Structure of a novel polynuclear europium compound with *N*-phosphonomethylglycine: heptaaquaperchloratodi-μ_4-*N*-phosphonomethylglycine-dieuropium(III) triperchlorate monohydrate, $[Eu_2(HO_3PCH_2NH_2CH_2CO_2)_2(H_2O)_7(ClO_4)] \cdot 3ClO_4 \cdot H_2O$†

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The solid-state structure of the europium(III) complex with *N*-phosphonomethylglycine (PMG) has been obtained from aqueous solution, at pH *ca.* 1.6, where a 1 : 1 M : L molar ratio has been kept. The crystal structure of the $[Eu_2(HO_3PCH_2NH_2CH_2CO_2)_2(H_2O)_7(ClO_4)] \cdot 3ClO_4 \cdot H_2O$ compound has been determined by single-crystal X-ray diffraction. In the structure of the title compound a two-dimensional polymer is formed, with an unexpected architecture. The oxygen atom of one of four perchlorate groups is engaged in the coordination besides that of the PMG groups. The glyphosate molecules are present as zwitterions. The polymeric chains are composed of two types of dimeric subunits. The first one is created by simple and chelating carboxyl bridges, and the second by phosphonate groups; in the latter type the dimeric unit coordination of metal ions is completed by two oxygen atoms of two perchlorate groups. In the first subunit four, and in the second subunit three water molecules are coordinated by each europium atom. The eighth water molecule and three of four perchlorate groups are outside the metal coordination. Therefore, two non-equivalent metal sites, eight- and nine-fold coordinated, exist in the structure. The structure is stabilized by an extended network of hydrogen bonds. The conformations of the two PMG molecules are quite different.

A significant increase of interest in aminophosphonate acids arose at the beginning of the 1970s when the compounds turned out to have various important biological properties. Due to their biological activity as metabolic process inhibitors, aminophosphonate acids began to be used as antibacterial agents, neuroactive compounds, anticancer drugs or pesticides.[1,2] *N*-Phosphonomethylglycine (PMG) plays a special role amongst aminophosphonate acids. Glyphosate was first described by Toy and Wing.[3] Frantz was the first to describe it as a component of the extremely potent herbicide known as Roundup[4] on the market. The potency of PMG, which is easily transported to each part of a plant and next decomposed in the soil,[5] can be partly explained by its complexing processes with metal ions.

Glyphosate chelate chemistry has focussed mainly on solution studies with only a few reports concerning the synthesis and structure of PMG in solid complexes.[6,7] Free acid single-crystal X-ray studies[8] and assignment of ^{31}P NMR shifts for the solution complex of platinum(II) : PMG[9] proved that free glyphosate acid exists in the zwitterionic form as $NH_2^+(CH_2COOH)(CH_2PO_3H^-)$. The Ca : PMG compound[6] crystal structure data show a zwitterionic form of the ligand in that compound, too.

Since lanthanide ions are often used as spectral probes in investigations of biological systems,[10] we successfully undertook the synthesis and study of the spectroscopic properties (IR, emission and absorption spectroscopy) of the europium(III) complex of PMG in the solid state.[11] This paper aims to determine the crystal structure of the title compound, which is the first example of a lanthanide complex with a potentially poly-dentate (N, O_C, O_P) ligand type.

Experimental

The europium(III) compound with *N*-phosphonomethylglycine of formula $[Eu_2(HO_3PCH_2NH_2CH_2CO_2)_2(H_2O)_7(ClO_4)] \cdot 3ClO_4 \cdot H_2O$ (further denoted as Eu : PMG) was obtained from an aqueous solution of europium perchlorate ($c \approx 10^{-2}$ M) at pH $\approx$ 1.6, with the 1 : 1 molar ratio of M : L being kept constant. The concentration of metal in the crystals was determined complexometrically and that of Eu, P and Cl was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Other elements were determined by elemental analysis. The results were as follows (the calculated values are given in parentheses): 25.81 (26.39)% of Eu, 4.9 (5.38)% of P, 9.87 (12.31)% of Cl, 6.57 (6.36)% of C and 2.28 (2.43)% of N. A relatively high error on the chloride estimation, because of the presence of ClO_4^-, should be noted. The crystals were grown over a long period (half a year) at constant temperature (25 °C). Variation of the temperature leads to formation of powder samples. The NMR solution studies are underway.

X-Ray data were collected and processed with MoKα radiation at 293 K on a Kuma Diffraction KM-4 diffractometer using the original KM4B8 data collection program[12] and

† Electronic supplementary information (ESI) available: displacement parameters and hydrogen bonding parameters. See http://www.rsc.org/suppdata/nj/b0/b000230p/

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DATPROC9 data processing program.[13,14] The intensities were corrected for Lorentz and polarization effects and for empirical absorption using the XEMP program.[15] The structure was solved by direct methods, using the XS program, and refined on F values by full-matrix least squares using the XLS3 program from the SHELXTL/PC system[15] and SHELXL program[15] from the SHELX-97 system, with anisotropic temperature factors. Hydrogen atoms were not included in the refinement. Editing of the data in Table 2 was done using the CSU program.[16]

CCDC reference number 440/179. See http://www.rsc.org/suppdata/nj/b0/b000230p/ for crystallographic files in .cif format.

Results and discussion

Eu : PMG crystallizes in the monoclinic system and $P2_1/c$ space group. The crystal data, data collection and structure refinement details are given in Table 1. Selected geometric parameters (bond lengths, bond angles and torsion angles) are given in Table 2.

Four $[Eu_2(HO_3PCH_2NH_2CH_2CO_2)_2(H_2O)_7(ClO_4)] \cdot 3ClO_4 \cdot H_2O$ units occur in the unit cell. The complex is a polymer consisting of two types, (1) carboxyl and (2) phosphonate, of centrosymmetric dimeric subunits (Fig. 1). The first type of dimeric subunit (1) has two metal ions, bound by four carboxyl groups from four different ligand molecules. Two of the four carboxylate groups act as an open bidentate bridge (I kind[17]) between adjacent europium(III) ions, whereas the remaining carboxylate groups coordinate two adjacent europium(III) ions by forming a cyclic bridge (II kind[17]), which creates four-membered chelate rings. In the latter case, one of the two carboxylic oxygen atoms interacts with two lantha

Table 1 Summary of crystal data, data collection and refinement details

Formula	$C_6H_{30}N_2O_{34}P_2Cl_4Eu_2$
Formula weight	1151.74
T/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	17.788(4)
b/Å	10.706(2)
c/Å	18.560(4)
β/°	113.37(3)
U/Å^3	3244.56(12)
Z	4
μ/mm^{-1}	4.382
Reflections collected	5990
Independent reflections	5820
R_{int}	0.0728
R, wR^a	0.0656, 0.1614

^{a} $R = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$; $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$

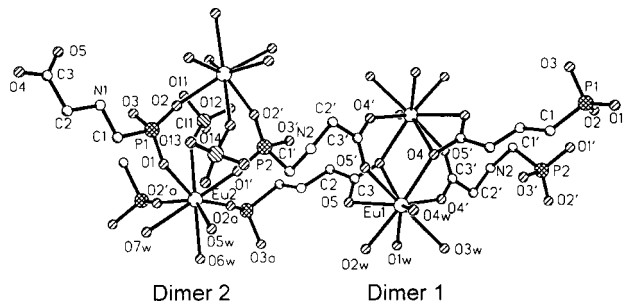

Fig. 1 SHELXTL (XP) drawing of the molecular structure with the atom labeling scheme, showing the two dimeric subunits. Isotropic displacement parameters are used and labels of the O atoms are omitted, for clarity. The polymer layer is parallel to the (102) plane, as it is shown in Fig. 2.

nide ions. The coordination number of Eu(III) ions in dimer (1) is 9, because each metal ion is additionally coordinated by four water molecules. The same carboxyl group coordination types (I and II) occur in polymeric lanthanide complexes with glycine (Gly)[18] and *N*-methylglycine (MGly).[19] The main difference between those structures and the Eu : PMG structure is that in Eu : PMG the two europium ions in the dimeric subunit (1) are equally bonded to the carboxylate groups, while the lanthanides in glycine (linear polymer) and *N*-methylglycine (linear polymer) complexes occupy two non-equivalent positions. It is possible that creation of dimer (2), in which another pair of metal ions is bridged by phosphonate groups, and formation of a network of branched polymers could stiffen the structure, thus creating better conditions for the metal ions to be equivalent within a dimer. In this aspect the structure of the Eu : PMG complex is closer to that of the Nd(III) complex with glycylglycine (Glygly).[20] In the latter compound, as in the Eu : PMG complex, a polymeric structure is created with centrosymetric dimeric M–(O–C–O)$_4$–M subunits and the carboxyl group (I,II) coordination types are identical. Thus, the structure presented here provides essential proof for the enhancing role of the phosphonate group in the creation of a two-dimensional polymer.

The coordination number of the metal in dimer (2) is 8. The second dimeric subunit type (2) is made up of two simple phosphonate bridges from two different glyphosate molecules. Each eight-fold coordinated lanthanide ion in dimer (2) is bonded to four oxygen atoms from four phosphonate groups (two bidentate oxygens and two monodentate oxygen atoms linking different dimer types together), three oxygen atoms from water molecules and one oxygen atom from an inner coordination sphere perchlorate group. The coordination of the ClO_4^- group with a metal ion is quite unexpected, because perchlorate ions are known to only rarely create inner sphere complexes. This is only the second case of this type of coordination in complexes with amino acid derivatives. The first reported case concerned an orthorhombic praseodymium complex with glutamic acid obtained from water solution.[21] The same kind of phosphonate bridge as in the Eu : PMG system can be found in the linear polymer of $[Lu(PO_3HCH_2CH_2NH_3)_3](ClO_4)_3 \cdot 3D_2O$,[22] where Lu(III) is six-coordinate. In the above Lu : ciliatine complex the amino group is protonated and the ligand has a zwitterionic form. The lanthanide ions are linked together by two phosphonate oxygen atoms.

The title compound has a two-dimensional polymeric structure branching into layers parallel to the (102) plane (Fig. 2). Each glyphosate molecule is linked with europium ions *via* carboxyl and phosphonate group oxygen atoms (Fig. 3). The PMG amino group is protonated ($>NH_2^+$), the carboxyl group is deprotonated and the phosphonate group is partially deprotonated, which is demonstrated well in the P–O bond lengths (Table 2). Free glyphosate crystallizes as a zwitterion of type $^-HO_3PCH_2NH_2^+CH_2COOH$.[8] Single-crystal X-ray studies proved that the proton resides on the amino nitrogen and is provided by the phosphonate group.[8]

Comparison of the P–O bond lengths in free PMG, the Eu : PMG and Ca : PMG complexes, and the only known Eu(III) complex with phosphonate acid (ciliatine) is given in Table 3. A 1.58 Å bond length indicates a single P–OH bond. The coordination of calcium ions in Ca : PMG takes place *via* all three phosphonate group oxygen atoms as well as *via* a carboxyl group oxygen atom.[6] The differences in C–O bond lengths and C–C–O angles for free PMG and its complexes are given in Table 4.

The metal–metal distances in the investigated compound are 4.011 Å (Eu1···Eu1a) for the carboxyl dimer (1) and 5.940 Å (Eu2···Eu2a) for the phosphonate dimer (2). The Ln···Ln distance in dimer (1) is comparable to that in complexes Eu : MGly (4.014 Å) and Nd : Glygly (3.996 Å), and shorter

Table 2 Selected bond lengths (Å) and angles (°)

Eu1–O4	2.669(17)	Eu2–O7w	2.526(13)	P1–O1	1.499(14)
Eu1–O5	2.492(14)	Eu2–O13	2.599(22)	P1–O2	1.466(12)
Eu1–O1w	2.421(16)	Eu2–O2^{iv}	2.324(10)	P1–O3	1.593(15)
Eu1–O2w	2.421(14)	Eu2–O2′^{iv}	2.306(11)	P1–C1	1.809(15)
Eu1–O3w	2.454(17)	C11–O11	1.406(51)	P2–O1′	1.510(13)
Eu1–O4w	2.468(17)	C11–O12	1.310(35)	P2–O2′	1.483(14)
Eu1–O4^{i}	2.452(16)	C11–O13	1.423(19)	P2–O3′	1.596(12)
Eu1–O4′^{ii}	2.373(14)	C11–O14	1.321(27)	P2–C1′	1.802(23)
Eu1–O5′^{iii}	2.400(15)	C12–O21	1.381(19)	O4–C3	1.259(21)
Eu2–O1	2.315(12)	C12–O22	1.448(17)	O5–C3	1.244(30)
Eu2–O1′	2.244(12)	C12–O23	1.406(27)	O4′–C3′	1.285(25)
Eu2–O5w	2.507(20)	C12–O24	1.436(23)	O5′–C3′	1.245(28)
Eu2–O6w	2.465(18)				
O4–Eu1–O5	50.4(4)	O1–Eu2–O2^{iv}	149.1(5)		
O4–Eu1–O1w	86.5(6)	O1–Eu2–O2′^{iv}	93.4(5)		
O4–Eu1–O2w	120.7(5)	O1′–Eu2–O5w	72.7(5)		
O4–Eu1–O3w	143.5(5)	O1′Eu2–O6w	120.4(5)		
O4–Eu1–O4w	140.2(5)	O1′–Eu2–O7w	134.7(5)		
O4–Eu1–O4^{i}	76.6(5)	O1′Eu2–O13	78.1(6)		
O4–Eu1–O4′^{ii}	73.3(5)	O1′–Eu2–O2^{iv}	81.8(6)		
O4–Eu1–O5′^{iii}	73.9(5)	O1′–Eu2–O2′^{iv}	148.5(6)		
O5–Eu1–O1w	68.6(6)	O5w–Eu2–O6w	70.7(6)		
O5–Eu1–O2w	70.4(6)	O5w–Eu2–O7w	68.9(6)		
O5–Eu1–O3w	136.9(5)	O5w–Eu2–O2^{iv}	114.7(6)		
O5–Eu1–O4w	128.1(5)	O5w–Eu2–O2′^{iv}	139.8(6)		
O5–Eu1–O4^{i}	121.5(5)	O6w–Eu2–O7w	67.3(5)		
O5–Eu1–O4′^{ii}	107.5(5)	O6w–Eu2–O13	143.3(6)		
O5–Eu1–O5′^{iii}	70.6(3)	O6w–Eu2–O2^{iv}	73.8(6)		
O1w–Eu1–O3w	72.3(6)	O6w–Eu2–O2′^{iv}	83.8(6)		
O1w–Eu1–O4w	132.5(6)	O11–C11–O12	101.7(25)		
O1w–Eu1–O4^{i}	137.2(6)	O11–C11–O13	102.7(21)		
O1w–Eu1–O4′^{ii}	67.7(6)	O11–C11–O14	107.6(24)		
O1w–Eu1–O5′^{iii}	137.5(6)	O12–C11–O13	113.3(18)		
O2w–Eu1–O3w	82.6(6)	O12–C11–O14	115.4(22)		
O2w–Eu1–O4w	72.9(6)	O13–C11–O14	114.3(17)		
O2w–Eu1–O4^{i}	147.4(6)	O1–P1–O2	120.3(8)		
O2w–Eu1–O4′^{ii}	138.8(7)	O1–P1–O3	107.0(7)		
O2w–Eu1–O5′^{iii}	84.0(6)	O1–P1–C1	106.0(8)		
O3w–Eu1–O4w	70.1(5)	O2–P1–O3	109.6(7)		
O3w–Eu1–O4^{i}	100.0(5)	O2–P1–C1	109.6(8)		
O3w–Eu1–O4′^{ii}	72.3(5)	O3–P1–C1	103.1(8)		
O3w–Eu1–O5′^{iii}	140.3(5)	O1′–P2–O2′	117.6(8)		
O4w–Eu1–O4^{i}	77.4(5)	O1′–P2–O3′	110.1(8)		
O4w–Eu1–O4′^{ii}	123.7(5)	O1′–P2–C1′	105.2(8)		
O4w–Eu1–O5′^{iii}	70.5(5)	O2′–P2–O3′	109.5(7)		
O4^{i}–Eu1–O4′^{ii}	69.9(6)	O2′–P2–C1′	110.6(8)		
O4^{i}–Eu1–O5′^{iii}	74.4(5)	O3′–P2–C1′	103.0(8)		
O4′^{i}–Eu1–O5′^{iii}	135.8(5)	Eu2–O1–P1	155.5(8)		
O1–Eu2–O1′	84.2(5)	Eu1–O4–C3	88.7(12)		
O1–Eu2–O5w	85.8(5)	Eu1–O5–C3	97.4(13)		
O1–Eu2–O6w	136.5(5)	Eu2–O1′–P2	172.3(9)		
O1–Eu2–O7w	70.2(5)	Eu2–O13–C11	152.2(13)		
O1–Eu2–O13	71.9(6)				
Eu1–O4–C3–C2	−175.2(16)	Eu1–O5–C3–C2	175.0(15)		
Eu2–O1–P1–O2	−52.2(22)	Eu2–O1–P1–O3	71.2(21)		
Eu2–O1–P1–C1	−177.1(18)	Eu2–O1′–P2–O2′	37.1(69)		
Eu2–O1′–P2–O3′	−91.2(68)	P1–O1–Eu2–O1′	49.4(20)		
P1–C1–N1–C2	173.3(12)	P2–O1′–Eu2–O1	−50.1(68)		
P2–C1′–N2–C2′	−50.8(18)	O1–P1–C1–N1	−175.3(11)		
O2–P1–N1–C1	−129.8(14)	O2–P1–C1–N1	53.5(14)		
O3–P1–O1–Eu2	73.4(20)	O3–P1–C1–N1	−63.1(13)		
O4–C3–C2–N1	−170.4(17)	O1′–P2–C1′–N2	−159.3(13)		
O2′–P2–C1′–N2	−31.5(15)	O3′–P2–O1′–Eu2	−88.8(66)		
O3′–P2–C1′–N2	85.4(13)	O3′–O1′–Eu2–O1	−130.5(13)		
O4′–C3′–C2′–N2	163.7(16)	O5′–C3′–C2′–N2	−18.4(25)		
N1–C1–P1–O1	−175.3(11)	N1–C1–P1–O2	53.5(14)		
N1–C1–P1–O3	−63.1(13)	N1–C2–C3–O4	−171.5(18)		
N1–C2–C3–O5	11.1(24)	N2–C1′–P2–O1′	−159.3(12)		
N2–C1′–P2–O2′	−31.5(15)	N2–C1′–P2–O3′	85.4(13)		
N2–C2′–C3′–O4′	165.5(17)	N2–C2′–C3′–O5′	−22.4(25)		
C1–P1–O1–Eu2	−177.1(18)	C1–N1–C2–C3	−170.7(14)		
C2–N1–C1–P1	173.3(11)	C2–C3–O4–Eu1	−175.3(16)		
C2–C3–O5–Eu1	175.0(15)	C3–O4–Eu1–O5	−1.2(12)		
C3–O5–Eu1–O4	1.8(12)	C1′–P2–O1′–Eu2	158.4(66)		
C1′–N2–C2′–C3′	−63.8(20)	C2′–N2–C1′–P2	−50.8(18)		

Symmetry codes:
(*i*) $-x, -1-y, -z$; (*ii*) $-1+x, -1/2-y, -1/2+z$; (*iii*) $1-x, -1/2+y, 1/2-z$; (*iv*) $1-x, 1/2+y, 1/2-z$.

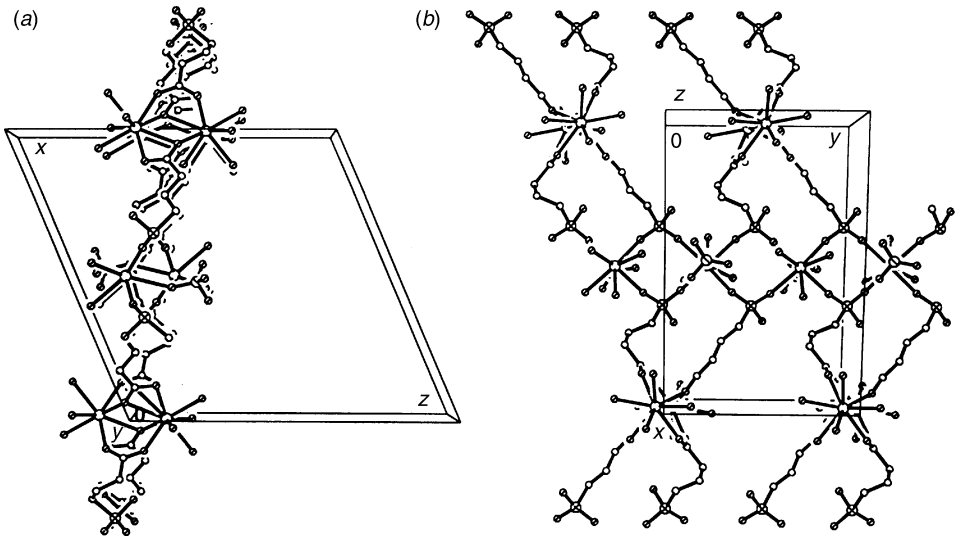

Fig. 2 SHELXTL (XP) drawing of a polymer layer parallel to the (102) planes: (*a*) in the unit cell projection viewed along the [010] direction; (*b*) in the unit cell projection viewed along the [100] direction.

than in the Nd : Gly (4.248 Å) compound. The distance in dimer (2) (5.940 Å) is much larger than that (5.093 Å) in the complex with ciliatine, where the coordination number is 6. The Eu1–O_C bond lengths in dimer (1) range from 2.373(14) Å to 2.669(17) Å, as in the case of Eu : MGly [2.387(12)–2.751(4) Å], while differences between Ln–O_C type bonds are slightly larger [2.397(3)–2.751(4) Å] in the glycylglycine compound. The longest bond in Eu : PMG and Eu : MGly is that of lanthanide with the bidentate oxygen atom of the three-bond carboxyl group, while in NdGlygly it is that of neodymium with the monodentate oxygen atom of the three-bond carboxyl group.

Eu2–O_P bond lengths in dimer (2) range from 2.24(1) to 2.32(1) Å and are much larger than those in the Lu:ciliatine complex, where they range from 2.196(6) to 2.210(5) Å. The longest bond in dimer (2) is the one between the Eu(III) ion and a perchlorate group oxygen atom [Eu2–O13 = 2.60(2) Å]. It is worth noticing that M–O_w and M–O_C bond lengths are comparable in dimer (1), whereas in dimer (2) the M–O_w distances are longer than M–O_P and similar to those in dimer (1). The lanthanide ion bond with phosphonate oxygen atom in the investigated complex is stronger than that of carboxyl oxygen, which is reflected in the $^5D_0 \rightarrow {}^7F_0$ band positions in the emission spectrum, depending on different lanthanide ion environments.[11] The difference in their energy of 36 cm^{-1} can be considered as a nephelauxetic effect for two different europium environments provided by carboxyl group coordination in Eu1 and phosphonate group coordination in Eu2. Table 5 summarizes the fitting of coordination polyhedron for Eu1 and Eu2. The outer coordination sphere in Eu : PMG is made up of three perchlorate ions and one water molecule.

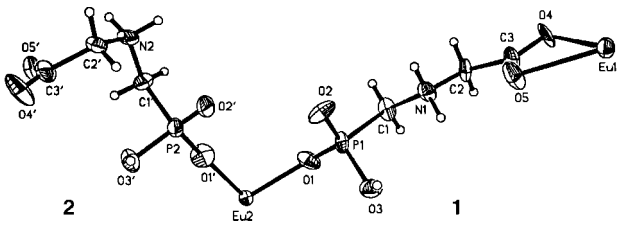

Fig. 3 SHELXTL (XP) drawing of two symmetrically independent ligand molecules (PMG) connected to the Eu2 and Eu1 atoms, with their atom labeling scheme. The remaining atoms are omitted, for clarity. The displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

The structure of $[Eu_2(HO_3PCH_2NH_2CH_2CO_2)_2(H_2O)_7(ClO_4)] \cdot 3ClO_4 \cdot H_2O$ is considerably different from that of $Ca[O_2CCH_2NH_2CH_2PO_3] \cdot 2\ H_2O$. The structure of the Ca : PMG compound is a three-dimensional polymer (not two-dimensional). Each calcium atom is bonded to four different glyphosate molecules and each glyphosate is bonded to four different calcium atoms (instead of two in the Eu compound). The calcium atom is seven-coordinate with four phosphate oxygens from three different glyphosates, one carboxylate oxygen from another glyphosate, and two water oxygens (the coordination number of Eu is eight). The carboxyl oxygen atom and all phosphonate oxygen atoms are involved in the coordination process, and the phosphonate group is responsible for bridging. The bridge type is also different (cyclic bridge).[6]

Between the carboxyl oxygen atom, phosphonate oxygen atom, amino nitrogen and coordinated water molecules in Eu : PMG hydrogen bonds form, just as in the free *N*-phosphonomethylglycine crystal structure and its calcium complex. Additionally, perchlorate groups are involved in hydrogen bond creation in Eu : PMG. The polymeric character of Eu : PMG as well as the hydrogen bond network form quite a rigid structure, which is indicated by small displacement parameters (see Electronic Supplementary Information).

The two PMG molecules in the title complex are shown in Fig. 3, connected by Eu2 and Eu1 atoms, and their torsion angles are given in Table 2. The first molecule (**1**) begins at the O1 atom and the second (**2**) at the O1′ atom. *Their conforma-*

Table 3 Comparison of P–O bond lengths (Å) in free PMG and different complexes

	P1–O1	P1–O2	P1–O3	P2–O*x*′[a]	P–O mean$_1$[b]	P–O mean$_2$[c]	P–O mean$_3$[d]
Free PMG	1.576(3)	1.500(3)	1.501(3)				
Eu : PMG	1.50(1)	1.47(1)	1.59(1)	1.51(1) 1.48(1) 1.60(1)			
Ca : PMG	1.516(1)	1.518(1)	1.519(1)				
Eu : ciliatine					1.491(5)	1.497(9)	1.579(8)

[a] x = 1–3; [b] P1–O1, P2–O4 and P3–O7; [c] P1–O2, P2–O5 and P3–O8; [d] P1–O3, P2–O6 and P3–O9.

Table 4 Differences in C–O bond lengths and C–C–O bond angles of the carboxylate group in free PMG and PMG complexes

	C–O/Å	C–C–O/°
Free PMG	0.1	14
Eu : PMG	0.04 (type I) 0.02 (type II)	3
Ca : PMG	0.01	1

tions are quite different. Although the dihedral angles O1–P1–C1–N1 (−175.3°) and O1′–P2–C1′–N2 (−159.3°) are similar, which means that O1 and N1 and also O1′ and N2 are in nearly perfect *anti* conformations relative to each other, as in the free ligand and in the Ca(II) complex, the basic difference between the conformations of **1** and **2** occurs in the dihedral angles C1–N1–C2–C3 (170.7°) and C1′–N2–C2′–C3′ (−63.8°). This means that in **1** C1 and C3 are in a nearly perfect *anti* conformation (in the calcium glyphosate structure they are in an approximately *anti* conformation with a torsion angle of 143°), while in **2** C1′ and C3′ are in an approximately *gauche* conformation, as in the free ligand with a respective torsion angle of 74.6°. Essential differences occur also between other torsion angles in **1** and **2** (see Table 2). For example, the P1–C1–N1–C2 torsion angle in **1** equals 173.3° (P and C2 atoms in an *anti* conformation relative to each other), and the P2–C1′–N2–C2′ torsion angle in **2** is −50.8° (P2 and C2′ in an approximately *gauche* conformation). It should be mentioned that—for these comparisons—the signs of all torsion angles in the crystal of the title compound can be changed, because the structure is centrosymmetric.

Conclusions

1. Based on the $[Eu_2(HO_3PCH_2NH_2CH_2CO_2)_2(H_2O)_7(ClO_4)] \cdot 3ClO_4 \cdot H_2O$ X-ray data, the formation of a two-dimensional polymer consisting of two dimeric subunits, created by carboxyl and phosphonate bridges, was shown.
2. Perchlorate ions are involved in the inner coordination sphere of Eu(III), two in each dimeric subunit formed by phosphonate groups.
3. The rigid two-dimensional polymeric structure leads to formation of centrosymmetric dimeric units as in the polymeric structure of the Nd(III) complex with the dipeptide Glygly.
4. The conformations of the two PMG molecules are quite different.

Table 5 The calculated shape characteristics of polyhedrons of Eu : PMG (Δ indicates the deviation from an ideal polyhedron)

Eu_1	Eu_2
0.0822 Δ_{TCTP}	0.0945 Δ_{SAP}
0.1838 Δ_{CSAP}	0.1052 Δ_{Dod}
	0.0695 Δ_{BCTP}

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