

# Crystal Structure of a Praseodymium Glutamate Perchlorate Hydrate, $\text{Pr}_2(\text{L-Glu})_2(\text{ClO}_4)_4 \cdot 11\text{H}_2\text{O}$

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Csöreg, I., Kierkegaard, P., Legendziewicz, J. and Huskowska, E., 1987. Crystal Structure of a Praseodymium Glutamate Perchlorate Hydrate,  $\text{Pr}_2(\text{L-Glu})_2(\text{ClO}_4)_4 \cdot 11\text{H}_2\text{O}$ . – Acta Chem. Scand., Ser. A 41: 453–460.

The structure of the complex of  $\text{Pr}_2(\text{OOC-CH}(\text{NH}_3^+)-\text{C}_2\text{H}_4-\text{COO})_2(\text{ClO}_4)_4 \cdot 11\text{H}_2\text{O}$  has been studied by X-ray diffraction. The space group is orthorhombic ( $P2_12_12_1$ ) and  $Z = 4$ . The unit cell dimensions are  $a = 11.0651(5)$ ,  $b = 14.4576(7)$  and  $c = 22.5958(9)$  Å. The two crystallographically independent Pr(III) ions are bridged by four carboxylate groups. The pair of metal ions is coordinated to a total of sixteen oxygen atoms, two of which are coordinated to both cations, making the coordination number equal to nine for each. One of the ligand oxygen atoms is provided by a perchlorate group. The mean value of the Pr–O distances is 2.52 Å. In the crystalline state, the L-glutamic acid residues interlink the lanthanide ion pairs to form infinite layers perpendicular to the long  $c$  axis. One of the perchlorate anions is coordinated directly to a  $\text{Pr}^{3+}$  ion, while the remaining ones are stacked between the layers and show partial disorder. The structural model has been refined to a final linear  $R$  value of 0.0275 for 6633 reflections.

Calcium(II) ions play an important regulatory role in many biological processes. There are, however, no suitable physical techniques for studying  $\text{Ca}^{2+}$ . This problem has been partly overcome by use of lanthanide cations as substitutes for calcium ions.<sup>1–6</sup> The trivalent rare earth ions resemble  $\text{Ca}^{2+}$  in size and also in their preference for oxygen donors in complex formation.<sup>3–4</sup> In biological processes, calcium ions commonly exert their effects by binding to proteins, normally via aspartate or glutamate residues. In order to obtain information about the chemical and structural nature of calcium binding sites, we have investigated complexes of lanthanides with amino acids as ligands. The interaction between amino acids and lanthanide ions in solution has been extensively studied by a variety of different spectroscopic methods,<sup>7–15</sup> but only a few publications deal with investigations of these compounds in the solid state.<sup>16–19</sup> The present work is part of a programme of research into the structural and spectroscopic aspects of interactions be-

tween trivalent lanthanoid cations and amino acids in the solid state.

## Experimental

**Sample preparation.** The title complex was prepared by dissolving equimolar amounts of  $\text{Pr}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  [synthesized from praseodymium oxide (Merck) as described earlier<sup>20</sup>] and L-glutamic acid (Reanal, Budapest) in water. Crystals suitable for X-ray work were grown by slow evaporation of an aqueous solution with pH ~3.5. The crystal density, measured by the flotation method in a mixture of bromoform and 1,2-dibromoethane, is  $2.11 \text{ g cm}^{-3}$ .

**X-Ray data collection and reduction.** A light green single crystal of the title complex ( $\text{C}_{10}\text{H}_{38}\text{O}_{35}\text{N}_2\text{Cl}_4\text{Pr}_2$ ,  $M_w = 1170.03$ ,  $D_c = 2.15 \text{ g cm}^{-3}$ ) with the approximate dimensions  $0.60 \times 0.40 \times 0.64 \text{ mm}$ , sealed in epoxy resin, was used for X-ray data collection. The intensities of

7158 reflections ( $\theta < 32.5^\circ$ ) were measured at room temperature with a Siemens/AED2 computer-controlled diffractometer using MoK $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) and the  $\omega$ - $2\theta$  scan technique. The net intensities were corrected for Lorentz and polarization effects as well as for absorption ( $\mu = 30.69 \text{ cm}^{-1}$ ). The space group is

orthorhombic ( $P2_12_12_1$ ) and  $Z = 4$ . The unit cell dimensions are  $a = 11.0651(5)$ ,  $b = 14.4576(7)$  and  $c = 22.5958(9) \text{ \AA}$ . The cell parameters were refined using the angular settings of 36 well-centered reflections ( $22^\circ < 2\theta < 53^\circ$ ) accurately measured on the diffractometer.

*Table 1.* Fractional atomic coordinates and equivalent isotropic/isotropic temperature factors<sup>a</sup> for the non-hydrogen atoms. The e.s.d.'s are given in parentheses. The atoms are numbered according to Fig. 1. For the atomic positions with partial site occupancy due to the disorder in the crystal,<sup>a</sup> the site occupancy factor (s.o.f.) is also given.

Atom	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}^b/U/\text{\AA}^2$	s.o.f.
Pr(1)	0.16000(2)	0.17655(1)	0.16799(1)	0.0164(0)	
O(1W)	0.2973(4)	0.2405(3)	0.0881(2)	0.033(1)	
O(2W)	0.0893(4)	0.3314(3)	0.1358(2)	0.040(1)	
O(3W)	-0.0549(4)	0.1577(4)	0.1278(2)	0.049(2)	
Pr(2)	0.21239(2)	0.04820(1)	0.32856(1)	0.0189(1)	
O(4W)	0.2626(4)	0.1588(3)	0.4096(2)	0.041(1)	
O(5W)	0.0770(4)	0.0046(3)	0.4131(2)	0.036(1)	
O(6W)	0.2736(5)	-0.1110(3)	0.3618(2)	0.051(2)	
O(7W)	0.4370(4)	0.0588(4)	0.3505(3)	0.048(2)	
O(1)	0.3310(3)	0.0694(3)	0.1679(2)	0.027(1)	
O(2)	0.3215(4)	-0.0245(3)	0.2477(2)	0.036(1)	
C(1)	0.3634(4)	0.0010(3)	0.1983(2)	0.024(1)	
C(2)	0.4599(4)	-0.0621(3)	0.1709(2)	0.025(1)	
N(2)	0.5248(4)	-0.0072(4)	0.1250(2)	0.037(2)	
C(3)	0.5482(5)	-0.1041(3)	0.2167(2)	0.029(1)	
C(4)	0.6096(5)	-0.1905(3)	0.1942(2)	0.028(1)	
C(5)	0.6811(4)	-0.2408(3)	0.2401(2)	0.021(1)	
O(5)	0.6988(4)	-0.2049(3)	0.2900(2)	0.037(1)	
O(6)	0.7262(3)	-0.3196(2)	0.2294(2)	0.024(1)	
O(1')	0.0439(3)	0.1592(3)	0.3309(2)	0.028(1)	
O(2')	0.0279(4)	0.2383(3)	0.2454(2)	0.028(1)	
C(1')	0.0056(4)	0.2244(3)	0.2990(2)	0.020(1)	
C(2')	-0.0699(4)	0.2982(3)	0.3287(2)	0.022(1)	
N(2')	-0.1280(4)	0.2556(3)	0.3824(2)	0.035(1)	
C(3')	0.0114(5)	0.3792(4)	0.3491(2)	0.028(1)	
C(4')	0.0680(4)	0.4335(3)	0.2975(2)	0.025(1)	
C(5')	-0.0259(4)	0.4787(3)	0.2586(2)	0.021(1)	
O(5')	-0.0405(4)	0.4506(3)	0.2072(2)	0.038(1)	
O(6')	-0.0874(3)	0.5434(3)	0.2795(2)	0.029(1)	
Cl(1)	0.2196(1)	0.0135(1)	0.0363(1)	0.0284(2)	
O(11)	0.1462(4)	0.0699(3)	0.0756(2)	0.034(1)	
O(12)	0.1605(5)	0.0071(4)	-0.0203(2)	0.059(2)	
O(13)	0.3367(4)	0.0554(3)	0.0285(2)	0.039(1)	
O(14)	0.2356(5)	-0.0761(3)	0.0612(3)	0.056(2)	
Cl(2)	0.3171(1)	0.6618(1)	0.2571(1)	0.0398(3)	
O(21)	0.4378(5)	0.6343(5)	0.2621(4)	0.085(3)	
O(22a)	0.3064(9)	0.7583(7)	0.2635(4)	0.081(3)	0.8289
O(22b)	0.2577(24)	0.7370(18)	0.2881(11)	0.042(5)	0.1751
O(23)	0.2701(7)	0.6154(6)	0.3097(4)	0.090(3)	
O(24a)	0.2419(12)	0.6255(9)	0.2111(6)	0.076(3)	0.6333

Table 1. (contd)

Atom	x/a	y/b	z/c	$U_{eq}^b/U/\text{\AA}^2$	s.o.f.
O(24b)	0.3272(24)	0.6910(19)	0.1916(11)	0.075(6)	0.2722
O(24c)	0.2032(34)	0.6174(27)	0.2377(18)	0.092(10)	0.2332
O(24d)	0.2827(27)	0.6426(21)	0.1946(13)	0.031(6)	0.1225
Cl(3)	0.3952(2)	0.7070(1)	0.4664(1)	0.0479(4)	
O(31)	0.2808(6)	0.7549(6)	0.4641(3)	0.082(3)	
O(32)	0.4728(9)	0.7504(9)	0.5068(4)	0.111(4)	
O(33)	0.4491(6)	0.7036(6)	0.4112(3)	0.089(3)	
O(34a)	0.3838(11)	0.6185(9)	0.4961(5)	0.084(3)	0.6822
O(34b)	0.3622(27)	0.6082(20)	0.4573(12)	0.090(8)	0.2886
Cl(4)	0.5634(2)	0.2391(1)	0.4741(1)	0.0459(4)	
O(41)	0.4922(8)	0.1591(6)	0.4822(5)	0.110(4)	
O(42a)	0.6927(11)	0.2154(9)	0.4789(6)	0.075(3)	0.6428
O(42b)	0.6705(31)	0.2171(23)	0.5049(14)	0.101(9)	0.3131
O(43a)	0.5459(11)	0.3025(9)	0.5225(6)	0.095(4)	0.7204
O(43b)	0.5072(41)	0.3331(34)	0.4856(21)	0.105(13)	0.2081
O(43c)	0.4714(41)	0.3148(32)	0.4478(21)	0.081(11)	0.1609
O(44a)	0.5373(13)	0.2779(10)	0.4242(6)	0.082(4)	0.5900
O(44b)	0.5959(17)	0.2417(13)	0.4081(8)	0.072(4)	0.3817
O(8W)	-0.1603(7)	0.0526(6)	0.4156(4)	0.092(3)	
O(9W)	0.7248(6)	-0.0754(5)	0.0625(4)	0.082(3)	
O(10W)	0.8881(7)	0.0463(8)	0.0106(5)	0.113(4)	
O(11W)	0.6303(10)	-0.0582(6)	0.3729(4)	0.120(4)	

<sup>a</sup>See text for explanation. <sup>b</sup> $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* \cdot a_j^* \cdot a_i \cdot a_j$ .

**Solution and refinement of the structure.** The positions of the two praseodymium ions, derived from Patterson synthesis, served as a starting point for the solution of the structure. Difference Fourier syntheses and full-matrix least-squares

calculations with the SHELX program system<sup>21</sup> were used to complete and refine the structural model. Three of the perchlorate groups show partial disorder, which could be partly resolved into major disorder sites. However, those dis-

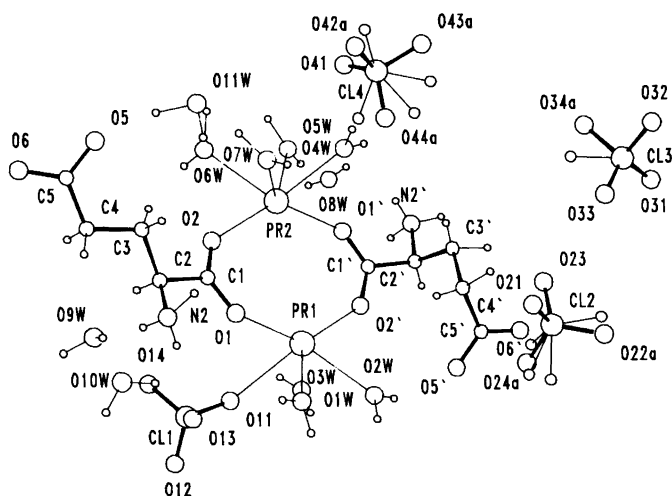


Fig. 1. Perspective view of the asymmetric unit, showing also the major disorder sites in the perchlorate groups. The atoms are numbered as in the text.

Table 2. The geometry of the coordination around the Pr(III) ions. Pr–O distances and O–Pr–O angles with e.s.d.'s in parentheses. The atoms are numbered as in Fig. 1. The oxygen positions are generated using the coordinates in Table 1 together with the following symmetry operations:

Superscript	Atom at
None	$x, y, z;$
<i>a</i>	$-x+1, y+\frac{1}{2}, -z+\frac{1}{2};$
<i>b</i>	$-x, y-\frac{1}{2}, -z+\frac{1}{2}.$

Atoms	Distance/Å	Atoms	Distance/Å
Pr(1)–O(1W)	2.534(4)	Pr(2)–O(4W)	2.495(4)
Pr(1)–O(2W)	2.500(4)	Pr(2)–O(5W)	2.508(4)
Pr(1)–O(3W)	2.561(4)	Pr(2)–O(6W)	2.513(4)
Pr(1)–O(11)	2.599(4)	Pr(2)–O(7W)	2.539(4)
Pr(1)–O(1)	2.446(3)	Pr(2)–O(1')	2.460(4)
Pr(1)–O(2')	2.448(4)	Pr(2)–O(2)	2.429(4)
Pr(1)–O(5) <sup>a</sup>	2.505(4)	Pr(2)–O(5') <sup>b</sup>	2.502(4)
Pr(1)–O(6') <sup>b</sup>	2.400(4)	Pr(2)–O(6) <sup>a</sup>	2.414(3)
Pr(1)–O(6) <sup>a</sup>	2.639(3)	Pr(2)–O(6') <sup>b</sup>	2.806(4)

Atoms	Angle/°	Atoms	Angle/°
O(2')–Pr(1)–O(11)	139.0(1)	O(1)–Pr(1)–O(11)	70.7(1)
O(1)–Pr(1)–O(2')	133.9(1)	O(3W)–Pr(1)–O(11)	66.3(2)
O(3W)–Pr(1)–O(2')	74.8(2)	O(3W)–Pr(1)–O(1)	130.6(2)
O(2W)–Pr(1)–O(11)	106.1(2)	O(2W)–Pr(1)–O(2')	71.4(2)
O(2W)–Pr(1)–O(1)	145.9(2)	O(1W)–Pr(1)–O(11)	71.3(1)
O(1W)–Pr(1)–O(2')	137.2(1)	O(1W)–Pr(1)–O(1)	76.5(1)
O(1W)–Pr(1)–O(3W)	110.1(2)	O(1W)–Pr(1)–O(2W)	70.6(2)
O(1W)–Pr(1)–O(5) <sup>a</sup>	69.3(2)	O(1W)–Pr(1)–O(6) <sup>a</sup>	109.4(1)
O(1W)–Pr(1)–O(6') <sup>b</sup>	147.7(1)	O(2W)–Pr(1)–O(3W)	71.3(2)
O(2W)–Pr(1)–O(5) <sup>a</sup>	73.0(2)	O(2W)–Pr(1)–O(6) <sup>a</sup>	113.4(1)
O(2W)–Pr(1)–O(6') <sup>b</sup>	138.6(2)	O(3W)–Pr(1)–O(5) <sup>a</sup>	141.8(2)
O(3W)–Pr(1)–O(6) <sup>a</sup>	139.2(2)	O(3W)–Pr(1)–O(6') <sup>b</sup>	77.2(2)
O(1)–Pr(1)–O(5) <sup>a</sup>	87.2(2)	O(1)–Pr(1)–O(6) <sup>a</sup>	69.2(1)
O(1)–Pr(1)–O(6') <sup>b</sup>	75.6(1)	O(5) <sup>a</sup> –Pr(1)–O(6) <sup>a</sup>	49.9(1)
O(5) <sup>a</sup> –Pr(1)–O(2')	81.5(2)	O(5) <sup>a</sup> –Pr(1)–O(6') <sup>b</sup>	124.8(1)
O(5) <sup>a</sup> –Pr(1)–O(11)	138.3(2)	O(6) <sup>a</sup> –Pr(1)–O(2')	69.5(1)
O(6) <sup>a</sup> –Pr(1)–O(6') <sup>b</sup>	75.0(1)	O(6) <sup>a</sup> –Pr(1)–O(11)	138.2(1)
O(2')–Pr(1)–O(6') <sup>b</sup>	74.9(1)	O(6') <sup>b</sup> –Pr(1)–O(11)	84.4(1)
O(2)–Pr(2)–O(1')	132.4(1)	O(7W)–Pr(2)–O(1')	134.3(2)
O(7W)–Pr(2)–O(2)	71.7(2)	O(6W)–Pr(2)–O(1')	142.7(2)
O(6W)–Pr(2)–O(2)	72.2(2)	O(6W)–Pr(2)–O(7W)	74.5(2)
O(5W)–Pr(2)–O(1')	72.3(1)	O(5W)–Pr(2)–O(2)	139.5(2)
O(5W)–Pr(2)–O(7W)	116.8(2)	O(5W)–Pr(2)–O(6W)	72.8(2)
O(4W)–Pr(2)–O(1')	74.6(2)	O(4W)–Pr(2)–O(2)	136.0(2)
O(4W)–Pr(2)–O(7W)	66.4(2)	O(4W)–Pr(2)–O(6W)	107.9(2)
O(4W)–Pr(2)–O(5W)	74.6(2)	O(4W)–Pr(2)–O(6) <sup>a</sup>	80.1(2)
O(4W)–Pr(2)–O(5') <sup>b</sup>	140.2(2)	O(4W)–Pr(2)–O(6') <sup>b</sup>	139.9(2)
O(5W)–Pr(2)–O(6) <sup>a</sup>	141.3(2)	O(5W)–Pr(2)–O(5') <sup>b</sup>	69.5(2)
O(5W)–Pr(2)–O(6') <sup>b</sup>	111.2(1)	O(6W)–Pr(2)–O(6) <sup>a</sup>	144.2(2)
O(6W)–Pr(2)–O(5') <sup>b</sup>	77.6(2)	O(6W)–Pr(2)–O(6') <sup>b</sup>	111.7(2)
O(7W)–Pr(2)–O(6) <sup>a</sup>	77.4(2)	O(7W)–Pr(2)–O(5') <sup>b</sup>	147.3(2)
O(7W)–Pr(2)–O(6') <sup>b</sup>	130.8(2)	O(2)–Pr(2)–O(6) <sup>a</sup>	78.2(2)
O(2)–Pr(2)–O(5') <sup>b</sup>	83.7(2)	O(2)–Pr(2)–O(6') <sup>b</sup>	65.2(1)
O(6) <sup>a</sup> –Pr(2)–O(1')	73.1(1)	O(6) <sup>a</sup> –Pr(2)–O(5') <sup>b</sup>	119.0(1)
O(6) <sup>a</sup> –Pr(2)–O(6') <sup>b</sup>	71.7(1)	O(1')–Pr(2)–O(5') <sup>b</sup>	78.4(2)
O(1')–Pr(2)–O(6') <sup>b</sup>	70.2(1)	O(5') <sup>b</sup> –Pr(2)–O(6') <sup>b</sup>	48.0(1)

order positions for which the refined site occupancy factor became less than 0.10 were not taken into account in the refinements. In the last stage the non-hydrogen atoms with full site occupancy were refined together with their anisotropic temperature factors. The perchlorate oxygen positions with partial occupancy due to the disorder in the crystal structure were refined together with their isotropic temperature factors. Their site occupancy factors, fixed in the last refinement, had been refined in the previous cycles. For the hydrogen positions, derived from difference electron density calculations, only two group isotropic temperature factors were refined: one for the hydrogens of the glutamic acid residues and one for the hydrate H atoms.

The structure was refined for both *L* and *D* configurations of the amino acid residues. The last refinements, based on 6633 structure factors with  $F/\sigma(F) > 10$ , in which an empirical extinction correction factor<sup>21</sup> was also refined, converged to give the final linear agreement factors  $R = 0.0275$  and 0.0353 for the structural models with *L* and *D* glutamic acid residues, respectively. The weighted reliability indices,  $R_w = \Sigma \sqrt{w} \cdot |\Delta F| / \Sigma \sqrt{w} \cdot |F_0|$  and  $R_G = [\Sigma w \cdot |\Delta F|^2 / \Sigma w \cdot |F_0|^2]^{1/2}$  became 0.0329 and 0.0451 for the *L* configuration and 0.0402 and 0.0513 for the other one. The weights were calculated as  $w = 0.647 / [\sigma^2(F) +$

$0.00154 F^2]$  and  $w = 3.566 / [\sigma^2(F) + 0.000276 F^2]$ , respectively. We may conclude from these significant differences between respective *R*-values that the glutamic acid residues in the present structure have the *L* configuration, as expected. This is confirmed to a significance level of 0.005 by a Hamilton test<sup>22</sup> on the relation of  $R_G$ 's for the *L* and *D* configurations. The final atomic coordinates, listed in Table 1, refer to the correct *L* configuration (cf. Fig. 1).

Lists of structure factors, intramolecular bond distances and bond angles, fractional atomic coordinates of the hydrogen atoms and anisotropic thermal parameters of the non-hydrogen atoms with full site occupancy have been deposited with the British Library Lending Division. Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England or from the authors.

#### *Crystallographic description of the structure, and discussion*

The two Pr(III) ions are bridged by four carboxylate groups. The coordination sphere is completed by four oxygens per metal ion. These are hydrate oxygens, except for one O atom, coordinated to Pr(1), which is provided by a perchlorate group (Fig. 2). It is worth mentioning that lanthanide coordination compounds involving a perchlorate group in the first coordination sphere are rare. Nevertheless, the possibility of lanthanide- $\text{ClO}_4^-$  inner-sphere complex formation was already suggested from IR studies, and from fluorescence spectrum and life-time measurements on organic complexes of europium and neodymium perchlorates,<sup>23-25</sup> a crystallographic study of the complex  $\text{Eu}(\text{ClO}_4)_3 \cdot \text{L} \cdot \text{CH}_3\text{CN}$  (where *L* = 4,7,13,16,21,24-hexoxa-1,10-diazabicyclo[8,8,8]hexacosane) has also revealed the presence of the  $[\text{Eu}(\text{ClO}_4)\text{L}]^{2+}$  cation.<sup>26</sup> However, it should be pointed out that in all these cases the complexes were prepared from, and/or the measurements were carried out in non-aqueous solutions. The formation of inner-sphere perchlorate complexes was to some extent also indicated by  $^1\text{H}$  and  $^{35}\text{Cl}$  NMR studies of  $\text{Yb}^{3+}-\text{ClO}_4^-$  and  $\text{Lu}^{3+}-\text{ClO}_4^-$  systems in water-acetone mixtures.<sup>27-28</sup> In aqueous perchlorate solutions, on the other hand, all reports agree on the outer-sphere nature of lanthanoid complexation.<sup>29-30</sup>

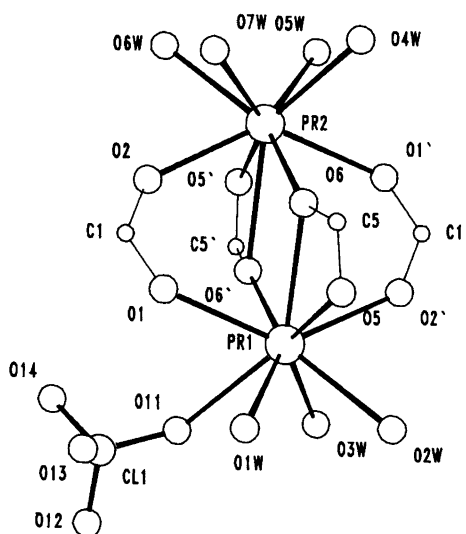


Fig. 2. Coordination around the two praseodymium ions of the asymmetric unit.

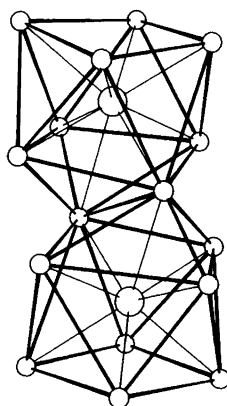
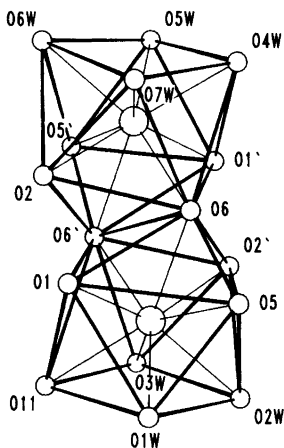


Fig. 3. Stereoscopic view of the coordination polyhedra around the pair of praseodymium ions.

The present structure provides the first example known to the authors of a perchlorate group coordinated directly to a rare earth cation when competing water molecules are present.

The pair of metal ions coordinates to a total of sixteen ligand atoms, two of which are coordinated to both cations, making the coordination number equal to nine for each (Fig. 2). The coordination polyhedra around the pair of Pr(III) ions (Fig. 3) can possibly be approximated by two strongly distorted mono-capped square antiprisms ( $C_{4v}$ ) which share one edge. The shortest polyhedron edges are as short as 2.172(5) [O(5)–O(6)] and 2.176(5) Å [O(5')–O(6')], and the longest ones are 3.414(5) [O(1)–O(5)] and

3.282(6) Å [O(2)–O(5')] around the Pr(1) and Pr(2) ions, respectively. The arithmetic mean of the lengths of the polyhedron edges (with r.m.s.d. in square brackets) is 2.97[25] Å. The Pr–O distances range between 2.40 and 2.81 Å, the mean value being 2.52[9] Å (Table 2). The distances to the ninth ligand atom (which caps the square face), Pr(1)–O(6) = 2.639(3) and Pr(2)–O(6') = 2.806(6) Å, are somewhat longer than the other Pr–O distances (Table 2). The bond lengths and bond angles in the glutamic acid residues conform to the expected values. The characteristic mean bond lengths (where averaged over more than three values, the r.m.s.d.'s are indicated in angular brackets) are C–C 1.524[24],

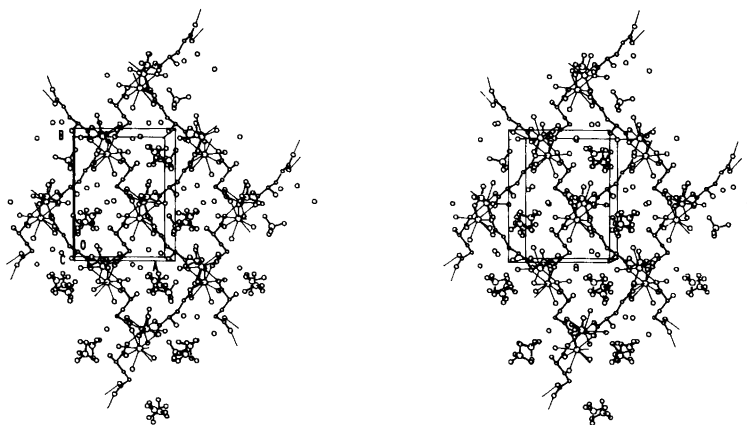


Fig. 4. Stereoscopic drawing of the crystal structure viewed along the *c*-axis. The hydrogens are omitted for clarity.

C–O 1.256[8] and C–N 1.498 Å. The C–O distances in the four carboxylate groups clearly show these groups to be ionized.

Due to the rotation of the perchlorate groups, which causes disorder in the crystal structure, twenty-five positions are taken into account for sixteen oxygen atoms (Table 1). The mean Cl–O bond length calculated for these twenty-five positions, 1.45[6] Å, agrees well with the commonly accepted average distance, 1.44 Å,<sup>31</sup> for such a bond. The hydrogen positions were derived from difference electron density maps. Some hydrate oxygens, however, had more than two peaks at reasonable distances, possibly suggesting disorder for these H atom positions. In these cases peaks with the highest relative electron density were chosen as H positions, and no disorder sites for hydrogens were included in the refined structural model.

In the crystal structure, the L-glutamic acid residues interlink the pairs of metal ions to form infinite layers perpendicular to the long *c* axis. Due to the bifunctionality of the glutamate groups, the pattern formed by the layers resembles a diamond (Fig. 4). The perchlorate anions, except for one which is attached directly to Pr(1), are stacked between the layers. Seven of the eleven hydrate molecules of the asymmetric unit are coordinated directly to the lanthanide ions, and together with the remaining ones increase the stability of the crystals by forming hydrogen bonds. The present crystal structure is similar to, but not isomorphous with, the crystal structures of the related dysprosium and holmium compounds which we have recently studied.<sup>32</sup> These latter structures will be published elsewhere.

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

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Received June 29, 1987.