O(4W) –Ho(1)–O(5a)	138.2	0.3	O(4W) –Ho(1)–O(6a)	141.6	0.3
O(4W) –Ho(1)–O(2b)	138.6	0.3	O(4W) –Ho(1)–O(6b)	98.4	0.4
O(2a) –Ho(1)–O(5a)	103.2	0.3	O(2a) –Ho(1)–O(6a)	72.5	0.3
O(2a) –Ho(1)–O(2b)	140.9	0.3	O(2a) –Ho(1)–O(6b)	74.2	0.3
O(5a) –Ho(1)–O(6a)	52.6	0.3	O(5a) –Ho(1)–O(2b)	73.4	0.3
O(5a) –Ho(1)–O(6b)	119.6	0.3	O(6a) –Ho(1)–O(2b)	75.4	0.3
O(6a) –Ho(1)–O(6b)	70.5	0.3	O(2b) –Ho(1)–O(6b)	74.3	0.3
O(5W) –Ho(2)–O(6W)	132.6	0.3	O(5W) –Ho(2)–O(7W)	74.4	0.4
O(5W) –Ho(2)–O(8W)	75.4	0.3	O(5W) –Ho(2)–O(1a)	136.9	0.3
O(5W) –Ho(2)–O(6a)	140.9	0.3	O(5W) –Ho(2)–O(1b)	71.9	0.4
O(5W) –Ho(2)–O(5b)	67.8	0.3	O(5W) –Ho(2)–O(6b)	91.8	0.3
O(6W) –Ho(2)–O(8W)	72.3	0.3	O(6W) –Ho(2)–O(1a)	68.9	0.3
O(6W) –Ho(2)–O(6a)	77.2	0.3	O(6W) –Ho(2)–O(1b)	119.9	0.4
O(6W) –Ho(2)–O(5b)	127.7	0.3	O(6W) –Ho(2)–O(6b)	135.7	0.3
O(7W) –Ho(2)–O(8W)	87.1	0.3	O(7W) –Ho(2)–O(1a)	139.0	0.3
O(7W) –Ho(2)–O(6a)	100.8	0.3	O(7W) –Ho(2)–O(1b)	68.1	0.4
O(7W) –Ho(2)–O(5b)	139.1	0.3	O(7W) –Ho(2)–O(6b)	143.8	0.3
O(8W) –Ho(2)–O(1a)	79.9	0.3	O(8W) –Ho(2)–O(6a)	143.7	0.3
O(8W) –Ho(2)–O(1b)	143.0	0.3	O(8W) –Ho(2)–O(5b)	69.2	0.3
O(8W) –Ho(2)–O(6b)	121.7	0.3	O(1a) –Ho(2)–O(6a)	70.9	0.3
O(1a) –Ho(2)–O(1b)	136.6	0.3	O(1a) –Ho(2)–O(5b)	70.7	0.3
O(1a) –Ho(2)–O(6b)	72.8	0.3	O(6a) –Ho(2)–O(1b)	70.5	0.3
O(6a) –Ho(2)–O(5b)	118.2	0.3	O(6a) –Ho(2)–O(6b)	69.8	0.3
O(1b) –Ho(2)–O(5b)	112.1	0.3	O(1b) –Ho(2)–O(6b)	75.9	0.4
O(5b) –Ho(2)–O(6b)	53.5	0.3	O(1'W)–Ho(3)–O(2'W)	77.2	0.4
O(1'W)–Ho(3)–O(3'W)	134.2	0.3	O(1'W)–Ho(3)–O(4'W)	70.3	0.4
O(1'W)–Ho(3)–O(1c)	72.9	0.3	O(1'W)–Ho(3)–O(5c)	64.0	0.3
O(1'W)–Ho(3)–O(6c)	83.4	0.3	O(1'W)–Ho(3)–O(2d)	131.5	0.3
O(1'W)–Ho(3)–O(6d)	141.1	0.3	O(2'W)–Ho(3)–O(3'W)	73.8	0.3
O(2'W)–Ho(3)–O(4'W)	77.4	0.3	O(2'W)–Ho(3)–O(1c)	142.2	0.3
O(2'W)–Ho(3)–O(5c)	71.9	0.3	O(2'W)–Ho(3)–O(6c)	122.2	0.3

contd

Table 3. (contd)

Atoms involved	Angle	E.s.d.	Atoms involved	Angle	E.s.d.
O(2'W)–Ho(3)–O(2d)	76.9	0.3	O(2'W)–Ho(3)–O(6d)	141.6	0.3
O(3'W)–Ho(3)–O(4'W)	69.4	0.4	O(3'W)–Ho(3)–O(1c)	112.4	0.4
O(3'W)–Ho(3)–O(5c)	134.3	0.3	O(3'W)–Ho(3)–O(6c)	142.3	0.3
O(3'W)–Ho(3)–O(2d)	74.4	0.3	O(3'W)–Ho(3)–O(6d)	76.3	0.3
O(4'W)–Ho(3)–O(5c)	129.1	0.3	O(4'W)–Ho(3)–O(6c)	143.1	0.3
O(4'W)–Ho(3)–O(2d)	140.0	0.3	O(4'W)–Ho(3)–O(6d)	113.5	0.3
O(1c) –Ho(3)–O(5c)	113.3	0.3	O(1c) –Ho(3)–O(6c)	76.9	0.3
O(1c) –Ho(3)–O(2d)	140.9	0.3	O(1c) –Ho(3)–O(6d)	72.4	0.3
O(5c) –Ho(3)–O(6c)	50.8	0.3	O(5c) –Ho(3)–O(2d)	69.2	0.3
O(5c) –Ho(3)–O(6d)	115.9	0.3	O(6c) –Ho(3)–O(2d)	76.9	0.3
O(6c) –Ho(3)–O(6d)	72.0	0.3	O(2d) –Ho(3)–O(6d)	72.2	0.3
O(5'W)–Ho(4)–O(6'W)	135.2	0.4	O(5'W)–Ho(4)–O(7'W)	73.9	0.4
O(5'W)–Ho(4)–O(8'W)	74.5	0.4	O(5'W)–Ho(4)–O(2c)	137.4	0.4
O(5'W)–Ho(4)–O(6c)	143.0	0.3	O(5'W)–Ho(4)–O(1d)	74.0	0.4
O(5'W)–Ho(4)–O(5d)	68.6	0.3	O(5'W)–Ho(4)–O(6d)	90.9	0.3
O(6'W)–Ho(4)–O(7'W)	73.8	0.4	O(6'W)–Ho(4)–O(8'W)	69.3	0.4
O(6'W)–Ho(4)–O(2c)	66.3	0.3	O(6'W)–Ho(4)–O(6c)	72.7	0.3
O(6'W)–Ho(4)–O(1d)	118.9	0.3	O(6'W)–Ho(4)–O(5d)	127.5	0.3
O(6'W)–Ho(4)–O(6d)	133.3	0.3	O(7'W)–Ho(4)–O(8'W)	78.3	0.4
O(7'W)–Ho(4)–O(2c)	140.1	0.3	O(7'W)–Ho(4)–O(6c)	99.3	0.3
O(7'W)–Ho(4)–O(1d)	66.8	0.4	O(7'W)–Ho(4)–O(5d)	140.5	0.3
O(7'W)–Ho(4)–O(6d)	140.9	0.3	O(8'W)–Ho(4)–O(2c)	87.2	0.4
O(8'W)–Ho(4)–O(6c)	141.0	0.3	O(8'W)–Ho(4)–O(1d)	138.0	0.4
O(8'W)–Ho(4)–O(5d)	80.3	0.4	O(8'W)–Ho(4)–O(6d)	132.8	0.4
O(2c) –Ho(4)–O(6c)	69.7	0.3	O(2c) –Ho(4)–O(1d)	134.7	0.3
O(2c) –Ho(4)–O(5d)	70.6	0.3	O(2c) –Ho(4)–O(6d)	73.8	0.3
O(6c) –Ho(4)–O(1d)	70.0	0.3	O(6c) –Ho(4)–O(5d)	118.0	0.3
O(6c) –Ho(4)–O(6d)	71.4	0.3	O(1d) –Ho(4)–O(5d)	112.5	0.3
O(1d) –Ho(4)–O(6d)	74.5	0.3	O(5d) –Ho(4)–O(6d)	52.9	0.3

[a]A list of the corresponding Dy–O distances and O–Dy–O angles (Table 3a) is included in the supplementary material.

Table 4. Oscillator strength values of *f-f* transitions for the $Dy_2(L\text{-}Glu)_2(ClO_4)_4 \cdot 9H_2O$ single crystal. The values of the τ_λ and Ω_λ parameters are calculated on the basis of the Judd-Ofelt theory.[a]

Spectral region λ/Å	Energy level		$P_{exp} \cdot 10^8$	$P_{calc} \cdot 10^8$
16240–18400	$^6H_{11/2}$		132.75	146.72
12000–13760	$^6H_{9/2}$, $^6F_{11/2}$		366.72	368.40
10400–12000	$^6F_{9/2}$, $^6H_{7/2}$		283.80	386.47
8600–9700	$^6H_{5/2}$, $^6F_{7/2}$		285.10	317.92
7800–8425	$^6F_{5/2}$		160.20	153.14
7400–7800	$^6F_{3/2}$		33.12	28.79
4650–4850	$^4F_{9/2}$		19.03	24.78
4400–4650	$^4I_{15/2}$		49.29	54.07
4150–4400	$^4G_{11/2}$		15.20	8.85
3732–4065	$^4F_{7/2}$, $^4I_{13/2}$, $^4M_{21/2}$, $^4K_{17/2}$		278.30	274.32
3580–3707	$^4M_{19/2}$, $[^4P, ^4D]_{3/2}$, $^6P_{5/2}$, $^4I_{11/2}$		319.46	231.28
3430–3580	$^6P_{7/2}$		415.20	383.57
3320–3428	$[^4M, ^4I]_{15/2}$, $[^4F, ^4D]_{5/2}$, $^4i_{9/2}$		31.60	27.34
3190–3330	$^4G_{9/2}$, $^6P_{3/2}$, $^4M_{17/2}$, $[^4G, ^2F]_{7/2}$, $^4K_{15/2}$, $[^4D, ^4G]_{5/2}$, $^4D_{1/2}$, $^4L_{19/2}$		236.20	141.67
R.m.s. deviation			0.50×10^{-7}	
$\tau_2\times10^9$	2.02±1.20	$\Omega_2\times10^{20}$	1.35±0.8	
$\tau_4\times10^9$	4.00±0.52	$\Omega_4\times10^{20}$	2.67±0.35	
$\tau_6\times10^9$	5.73±0.56	$\Omega_6\times10^{20}$	3.82±0.37	

[a]See the text for explanation.

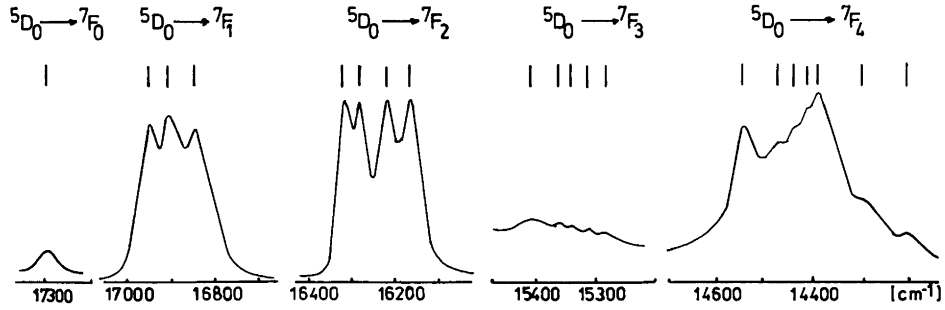

Fig. 4. Fluorescence spectra of the single crystal of europium glutamate perchlorate hydrate at 77 K in the region of $^5D_0 \rightarrow {}^7F_J$ transitions.

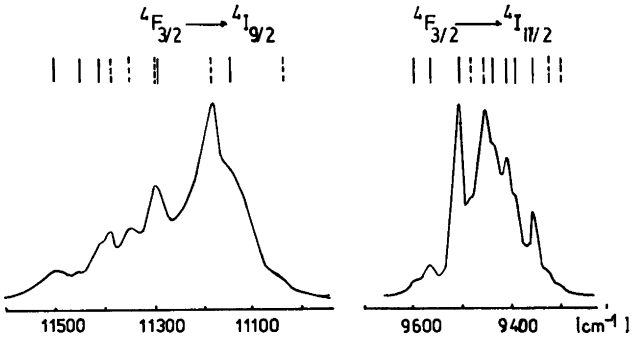

Fig. 5. Fluorescence spectra of the single crystal of neodymium glutamate perchlorate hydrate, taken at 77 K.

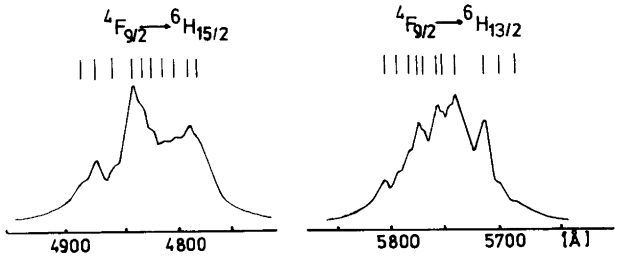

Fig. 6. Fluorescence spectra of the single crystal of dysprosium glutamate perchlorate hydrate, taken at 77 K.

beam. The spectra of the europium, neodymium and dysprosium single crystals were measured within the ranges of transitions $^5D_0 \rightarrow {}^7F_J$ (where $J = 0 - 4$), $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{11/2}$ and $^4F_{9/2} \rightarrow {}^6H_{11/2}$, $^6H_{15/2}$, respectively. Stark sublevels were determined in the spectra of these compounds. 1, 3, 4, 5 and 7 components were observed for $0 - J$ ($J = 0 - 4$) transitions in the europium compound (cf. Fig. 4); 9 and 11 bands for the neodymium single crystal (cf. Fig. 5); and 10 and 11 components for the $^4F_{9/2} \rightarrow {}^6H_{11/2}$, $^6H_{15/2}$ transitions in the dysprosium spectra. Noteworthy is the large width of the lines in these spectra. The band corresponding to $^5D_0 \rightarrow {}^7F_0$ transition is unusually broad in the spectrum of the europium compound. Such broadening of the lines is usually associated with the presence of pseudo-symmetry centres in the crystals and with partially disordered structures. Such an effect was observed by Kaminskii[22] in the crystals doped with Ln^{3+} ions, in which significant differences in crystal field between the particular sites were also observed. Lanthanoid cations occupying sites with different symmetry in ordered crystals give rise to additional lines, detectable even at 77 K.[23] Such additional lines have been detected at 77 K in the fluorescence spectra of neodymium with cryptands[24] and with glycine.[25] The presence of two crystallographically independent Nd^{3+} cations in these crystals has been confirmed by X-ray analysis. In the glutamate perchlorate crystals, however, neither europium nor neodymium give rise to additional lines under the same experimental conditions (77 K, 2 cm^{-1} resolution), not even when the excitation energy is changed. The X-ray analyses revealed four crystallographically independent cation sites in the glutamate perchlorates of holmium and dysprosium, with varying Ln–O contact distances. The coordination polyhedron in all cases is an intermediate between a capped square antiprism (CSAP) and a tricapped trigonal prism (TCTP). According to Drew[26] it can only be realized via the C_{2V} reaction pathway. Consequently, and also as a result of the relatively low crystallographic space group symmetry ($P2_1$), C_{2V} point symmetry is assumed for the Eu^{3+}, Nd^{3+} and Dy^{3+} ions in the present glutamate perchlorate crystals. The differences between the four independent cation positions seem to be only very small since they were not detectable at 77 K under the experimental conditions used. The large width of the fluorescence spectral lines may depend on the rare earth cations occuring in pairs[27] (linked together via O-C-O$^-$ groups) and to some extent also on the long range effect of the ClO_4^- disorder. It should be noted that both these statements are also valid for the crystal structures of $Nd(L\text{-}Ala)_2(ClO_4)_3 \cdot 4H_2O$ and $Eu(L\text{-}Ala)_2(ClO_4)_3 \cdot 4H_2O$; similar line-broadening effects were also detected in the fluorescence spectra of these latter compounds.[28]

Although the Dy^{3+} ion has a great number of absorbing levels in the 20000–30000 cm^{-1} spectral region, only the $^4F_{9/2}$ level shows notable fluorescence in the visible and near infrared regions, depending on the small energy gaps (~ 1500 cm^{-1}) between successive levels (cf. Table 4). Since the crystal contains amino acid residues with high-energy vibrations of NH-, CH-, and CO-groups, the higher levels are depopulated very fast, leading to population of the $^4F_{9/2}$

Table 5. Energy level diagram of the $Nd_2(L\text{-}Glu)_2(ClO_4)_4 \cdot 9H_2O$ crystal for the transitions $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{11/2}$.[a]

Observed fluorescence series I/cm^{-1}	Observed fluorescence series II/cm^{-1}	Positions of the levels/cm^{-1}
11500	11392	0
11453	11345	47
11400	11300	92
11298	11190	202
11152	11044	348
9595	9485	1906
9565	9455	1936
9507	9398	1994
	9358	2034
9435	9325	2067
9410	9300	2092

[a]Splitting of $^4F_{3/2}$ = 108 cm^{-1}.

level, which is separated by about 7000 cm^{-1} from the next lower level. The fluorescence decay time measured for the $Dy_2(L\text{-}Glu)_2(ClO_4)_4 \cdot 9H_2O$ crystal is 3.8 μs. This longer decay time, as compared with 2.26 μs observed for the $Dy(HCOO)_3 \cdot 2(HCONH_2)$ crystal,[29] suggests that the $^4F_{9/2}$ level is depopulated by non-radiative and radiative transitions rather than by a concentration quenching mechanism.

Acknowledgement. Financial support from the Swedish Natural Research Council (NFR) is gratefully acknowledged.

Supplementary material. Lists of geometric data for the coordination polyhedra around the dysprosium ions (Table 3a, 3 pages), intramolecular bond distances and bond angles (Tables 6 and 7, 16 pages) and anisotropic thermal parameters for the non-hydrogen atoms in both structures (Table 8, 12 pages) are deposited with the British Library Lending Division. Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CHI2HU, England or from one of the authors (I. C.). A list of the observed and calculated structure factors (70 pages) is available directly from one of the authors (I. C.) upon request.

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Received November 29, 1988.