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Novel polynuclear compound of europium with *N*-phosphonomethylglycine: spectroscopy and structure

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Abstract

Phosphonic acid analogues of amino acids display interesting biological activities, the possible applications of which range from medicine to agriculture. Aminophosphonates are found in tissues as free compounds but their most frequent forms of occurrence include complex structures, such as lipids, proteins and polysaccharides [1]. For the first time, to our knowledge, lanthanide compounds with *N*-phosphonomethylglycine were obtained and analyzed by X-ray diffraction methods. The compound is polynuclear, with unexpected architecture, and crystallizes in the $P2_1/c$ space group (cell parameters $a=17.788(4)$ Å, $b=10.706(2)$ Å, $c=18.560(4)$ Å, $\beta=113.37(3)°$, $Z=4$). Two nonequivalent metal sites exist in the structure. Both carboxyl and phosphonate groups of the ligand are involved in metal ion coordination forming two centrosymmetric dimers: one by the carboxyl (simple and chelating) bridges, and one by phosphonate groups. Moreover, in the latter dimer, coordination of metal ion is completed by three water molecules and one oxygen of perchlorate ion, thus the coordination number is 8. In the former dimer, additional water molecules are bonded and the coordination number of Eu becomes 9, with a little different distortion. The M–M distances are 4.012 and 5.940 Å for carboxyl and phosphonic dimers, respectively. The compound was characterized by IR and electron spectroscopy methods. Absorption, excitation and emission spectra were measured down to 77 K. Electron transition probabilities and splitting of levels were analyzed and compared to the structural data. Assignment of the vibronic components in electronic transitions, which obey the selection rule $\Delta J=0.2$ was made on the basis of IR spectra. © 1998 Elsevier Science S.A.

Keywords: Spectroscopy; Luminescence; Absorption; Eu(III); *N*-Phosphonomethylglycine

1. Introduction

In the last two decades great efforts have been made to investigate the structure, and physical and biological functions of aminophosphonic acid.

The biological activity, as inhibitors of metabolic processes, herbicides, neuroactive compounds, anticancer drugs, phototoxic agents, etc., was the reason of the increase of the interest [1]. Besides, in most of the above processes the complexation with metal ions certainly plays an important role and may partially explain the mechanism of the processes with metal involved. The main studies have focused on the solution chemistry, a few only concern the synthesis and structure of metal complexes in solids. Only few literature reports give X-ray data of divalent and trivalent metal compounds with *N*-phosphonomethylglycine (further denoted PMG). Since the lanthanide ions are often used as spectroscopic probes in studies of biologically important systems, we have undertaken studies of the structure and spectroscopic properties of the europium complex with PMG, the first example of a compound with this type of potentially tridentate (N, O_C, O_P) ligand.

2. Experimental

Europium compounds with *N*-phosphonomethylglycine (formula, $Eu_2(HO_3PCH_2NH_2CH_2COO)_2(H_2O)_8(ClO_4)_4$; further denoted EuPMG) was obtained from aqueous solutions of europium perchlorate ($c\approx10^{-2}$ M). The molar ratio of M:L was kept at 1:1. The concentration of metal in crystals was determined complexometrically and by inductively coupled plasma atomic emission spectrometry (ICP-AES) method. Other elements were determined by elemental analysis.

X-ray data were collected with Mo Kα radiation at 293

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K on a KUMA Diffraction KM-4 diffractometer. The number of collected reflection was 6347, with 5870 independent reflections, and 3655 observed reflections with $F_0 > 4\sigma(F_0)$.

Well-resolved absorption spectra were measured on a Cary-Varian 5 spectrophotometer equipped with an Oxford helium flow cryostat in the 80–293 K temperature range.

The excitation and emission spectra were obtained at 77 K and room temperature using an SLM Aminco SPF 500 spectrofluorometer. IR spectra were detected in the 30–4000 cm^{-1} region with a Brucker FS88, FTIR spectrometer.

3. Results and discussion

N-Phosphonomethylglycine is a member of the chelating group of aminopolyacid series which includes both aminocarboxylic acid and alkylphosphonic acid functions. The neutral acid exists in a zwitterionic form as $-HO_3PCH_2NH_2^+CH_2COOH$ [2–4]. In a coordination of metal ions, oxygen from phosphonate and carboxylate groups are involved; the amino N donors can also take part in this.

The structure of the title compound is polymeric with unexpected architecture in which, except for MPG groups, oxygen atoms of perchlorate groups are engaged (Fig. 1). This polymeric chain is composed of two types of dimeric subunits. The first type is created by carboxyl simple and chelating bridges, and the second type by phosphonate groups; in this latter dimeric unit coordination of metal ions is completed by two oxygens of two perchlorate groups. Two nonequivalent metal sites exist in the structure with eight- and nine-fold coordinated metal ions.

Each of the eight-fold coordinated metal ions (Eu_2) in a phosphonic dimer comprise, in its coordination sphere, four oxygens from phosphonic groups, three water molecules and one oxygen from perchlorate anion. The perchlorate ions are involved, to our knowledge, only in one type of orthorhombic praseodymium complex with glutamic acid crystallized from aqueous solution [5]. Nine-fold coordination of metal (Eu_1) in a carboxylic dimer unit is built up from four oxygens from carboxylic groups, additionally one oxygen of a chelating bridging type and four water molecules. The M–M distances are 4.012 and 5.940 Å for carboxyl and phosphonic dimers, respectively. Four $Eu_2(HO_3PCH_2NH_2CH_2COO)_2(H_2O)_8(ClO_4)_4$ units occur in the unit cell. In the title compound crystals, the carboxyl groups are deprotonated, and the phosphonic ones are partially protonated, which is clearly shown in the P–O bonding lengths. The mean values of M–L bonds are 2.464 and 2.417 Å for Eu_1 and Eu_2, and the differences between the longest and shortest ones are equal to 0.287 and 0.400 Å, respectively, for Eu_1 and Eu_2 coordination. This type of

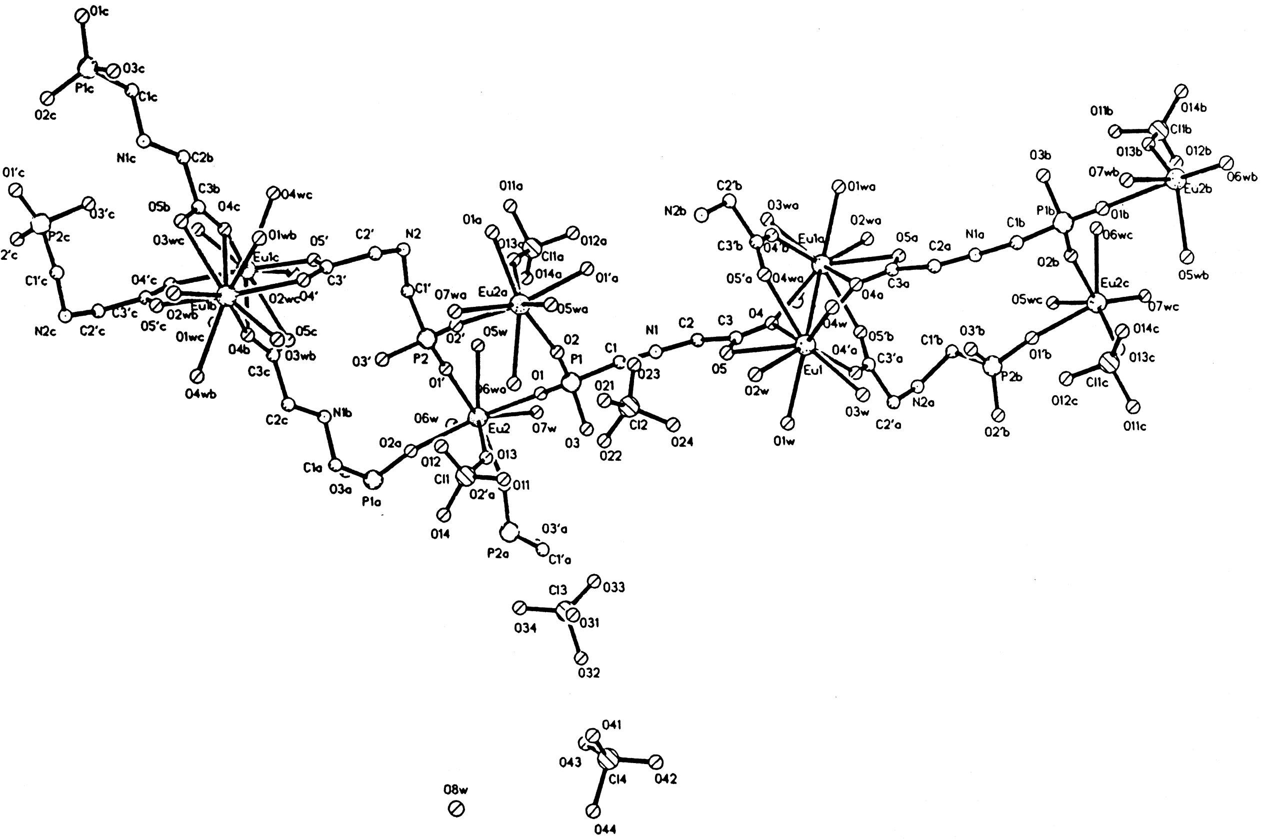

Fig. 1. Crystal structure of the $Eu_2(HO_3PCH_2NH_2CH_2COO)_2(H_2O)_8(ClO_4)_4$.

bridging structure differs from that seen in a calcium complex where phosphonic bridges are the chelating bridging ones, in contrast to our system.

Each calcium atom is bonded to four different glyphosate molecules, and each glyphosate is bonded to four different calcium atoms. The calcium atom is seven-fold coordinated with four oxygens from three different phosphonate groups, one carboxylate oxygen from another glyphosate, and two water oxygens [6,7]. The type of phosphonic bridge in the title compound is the same as in Cu^{2+}, Zn^{2+}, Co^{2+} complexes of aminomethylphosphonate [8–10].

The title compound structure differs drastically from the structure of Cu^{2+} chelate, where all ligand donor atoms are involved in metal ion coordination. The complex Cu(II)–PMG contains two discrete chelate rings around each metal ion, with members of the chain holding together by unidentate and bidentate coordination to a bridging phosphonate group [11].

The structure parameters must be reflected in the spectroscopy of the system under study. Europium(III) spectra in the visible and UV regions are reigned mainly by transitions from the $^7F_0$ ground state to the excited state multiplets; ^5D_J, ^5G_J and ^5L_J. Since the $^7F_1$ state lays very close in energy to the $^7F_0$ one (≈350 cm^{-1}), both these levels are populated at room temperature. Sometimes very weak transitions from Stark components of the $^7F_2$ level are also observed in the 5200–6000-Å energy region. Besides the f–f transitions, CT bands can locate in the UV region. Their energy depends on the optical electronegativity of ligand and the metal uncorrected value, according to the relation given by Ryan and Jørgensen [12].

Two symmetry centres of metal ions in two centrosymmetric dimers of the title compound are well confirmed by the emission and excitation spectra recorded at 77 K in the range of $^5D_0 \rightarrow {}^7F_0$ transition (see Figs. 2 and 3). The two components are quite well resolved with the half-band width equal to 23 and 20 cm^{-1} for the two europium centres.

The respective $^5D_0 \rightarrow {}^7F_0$ bands are located at the energies 17 301 and 17 265 cm^{-1} and are recorded at the same energies in absorption spectra. The bands are separated by 36 cm^{-1}, which can be considered as a nephelauxetic effect for two europium environments given by carboxyl group coordination in Eu_1 and phosphonic bonding with second europium ions.

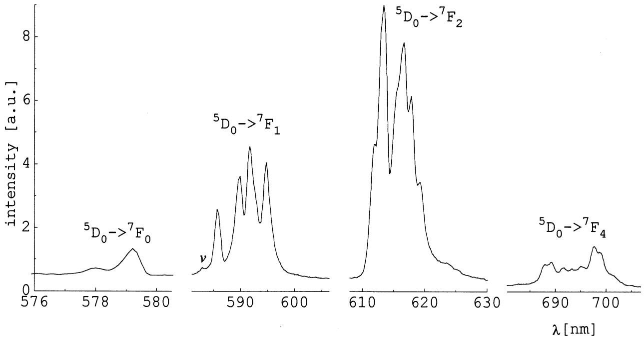

Fig. 2. Emission spectra of the $Eu_2(HO_3PCH_2NH_2CH_2COO)_2(H_2O)_8(ClO_4)_4$ at 77 K.

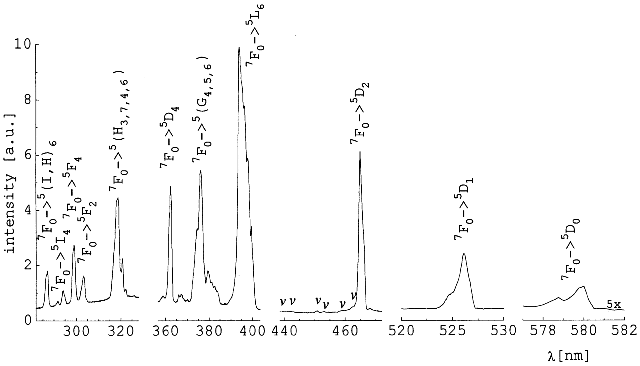

Fig. 3. Excitation spectra of the $Eu_2(HO_3PCH_2NH_2CH_2COO)_2(H_2O)_8(ClO_4)_4$ at 77 K.

Similarly, in other $^5D_0 \rightarrow {}^7F_J$ transitions the number of components exceeds that expected for two symmetry centres if one assumes the ideal coordination polyhedra with one exception (C_{2v} for Eu_2 and C_{4v} for Eu_1) (see Figs. 2 and 3).

Three possible coordination polyhedra could be built up for CN 8. The first type, dodecahedron (Dod), has symmetry close to D_{2d}, the second one (square antiprism, SAP) has D_{4h} symmetry and, finally, the bicapped trigonal prism (BCTP) is indicated by a fitting procedure (Table 1), which allows us to take into account the C_{2v} symmetry. For this (Eu_2) centre the most probable intensity of one component in the $^5D_0 \rightarrow {}^7F_0$ transition is significantly higher and allowed by selection rule. For the second type of metal coordination with CN 9, C_{4v} symmetry can be assumed for capped square antiprism (CSAP) and D_{3h} for tricapped trigonal prism (TCTP). The former symmetry, as well as C_{2v} for CN 8, corresponds quite well to the number of Stark components in the emission spectra at 77 K observed in our system (Fig. 2). In the bands which correspond to $^5D_0 \rightarrow {}^7F_J$ (where $J=0$, 1, 2, 4) transitions one can find two, five, six and eight lines. Judging from X-ray analysis, the symmetry of the europium ion in carboxyl surrounding is determined as D_{3h} (see Table 1), but deformation of the coordination polyhedra is relatively

Table 1
The calculated shape characteristics of polyhedrons and selected bond length of the $Eu_2(HO_3PCH_2NH_2CH_2COO)_2(H_2O)_8(ClO_4)_4$

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

$Eu_1–O_{mean(C)}=2.475$ Å; $Eu_1-O_{mean(H_2O)}=2.451$ Å; $Eu_2–O_{mean(P)}=2.297$ Å; $Eu_2-O_{mean(H_2O)}=2.510$ Å; $Eu_2–O_{13}=2.620$ Å.

strong and symmetry deviation parameter Δ is equal to 0.0822 Å^2. On the other hand, the spectroscopic measurement was made at 77 K, and temperature lowering can also distort the coordination polyhedra. Finally, the splitting of the levels rather confirms the C_{4v} symmetry. Since both types of coordination polyhedra are strongly distorted, it is very difficult to predict which components belong to which centre of Eu(III) ions in the range of $^5D_0 \rightarrow {}^7F_0$ transition. Most probably the weaker one belongs to carboxyl surrounding, since in D_{3h} symmetry (as well as in C_{3h}) 0–0 transition is forbidden by both magnetic and electric dipole selection rule. Similarly, in other $^5D_0 \rightarrow {}^7F_J$ transitions the analysis of separated components was very difficult. Separation of the components in the spectra which correspond to one europium site needs the selective excitation measurement of emission using separated lines at 17 301 and 17 265 cm^{-1}. However, we were able to grow up only a few very unstable single crystals which were very sensitive to the temperature changes. Moreover, they are also unstable when strong light beam is passing.

The majority of f–f transitions observed in absorption spectra of lanthanides are these of the electric dipole type, and their intensities can be calculated and reproduced by the Judd–Ofelt theory [13,14]. In europium ions few satisfy magnetic dipole selection rule and are well manifested in absorption and emission spectra. Results of intensity analysis of f–f transitions in the absorption spectra are presented in Table 2. Relative intensities of $^7F_0 \rightarrow {}^5L_6 / {}^7F_0 \rightarrow {}^5D_2$ bands at room temperature in the single crystal spectra and in oil are comparable, thus indicating relatively small effect of anisotropy (see Table 2). Moreover, relative intensities of separated $^7F_0 \rightarrow {}^5D_J$ transitions in absorption correspond quite well to those in excitation spectra, with the exception of UV region. Strong absorption was detected above 320 nm, which can be assigned to CT europium transition and transitions inside the ligand molecules. Note that this very intense absorption was not recorded in the excitation spectra up to 280 nm. Note also that splitting of bands at 77 K in excitation is even less detectable then that at room temperature in absorption. It is given by conditions of the measurement of excitation spectra with very low emission intensities. Our effort to measure the single crystal absorption spectra at 4 K failed. The spectrum of the powder of crystals in a thin layer of oil was detected at 80 K (see Fig. 4).

Table 2
Oscillator strength values of f–f transitions of the $Eu_2(HO_3PCH_2NH_2CH_2COO)_2(H_2O)_8(ClO_4)_4$ at 293K

Spectral region (Å)	$S'L'J'$	P ($\times 10^8$)
5803–5784	$^7F_0 \rightarrow {}^5D_0$	I 0.147
5784–5771		II 0.458
5430–5291	$^7F_1 \rightarrow {}^5D_1$	6.06
5291–5236	$^7F_0 \rightarrow {}^5D_1$	3.18
4670–4620	$^7F_0 \rightarrow {}^5D_2$	11.75
4034–3907	$^7F_0 \rightarrow {}^5L_6$	195.0
3899–3782	$^7F_1 \rightarrow {}^5G_2$; $^7F_0 \rightarrow {}^5G_2$	77.05
3782–3705	$^7F_0 \rightarrow {}^5G_4$, $^5G_5$, $^5G_6$	49.21
3710–3636	$^7F_1 \rightarrow {}^5D_4$	6.54
3636–3597	$^7F_0 \rightarrow {}^5D_4$	24.36

$^7F_0 \rightarrow {}^5L_6 / {}^7F_0 \rightarrow {}^5D_2 = 16.59$ for monocrystal at 293 K; $^7F_0 \rightarrow {}^5L_6 / {}^7F_0 \rightarrow {}^5D_2 = 20.92$ for powder at 293 K; $^7F_0 \rightarrow {}^5L_6 / {}^7F_0 \rightarrow {}^5D_2 = 17.73$ for powder at 80 K.

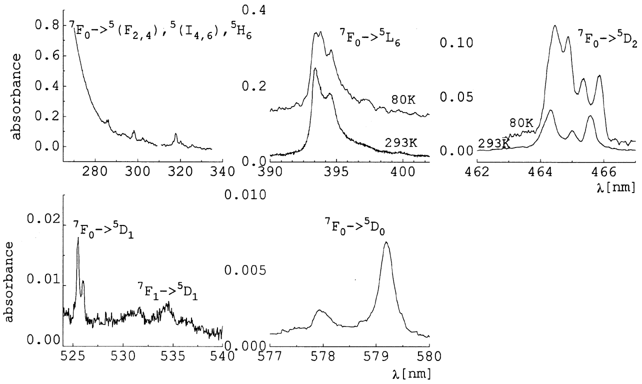

Fig. 4. Absorption spectra of the $Eu_2(HO_3PCH_2NH_2CH_2COO)_2(H_2O)_8(ClO_4)_4$ crystal at 273 K and powder of crystals in thin layer of oil at 80 K.

Low intensities of emission are caused by multiphonon relaxation processes which effectively quench europium emission from the $^5D_0$ level. The high energy OH vibrational mode promotes the nonradiative relaxation; moreover, ν_{CO} mode could also take part in that process. For that reason, emission spectra are almost undetectable at room temperature, fluorescence was measured at 77 K. Fig. 2 shows emission spectra recorded at 77 K. Quite good splitting of the emission lines was recorded. Strong electronic lines are accompanied by weak sidebands, the intensities of which are significantly higher in the excitation spectra. These lines could be a result of vibronic coupling and double excitation processes in the polymeric systems. Vibronic components occur between crystal field electronic levels with simultaneous excitation (or de-excitation) of a phonon or vibrational mode. Several vibronic transitions are promoted by internal ligand vibrations as well as by ($MO_{8/9}$) coordination cluster motions. Attribution of the vibronic components is given in Table 3. It is

Table 3
Vibronic components in luminescence and excitation spectra of the $Eu_2(HO_3PCH_2NH_2CH_2COO)_2(H_2O)_8(ClO_4)_4$ crystal

Transition	Energy (cm^{-1})	ΔE (from 0-phonon line) (cm^{-1})
$^5D_0 \rightarrow {}^7F_2$	$\underline{16\,811}$	
	17 154	343 δ(COO)
$^7F_0 \rightarrow {}^5D_2$	$\underline{21\,505}$	
	21 633	128 δ(LnOLn)
	21 798	293 ν(LnO)
	22 067	562 π(COO)
	22 185	680 τ(OCO)
	22 585	1080 $\nu_s(ClO_4)$?
	22 655	1150 ν(PO)
	22 740	1232 ν(Cl–O_4)?

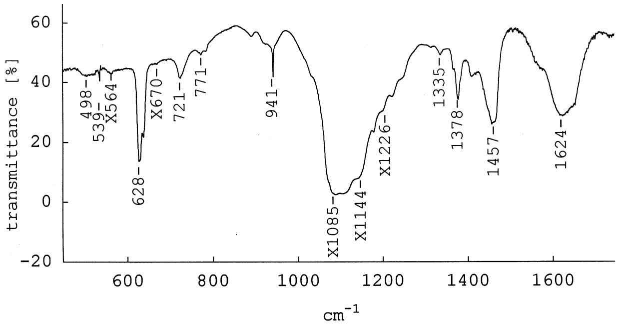

Fig. 5. IR spectra of the $Eu_2(HO_3PCH_2NH_2CH_2COO)_2(H_2O)_8(ClO_4)_4$ crystals at 273 K.

not the intention of the authors to perform vibrational analysis of the systems under study, but to find a good relation with the vibrational modes found in IR spectra (Fig. 5). Note that the strongest components can be assigned to the ν_{CO}, τ_{CO}, δ_{OCO}, $\rho_{(H_2O)}$ as well as to ν_{PO} modes, that means frequencies of these groups of ligand molecules which are involved in metal ion coordination. This effect corresponds well to the relation of Blasse [15,16] describing the vibration transition probabilities. The P_ν remains in a straight relation to $R = M–L$ distances, as well as to the matrix elements of electronic hypersensitive transition, and to the frequencies of vibrational transitions. The higher intensities of vibronic components in excitation spectra can be explained with regard to the CT state mechanism [17,18] in the creation of vibrational states proposed by Hoshina.

4. Conclusions

(1) A novel polynuclear europium compound with *N*-phosphonomethylglycine was obtained in the form of monocrystals.

(2) X-ray analysis shows creation of two types of dimeric units involving both carboxyl and phosphonate groups of the ligand. Further, polymeric chains composed of dimeric units are formed.

(3) Unexpectedly, perchlorate ions take part in metal ion coordination.

(4) The complex was characterised by absorption, emission and excitation spectra.

(5) Electron transition probabilities and splitting of the levels were analysed and compared to the structural data.

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