From structural properties of the Eu^{III} complex with ethylenediaminetetra(methylenephosphonic acid) (H₈EDTMP) towards biomedical applications[†]

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Crystals of Eu^{III} with ethylenediaminetetra(methylenephosphonic acid) (H₈EDTMP) and with ethylenediaminetetraacetic acid (H_4EDTA) have been synthesized in the same experimental conditions and their X-ray analyses have been performed. The EDTMP ligand wraps the Eu^{III} ion in a fashion similar to its carboxylic analogue, EDTA, *i.e.* coordinating through two nitrogen atoms and four oxygen atoms in such a way that only one oxygen atom from each phosphonate group is bonded to the central ion. The coordination sphere is completed by two oxygen atoms of the bidentate carbonate anion in the case of the Eu^{III}-EDTMP complex, whereas the inner sphere of the Eu^{III}-EDTA crystal is completed by three water molecules. Spectroscopic studies (UV-Vis and ³¹P NMR spectra) of Eu^{III}-EDTMP solutions at controlled pH showed that the replacement of inner sphere water molecules and/or OH hydroxy groups by a carbonate anion in the Eu^{III}-EDTMP complex at physiological pH results in the formation of $[Eu(EDTMP)(CO_3)]^7$ species which is thermodynamically stable and kinetically inert. The affinity of the carbonate anion towards the EuIII-EDTMP species was studied by analysis of f-f intensities and luminescence decay rates. The dissociation constant of the Eu^{III}-EDTMP-carbonate complex was found to be approximately 43 mM. The presented results may be helpful in understanding the role played by the ¹⁵³Sm^{III}-EDTMP complex known as Quadramet[®] in the seeking of metastatic tissue in bones as well as possibly giving some premises for future ligand design of these types of complexes with lanthanide radionuclides.

Introduction

Recently a great interest in studying lanthanide complexes with polyamino polyphosphonic ligands has been observed. One of the reasons for which these chelate complexes have been extensively investigated is their potential use in biomedical diagnosis1 and in cancer therapy.2,3 Contrary to the lanthanide complexes with 1,4,7,10-tetraazacyclododecane-1,4,7,10tetrakis(methylenephosphonic acid) (H₈DOTMP) or related cyclic ligands, which have been widely studied in solutions and in single crystals,^{1,4} knowledge of the possible structure of Ln^{III} species with acyclic polyaminopolyphosphonates is still fragmentary.⁵⁻⁹ In spite of this, the ¹⁵³Sm^{III} complex with ethylenediaminetetrakis(methylenephosphonic acid) (H₈EDTMP), known as Quadramet[®], is commonly used for the palliation of pain from metastatic bone cancer.^{2,3} Difficulties with estimating stability constants by means of the potentiometric method for lanthanide complexes with the EDTMP ligand are known.¹⁰⁻¹² The stability constants determined for the Ln^{III}-EDTMP system differ up to ten orders of magnitude depending on the experimental conditions.¹² It was shown that protonated species of the Ln^{III}-

EDTMP complexes are kinetically inert, whereas the deprotonation of the ligand leads to higher lability of species as found from the kinetic studies of the Eu^{III}–EDTMP system.⁹ The latter studies also proved that the kinetic behaviour of the Ln^{III}–EDTMP species is in contrast to that observed for the Ln^{III}–EDTA complexes.⁹ Some insight in the formation of lanthanide acyclic polyaminopolyphosphonate species in aqueous solution was gained previously by the luminescence spectroscopy studies.^{7,8} These studies performed on the 1 : 1 Eu^{III}–EDTMP complex have revealed that species which appear in aqueous solutions at pH above 6 are monomeric and contain, besides the EDTMP ligand, two water molecules in the inner sphere of the Eu^{III} ion.⁷

Previously, by applying the method of crystallization for anionic lanthanide complexes with polyaminopolycarboxylic acids described by Ruloff *et al.*,¹³ we demonstrated the usefulness of the guanidinium countercation for obtaining crystals with different coordination geometry.¹⁴ For this reason we have decided to use the guanidinium cation in the form of guanidinium carbonate for crystallization of highly negative anionic lanthanide complexes with polyphosphonic acids.¹⁵ Following this approach we have been able to obtain in the same experimental conditions crystals of the Eu^{III}–EDTMP complex and of its carboxylic analogue, Eu^{III}–EDTA. In this work we present their X-ray analyses and the spectroscopic results for both complexes in aqueous solutions and in the form of single crystals.

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 $[\]dagger$ Electronic supplementary information (ESI) available: Fig. S1: View of the unit cells of $[C(NH_2)_3]_7[Eu(EDTMP)(CO_3)]\cdot 10H_2O$ and $[C(NH_2)_3][Eu(EDTA)(H_2O)_3]$. See DOI: 10.1039/b606420e

Results and discussion

Crystal structures

The crystal structures of the Eu^{III} compounds with EDTMP EDTA, $[C(NH_2)_3]_7[Eu(EDTMP)(CO_3)] \cdot 10H_2O$ and and $[C(NH_2)_3][Eu(EDTA)(H_2O)_3]$ respectively, were determined. Both crystals were obtained by the same method of crystallization with the pH of the natant solution 10.7 in each case (see Experimental section for further details). The crystals are composed of the respective complex anions, guanidinium cations and water molecules. Both the complex anions are presented in Fig. 1, while the cell packing views are given in Fig. S1 (see ESI[†]). Selected bond lengths of both compounds are given in Table 1. The presence of the guanidinium cation in the Eu^{III}-EDTA crystal does not bring about a change of the composition of the coordination environment of Eu, which is the same (four O and two N atoms from the EDTA ligand and three water molecules) as in the earlier reported various salts of Eu^{III}-EDTA complexes.¹⁶ Since each of the counterions, namely Na⁺, K⁺, NH₄⁺ and a guanidinium cation, interacts with the anionic $[Eu(EDTA)(H_2O)_3]^-$ complex through different hydrogen-bonding networks, small differences in the Eu^{III}-ligand distances are observed in crystals of these salts.¹⁶ One may notice, for instance, a small decrease of the Eu^{III}–O(COO⁻) distances and elongation of the Eu^{III}–N as well as the Eu^{III} –O(H₂O) distances in the guanidinium crystal (this work) as compared with the sodium one.^{16a}

Although the EDTMP ligand has twice as many oxygen donor atoms as the EDTA ligand, it wraps the Eu^{III} ion in the same fashion as its carboxylic analogue, *i.e.* by two nitrogen atoms (N1, N2) and four oxygen atoms (O1, O6, O8, O10) in such a way that only one oxygen atom from each phosphonic group is coordinated to the central ion and the Eu–O(PO₃^{2–}) bond distances are similar (Table 1). All bond distances (C–C, C–P, C–N and P–O) within the ligand backbone are very similar to those determined for the free ligand (H₈EDTMP).¹⁷ The P–O bond distances when the O atoms are coordinated to the Eu^{III} ion are generally slightly elongated and resemble the P–O(H) distances in the free ligand.¹⁷

Due to the presence of bulkier, tetrahedral phosphonic groups and longer C–P bonds in the Eu^{III}–EDTMP crystal as compared with the planar carboxylic groups and shorter C–COO distances in the Eu^{III}–EDTA complex, free space available for other ligands (usually solvent molecules) around the central ion is more limited

Eu ^{III} –EDTMP		Eu ^{III} –EDTA	
Eu–O6	2.409(2)	Eu–O1	2.426(2)
Eu–O1	2.361(2)	Eu–O3	2.458(2)
Eu–O8	2.343(2)	Eu–O5	2.392(2)
Eu-O10	2.376(2)	Eu–O7	2.383(2)
Eu-O _{av}	2.372(28)	Eu–O _{av}	2.415(34)
Eu–O23	2.419(2)	Eu-OW1	2.464(2)
Eu–O22	2.446(2)	Eu–OW2	2.435(2)
Eu-O _{av}	2.432(19)	Eu–OW3	2.528(2)
		Eu–O _{av}	2.476(48)
Eu-N1	2.703(3)	Eu-N1	2.727(2)
Eu–N2	2.734(3)	Eu–N2	2.622(2)
Eu-N _{av}	2.718(22)	Eu-N _{av}	2.674(74)
Eu–Eu	9.998(3)	Eu–Eu	7.814(3)



Fig. 1 Molecular structure of (A) $[Eu(EDTMP)(CO_3)]^{7-}$ and (B) $[Eu(EDTA)(H_2O)_3]^{-}$ anions together with the atom numbering schemes.

in the phosphonate complex than in its carboxylate analogue. For instance, the coordination number of the lanthanide ion, eight, is one less in the Ln^{III} crystals with DOTMP^{4c} than that in DOTA (nine),¹⁸ the difference being brought about by coordination of one more water molecule in the case of the carboxylate complexes. The change of the coordination number of the Eu^{III} ion in its complexes with EDTMP and EDTA from eight to nine is also observed in the crystal structures presented in this work. Three water molecules which complete the first coordination sphere of the metal ion in the Eu^{III}–EDTA complex are replaced by two oxygen atoms (O22, O23) from the bidendate carbonate anion in the case of the Eu^{III}–EDTMP crystal. This is one of the reasons that the symmetry of the phosphonate complex is C_2 , while that of the carboxylate one is C_1 .

The coordination of the carbonate anion to the lanthanide ion in the present crystal, is however quite unexpected since up to date there are only few crystal structures known where the binding of carbonate to the lanthanide ion has been achieved at ambient conditions (temperature and pressure) of synthesis.¹⁹

It is perhaps of note that the X-ray analysis of the $[C(NH_2)_3]_7[Eu(EDTMP)(CO_3)] \cdot 10H_2O$ crystal has revealed, contrary to the X-ray results of the H₈EDTMP ligand,¹⁷ a slight nonequivalence of the phosphonate groups. This point may be illustrated by the values of angles between the vectors Eu–P and Eu–O21 (the latter determines the approximate twofold symmetry axis C_2 of the complex anion). Thus the angles are slightly greater in the case of P2 and P3 than those involving P1 and P4. They amount to 117.8° (O21–Eu–P2), 109.9° (O21–Eu–P3), 102.0°

(O21–Eu–P1) and 105.5° (O21–Eu–P4). On the other hand O22 and O23 atoms from the carbonate anion are nearer to the P2 and P3 phosphonate groups than to the P1 and P4 ones. In this way the carbonate anion is located in a quasi-saddle, with P1 and P4 phosphonate groups supporting the anion from both sides, and the CO_3^{2-} plane is almost parallel to the P2–P3–Eu plane and perpendicular to the P1–P4–Eu plane. Furthermore, the lateral support of the anion is strengthened by two guanidinium cations which bridge the phosphonate groups with the coordinated O carbonate atoms by relevant H-bonds. Namely one of the cations is H-bonded to O10 (of P4 group) and to O22, whereas the other links O6 (of P1) with O23. Such a system brings about the CO_3^{2-} coordination rigidity.

Spectral results

The f-f transition spectra of the Eu^{III} ion are one of the most convenient among the spectra of all lanthanide ions due to the fact that the ground ${}^{7}F_{0}$ and the emitting ${}^{5}D_{0}$ states of this ion are nondegenerate.²⁰ For this reason the number of components observed in the ${}^{7}F_{0} \leftrightarrow {}^{5}D_{0}$ transitions directly renders the number of chemically distinct environments of the Eu^{III} ion. These transitions are forbidden by the symmetry selection rule when the local symmetry of the Eu^{III} complex is high or when an inversion centre in the Eu^{III} species is present. The position of the ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$ transition is also used to study the nephelauxetic effect in europium compounds.²¹ This effect is interpreted as a covalent contribution to the bonding between the metal ion and the ligands and is probably connected with metal-ligand distances, coordination numbers and the total charge of the first coordination sphere. The ${}^7F_0 \rightarrow {}^5D_1$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transitions are magnetically allowed and therefore their intensities are essentially independent of the Eu^{III} environment. This feature of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition may be exploited to calibrate the intensities of other Eu^{III} f-f transitions in the emission spectra. The ${}^7F_0 \rightarrow {}^5D_2$ and ${}^5D_0 \rightarrow {}^7F_2$ transitions are known as hypersensitive transitions which means that their intensities are strongly influenced by the changes of the nearest surrounding of the Eu^{III} ion. The intensity of these transitions depend mainly on the symmetry of the Eu^{III} ion and/or the ligand polarizability.^{22,23}

On account of these characteristic f–f transition features it is of interest to compare spectral properties of both studied crystals as well as the relevant complexes in aqueous solutions, particularly the properties of the Eu^{III}–EDTA complex in aqueous solution which are rather well recognized.^{24,25}

Spectra of the f-f transitions. The corrected emission spectra of single crystals and of their natant solutions, *i.e.* solutions with $1 : 1 \text{ Eu}^{III}$ to ligand ratio basified with guanidinium carbonate to pH 10.7 as well as of solutions with pH adjusted by NaOH are presented in Fig. 2. As can be seen, the intensity of the $^{7}F_{0} \rightarrow {}^{5}D_{0}$ transition is much weaker in the crystal of the Eu^{III}–EDTMP complex than that observed in the Eu^{III}–EDTA crystal. This fact is in accordance with a higher symmetry of the Eu^{III} surrounding in the former crystal, as has been disclosed by the diffraction study presented in the preceding section. One may also notice a high correspondence between the spectra of the Eu^{III}–EDTMP–carbonate complex in solution and in the crystal whereas the corresponding spectra of the Eu^{III}–EDTA system differ considerably. The spectra of Eu^{III} solutions with both ligands at pH 10.7 vary strongly depending on whether the pH of the



Fig. 2 Emission spectra of Eu^{III} complexes with EDTMP and EDTA in the form of single crystals and in solutions.

solution was adjusted by guanidinium carbonate or NaOH. A distinct decrease of the ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$ intensity (for both ligands) in the solutions containing a carbonate anion as compared to the solutions with the pH fixed by NaOH results from the substitution of some water molecules and/or OH⁻ groups by the CO₃²⁻ anion. Contrary to the Eu^{III}–EDTA solutions of the sodium salt, for which no considerable changes of the shape of f–f bands are observed in the pH range between 5.4 and 10.7, a strong influence of pH changes on the Eu^{III}–EDTMP spectra is clearly seen.

To obtain additional information about the studied systems, particularly those with the EDTMP ligand, the absorption spectra of the Eu^{III}-EDTMP and Eu^{III}-EDTA complexes were measured. The spectra of the ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$, ${}^{7}F_{0} \rightarrow {}^{5}D_{1}$ and ${}^{7}F_{0} \rightarrow {}^{5}D_{2}$ transitions together with the peak maxima are presented in Fig. 3. As can be seen in Fig. 3(A), in the ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$ spectra of the Eu^{III} complexes with EDTMP and EDTA in solutions of which pH was adjusted by NaOH, two well separated peaks occur indicating two different coordination arrangements of the Eu^{III} ion in both systems. Introduction of the carbonate anion to Eu^{III} complexes with EDTMP and EDTA at pH 10.7 brings about changes in the inner sphere of the metal ion. In the ${}^{7}F_{0} \rightarrow {}^{7}D_{0}$ spectrum of the Eu^{III}–EDTMP complex a single peak with the same energy at maximum (17261 cm⁻¹) as that of the crystal appears. Moreover, it may be supposed that among the two peaks found in the ${}^{7}F_{0} \rightarrow$ ⁷D₀ spectra of Eu^{III}–EDTMP solutions adjusted by NaOH, the red-shifted peak with energy similar to that of the crystal, may belong to species in which two oxygen atoms from water molecules and/or hydroxy groups are located in similar positions as the O atoms from the carbonate anion in the crystal. Since the peak positions of the remaining $^7F_0 \rightarrow \, ^7D_1$ and $^7F_0 \rightarrow \, ^7D_2$ transitions in spectra of the Eu^{III}-EDTMP-carbonate complex in the solution and in the crystal are similar, one may presume the presence of the [Eu(EDTMP)(CO₃)]⁷⁻ entity, found from the X-ray analysis, also in solution.

The appropriate spectra of the Eu^{III}–EDTA complex of the crystal and of the solution from which the crystals were obtained differ considerably. As was found previously, in the case of the Eu^{III}–EDTA–carbonate solution besides species with inner sphere



Fig. 3 Absorption spectra of (A) ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$, (B) ${}^{7}F_{0} \rightarrow {}^{5}D_{1}$ and (C) ${}^{7}F_{0} \rightarrow {}^{5}D_{2}$ transitions of Eu^{III} complexes with EDTMP and EDTA ($c_{Eu} = 40 \text{ mM}, d = 5 \text{ cm}$ for Eu^{III}–EDTMP solutions; $c_{Eu} = 20 \text{ mM}, d = 5 \text{ cm}$ for Eu^{III}–EDTMP solutions; $c_{Eu} = 20 \text{ mM}, d = 5 \text{ cm}$ for Eu^{III}–EDTA solutions; $c_{Eu} = 1.368 \text{ M}, d = 0.063 \text{ cm}$ for Eu^{III}–EDTMP crystal; $c_{Eu} = 3.642 \text{ M}, d = 0.067 \text{ cm}$ for Eu^{III}–EDTA crystal); instead of the ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$ absorption spectrum which could not be recorded for the Eu^{III}–EDTMP crystal due to its low intensity, the luminescence excitation spectrum ($\lambda_{em} = 612 \text{ nm}$) of this transition is displayed.

water molecules replaced by a carbonate anion also a carbonate complex with the Eu^{III} ion is formed.²⁶

Intensities of the f-f transitions. The oscillator strength values (*P*) of the ${}^7F_0 \rightarrow {}^5D_J$ transitions of the Eu^{III} ion in the studied systems were also determined and are given in Table 2. The *P* values of the ${}^7F_0 \rightarrow {}^5D_1$ transition calculated for all complexes are nearly constant. The high correspondence between the respective ${}^7F_0 \rightarrow {}^5D_J$ oscillator strength values of the Eu^{III}-EDTMP-carbonate crystal and the Eu^{III}-EDTMP-carbonate solution is in accordance with the resemblance of the absorption and emission spectra for both these systems. The high *P* values of the hypersensitive ${}^7F_0 \rightarrow {}^5D_2$ transition of both the crystal and the solution in comparison with a much lower *P* value of the NaOH-adjusted solution at pH 10.7 may be related to the influence of the carbonate polarizability on the Eu^{III} ion.

Since the direction of *P* changes observed for the Eu^{III}– EDTMP complex in sodium solutions seems to be associated with the protonation of Eu^{III} species, therefore intensities of absorption and emission transitions as the functions of pH of Eu^{III}–EDTMP solutions were plotted. Plots of these relations together with percentage contents of analogous Sm^{III}–EDTMP species calculated from the stability constants given by de Witt *et al.*¹² are shown in Fig. 4. As may be seen in this Figure there is no pH region in which the deprotonated [Eu(EDTMP)]^{5–} species would exist without significant admixture of other species.



Fig. 4 Absorption and emission intensities of Eu^{III}–EDTMP solutions as a function of pH ($\lambda_{exc} = 394.8$ nm in emission spectra). The included percentage contents of Sm^{III}–EDTMP species^[a] were calculated from ref. 12.

Binding of H₂O and/or OH⁻. The luminescence lifetime measurements of the Eu^{III}–EDTMP complex in the crystal and solutions at pH 10.7 and 7.5 have been measured. It is worth noting that the estimation of the inner sphere water molecules

 Table 2
 Oscillator strength values (P) of Eu^{III} complexes with EDTMP and EDTA

Eu ^{III} –EDTMP			Eu ^m –EDTA				
	$^7F_0 \rightarrow ^5D_0$	$^7F_0 \rightarrow ^5D_1$	$^7F_0 \rightarrow {}^5D_2$		$^7F_0 \rightarrow ^5D_0$	$^7F_0 \rightarrow ^5D_1$	$^7F_0 \rightarrow ^5D_2$
pH	$10^{8}P$	$10^{8}P$	$10^{8}P$	pН	$10^{8}P$	$10^{8}P$	$10^{8}P$
5.40	0.24	1.65	10.40	4.50	0.59	1.43	8.59
5.98	0.51	1.68	8.13				
7.18	0.77	1.64	6.44	7.50	0.63	1.45	8.72
8.10	0.79	1.64	6.06				
9.15	0.86	1.64	6.00				
10.70	0.88	1.63	6.24	10.70	0.61	1.49	10.49
10.70^{a}	0.22	1.48	19.62	10.70^{a}	0.48	1.53	19.42
Crystal	0.12^{b}	1.60	21.01	Crystal	0.65	1.45	4.95

pH of solutions adjusted by NaOH ^a pH of solutions adjusted by (gua)₂CO₃. ^b P value estimated from the excitation spectrum.

Table 3 Emission lifetimes (τ) and hydration numbers (q) of the Eu^{III}–EDTMP complex

Added compound	pН	$\tau_{\rm H_2O}/\mu s$	$\tau_{\mathrm{D}_{2}\mathrm{O}}/\mu\mathrm{s}$	q
Crystal (none) (gua) ₂ CO ₃ Na ₂ CO ₃ NaOH (gua) ₂ CO ₃ Na ₂ CO ₃ NaOH	10.70 10.70 10.70 7.50 7.50 7.50	1036 1022 1038 422 826 864 420	2107 2047 2412 2066 2016 2193	0.22 0.18 1.83 0.46 0.39 1.79

in this complex is difficult due to the fact that the excited state of the Eu^{III} ion will be also quenched by the hydroxy groups. The hydration numbers (q), or more strictly, the numbers of OH oscillators (2q) were determined from eqn (1):²⁷

$$q = 1.11(\tau_{\rm H_2O}{}^{-1} - \tau_{\rm D_2O}{}^{-1} - 0.31) \tag{1}$$

where $\tau_{H_2O}^{-1}$ and $\tau_{D_2O}^{-1}$ are the luminescence decay rates measured in H_2O and D_2O solutions. This equation complies with the deactivation equal to 0.31 ms⁻¹ by water molecules of the second coordination sphere. The results are presented in Table 3.

The close similarity between luminescence lifetimes determined for the crystal and both carbonate solutions at pH 10.7 of the Eu^{III}–EDTMP complex in H₂O clearly indicates the substitution of all OH oscillators originating from water molecules and/or hydroxy groups by a carbonate anion. As may be suggested by the number of OH oscillators calculated for the solution of which pH 10.7 was adjusted by NaOH, the dominant species in that solution contains one inner sphere water molecule and one inner sphere hydroxy group.

The *q* numbers calculated for the solution adjusted by NaOH to pH 7.5 (at this pH the distribution of Sm^{III} species is 30.8% [SmL]⁵⁻ and 68.4% [SmH₋₁L]⁶⁻¹²) are very similar to those at pH 10.7. The relatively low precision of the method does not allow detecting the shifts of the equilibrium between the species with two coordinated water molecules and that with one H₂O and one OH⁻ group.

³¹**P** NMR spectra. Further information about the solution structure of the Eu^{III}–EDTMP complex has been provided by NMR spectroscopy. The ³¹P NMR spectra of Eu^{III}–EDTMP solutions for which the pH was adjusted by NaOH, Na₂CO₃ and [C(NH₂)₃]₂CO₃ are presented in Fig. 5. In the spectra of the NaOH adjusted solutions of the complex one strong phosphorus resonance appears. It is located at 12.7 ppm in the spectrum of



Fig. 5 ³¹P NMR spectra of Eu^{III}–EDTMP solutions.

the solution at pH 5.4, similarly as the peak of the free ligand (12.6 ppm, pH = 5.4) but its width is 302 Hz as compared to the 6 Hz of the free ligand peak. The large width of this peak indicates that this resonance originates from the complexed ligand. Apart from this peak, another weak peak at 51.6 ppm with 340 Hz width is also observed at pH 5.4. As the pH is increased to 7.2, the peak at 12.7 ppm disappears and that at 51.6 gains in intensity. This suggests that the former peak corresponds to the protonated species [EuHL]^{4–} and [EuH₂L]^{3–}, which vanish at higher pH, as the speciation curves of analogous Sm^{III}–EDTMP complex indicate.¹² The peak at 51.6 ppm in the spectrum at pH 5.4 corresponds then to the [EuL]^{5–} species.

As long as the concentration of [EuL]⁵⁻ species is considerable, the intramolecular exchange is fast due to the fact that four phosphorus atoms are averaged. A significant broadening of the peak which is associated with the nearly complete formation of the hydroxy species of the complex at pH 9.2 may then reflect that the ligand exchange rate slows down. The appearance of a broad band divided into two observed resonances at pH 10.7 may mean that the structure of the complex becomes more rigid, thus the formation of double hydroxy species cannot be excluded.

The stabilization of the hydroxy Eu^{III} –EDTMP species increases remarkably when the H₂O and OH⁻ groups are replaced by a carbonate anion as is well demonstrated by two well resolved phosphorus peaks in spectra of the [Eu(EDTMP)(CO₃)]^{7–} complex. The appearance of two P resonances separated by 44.7 and 52.7 ppm in spectra of sodium and guanidinium solutions respectively, allows to observe the nonequivalence of phosphonate groups in the [Eu(EDTMP)(CO₃)]^{7–} species as may be predicted from the X-ray analysis, as well as the influence of countercations on the signal positions in the ³¹P NMR spectra.

Binding of carbonate. Since the electronic and ³¹P NMR spectra of Eu^{III}–EDTMP solutions at pH around 7.5 adjusted by Na₂CO₃ or $[C(NH_2)_3]_2CO_3$ are very similar to those recorded for alkaline solutions with carbonates at pH 10.7, we deemed it advisable to undertake studies of the Eu^{III}–EDTMP complex interaction with the carbonate ion at physiological pH. Such studies with physiologically available anions have been recently carried on Ln^{III} complexes with polyaminopolycarboxylates and with cyclen derivatives.^{26,28-31}

To the Eu^{III}-EDTMP complex adjusted by NaOH up to pH 7.5 in a HEPES buffer different amounts of NaHCO₃ were added. Binding of the carbonate anion towards the Eu^{III}-EDTMP complex was monitored by the intensity changes of the hypersensitive transitions in absorption and emission, and also by luminescence lifetime measurements. The intensity changes were followed by the determination of oscillator strength values (P) of the ${}^{7}F_{0} \rightarrow$ ${}^{5}D_{2}$ transition whereas the intensities of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition were calibrated to the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ones. Plots of *P* and *k* (where k is a decay constant rate of the excited state) changes as a function of added NaHCO₃ are shown in Fig. 6. Fitting of the three curves to equations which combine the measured quantities with concentrations of EuL and A (where A is HCO₃⁻ anion) as well as the dissociation $K_{\rm D}$ and association $K_{\rm A}$ constants of the EuLA complex were performed. The $K_{\rm D}$ and $K_{\rm A}$ constants of the equilibrium given by eqn (2):

$$EuLA \Leftrightarrow EuL + A$$
 (2)

are expressed as:

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$$K_{\rm D} = [\text{EuL}][\text{A}] / [\text{EuLA}], K_{\rm A} = 1 / K_{\rm D}$$
(3)

Table 4 The dissociation (K_D) and association (K_A) constants determined from different optical measurements for the Eu^{III}–EDTMP–carbonate complex

	Method of $K_{\rm D}$ and $K_{\rm A}$ determinations			
	Intensities			
	Absorption	Emission	Luminescence lifetimes	
$rac{K_{ m D}/{ m mM}}{K_{ m A}/{ m M}^{-1}}$	40.3 24.8	14.8 67.6	46.1 21.7	

The determined $K_{\rm D}$ and $K_{\rm A}$ constants from different measurements for the Eu^{III}–EDTMP–carbonate complex are given in Table 4. While the data obtained from absorption intensities and luminescence lifetime measurements are in good agreement, the results estimated from emission intensities differ from them about three. The only probable reason of this disagreement was the timescale. The absorption spectra and luminescence lifetime measurements were taken after one day of solution preparation, whereas the emission spectra of those solutions were recorded a week later. A very slow establishing of the equilibrium was probably a reason of the lower value of the dissociation constant obtained from the emission intensities measurements.

Comparing the obtained values of the dissociation constants with the *K* values available from the literature^{26,29} we see that the discussed system is an order of magnitude more stable than the Eu^{III}–EDTA–carbonate complex ($K_{\rm D} = 298$ mM),²⁶ while similar or higher affinity of the carbonate anion towards europium chelates was estimated for the neutral and positively charged (+3) Eu^{III} complexes, as for example [Eu(DO3A)] ($K_{\rm D} = 35.3$ mM, where H₃DO3A is 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid)²⁶ and its alkylphenatridinium derivatives ($K_{\rm D} = 2.5$ and 0.2 mM).²⁹

Conclusions

The X-ray analysis of the EDTMP crystal with the Eu^{III} ion has shown a rare example of lanthanide ion coordination with a bifunctional carbonate anion. Therefore the inner sphere of the Eu^{III} ion in the $[C(NH_2)_3]_7[Eu(EDTMP)(CO_3)] \cdot 10H_2O$ crystal is filled by donor atoms (four O and two N) of the EDTMP ligand in a similar way as was revealed in the crystal structure of its



Fig. 6 Oscillator strengths and luminescence decay rates as function of added NaHCO₃ to the Eu^{III}–EDTMP complex at pH 7.5.

carboxylate analogue, EDTA, and additionally, by two oxygen atoms from the carbonate anion.

The comparison between spectral results of the crystal and Eu^{III} -EDTMP solutions of which the pH was adjusted by NaOH, Na₂CO₃ and [C(NH₂)₃]₂CO₃ allowed us to show that the formed anionic complex of [Eu(EDTMP)(CO₃)]^{7–}, though highly negative, is thermodynamically stable. A very good fitting of a carbonate anion into the coordination space vacated by water molecules and/or hydroxy groups is a reason that the kinetically labile complex becomes inert. The high affinity of the carbonate anion towards the Eu^{III}-EDTMP complex was confirmed by the determined low dissociation constant.

The presented results may be helpful in understanding of the uptake mechanism of the ¹⁵³Sm^{III}–EDTMP complex by metastatic bones and may provide some indications for future ligand design for therapeutic complexes with lanthanide radionuclides.

Experimental

Materials and samples preparation

Stock solutions of europium chloride and perchlorate were prepared from Eu₂O₃ (99.99% Stanford Materials) by dissolving it under heating in 2 mol dm⁻³ hydrochloric and perchloric acids, respectively. The Eu^{III} concentrations were determined complexometrically using xylenol orange as an indicator. For spectral measurements of Eu^{III} : L = 1 : 1.1 solutions ($c_{Eu} = 4.0 \times$ 10^{-2} M for Eu^{III}–EDTMP and $c_{\rm Eu} = 2.0 \times 10^{-2}$ M for Eu^{III}– EDTA) of which pH was adjusted by NaOH, the stock solutions of EDTMP (ABCR) and EDTA (Merck) adjusted to pH around 7 with NaOH were used. Stock solutions of EDTMP and EDTA with carbonate were prepared by neutralization of the ligand by Na₂CO₃ or guanidinium carbonate to pH 7.0. These solutions were added to $EuCl_3$ solutions in the ratio of Eu^{III} : L equal to 1: 1.1 ($c_{Eu} = 4.0 \times 10^{-2}$ M for Eu^{III}–EDTMP and $c_{Eu} = 2.0 \times 10^{-2}$ M for Eu^{III}-EDTA) and then the pH of the solutions was adjusted by Na₂CO₃ or guanidinium carbonate, respectively.

The buffered solutions of the Eu^{III}–EDTMP complex with different concentrations of HCO₃⁻ ligand were prepared as follows. The stock solutions of the Eu^{III}–EDTMP complex and of HEPES were adjusted with NaOH to pH 7.5 and then mixed together. To a fixed amount of the latter solution the calculated amount of NaHCO₃ was added and the solutions were diluted to 10 cm³. The final concentrations of particular components in such prepared solutions were: $c_{Eu} = 4.0 \times 10^{-2}$ M, $c_{HCO_3^-} = 0.90$ M, $c_{HEPES} = 0.50$ M.

For NMR and luminescence lifetimes measurements in D_2O each of the solutions prepared earlier in water was evaporated to dryness and then dissolved in D_2O . This procedure was repeated three times.

All measurements of solutions were performed after one day of equilibration.

Crystal synthesis

Crystals of Eu^{III}–EDTMP and Eu^{III}–EDTA complexes were prepared as follows. The ligand solutions of EDTMP (0.48 g, 1.1 mmol) and EDTA (0.64 g, 2.2 mmol) were neutralized with $[C(NH_2)_3]_2CO_3$ to pH around 7 and added to an aqueous solution of Eu(ClO₄)₃ (1 and 2 mmol), respectively. The resulting solutions were basified with guanidinium carbonate to pH 10.7. Colourless crystals of $[C(NH_2)_3]_7[Eu(EDTMP)(CO_3)] \cdot 10H_2O$ (I) and $[C(NH_2)_3]_7[Eu(EDTA)(H_2O)_3]$ (II) were formed during slow evaporation.

X-Ray crystal analysis

An appropriate crystal was cut from a larger one and mounted on a Kuma KM4 diffractometer equipped with a CCD counter. The collected data were corrected for polarization, Lorentz and absorption, the latter calculated from the crystal habits captured from photo scans. The positions of Eu were found from Patterson maps, and the remainder of non-H atoms from difference Fourier maps. The positions of the C-bonded hydrogen atoms were calculated geometrically. In **I** 16 H atoms from 8 water molecules were located and refined freely (except HW91 which had its temperature factor fixed). In **II** all 6 water H atoms were found and also refined freely. The refinement was full-matrix with all non-H atoms anisotropic. All computations were performed using SHELXS97 and SHELXL97 programs.³² The molecular graphics was prepared with DIAMOND.³³

Selected crystal data for I. $C_{14}H_{74}EuN_{23}O_{25}P_4$, M = 1240.80, monoclinic, space group $P2_1/n$, Z = 4, a = 12.407(4), b = 16.606(6), c = 24.071(9) Å, $\beta = 101.85(3)^\circ$, V = 4854(3) Å³, $\mu = 1.525$ mm⁻¹, $D_c = 1.698$ g cm⁻³, F(000) = 2568, crystal size $= 0.4 \times 0.25 \times 0.20$ mm, $\theta = 3-28.5^\circ$, index ranges: $-16 \le h \le 16, -21 \le k \le 17, -31 \le l \le 31$, reflections collected/unique = 31261/11207 ($R_{int} = 0.0415$). Final *R* indices [$I > 2\sigma(I)$] R(F) = 0.0336, $R_w(F^2) = 0.0617$ and R(F) = 0.0618, $R_w(F^2) = 0.0660$ (all data). Data completeness to $2\theta = 28.5^\circ$, 91.2%. Largest diff. peak and hole 1.021 and -0.590 e Å⁻³.

Selected crystal data for II. $C_{11}H_{24}EuN_5O_{11}$, M = 554.31, monoclinic, space group $P2_1/c$, Z = 4, a = 11.269(5), b = 8.646(4), c = 18.718(9) Å, $\beta = 90.07(4)^\circ$, V = 1823.7(15) Å³, $\mu = 3.509$ mm⁻¹, $D_c = 2.019$ g cm⁻³, F(000) = 1104, crystal size $= 0.4 \times 0.17 \times 0.1$ mm, $\theta = 3-28.5^\circ$, index ranges: $-14 \le h \le 14$, $-11 \le k \le 10$, $-23 \le l \le 24$, reflections collected/unique = 11182/4233 ($R_{int} = 0.0369$). Final *R* indices $[I > 2\sigma(I)] R(F) = 0.0211$, $R_w(F^2) = 0.0552$ and R(F) = 0.0234, $R_w(F^2) = 0.0565$ (all data). Data completeness to $2\theta = 28.5^\circ$, 92.0%. Largest diff. peak and hole 0.823 and -0.696 e Å⁻³.

CCDC reference numbers 297437 and 297438.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606420e

UV-Vis measurements

All electronic absorption spectra were recorded on a Cary 500 UV-VIS-near-IR spectrophotometer. Corrected emission spectra were taken on a SLM Aminco 500 spectrofluorometer. The luminescence of the Eu^{III} ion was excited with a wavelength of 394 nm. The luminescence decay curves were detected on Edinburgh Instruments FLS 920 Spectrometer with the monitored emission at 614 nm.

NMR measurements

The 31 P NMR spectra were recorded on a Bruker AMX 500 spectrometer at 298 K. 5% H₃PO₄ in D₂O solution was used as an external standard.

Calculations. The luminescence decay lifetimes of the emitting Eu^{III} level were obtained by fitting the decay curves to a single exponential function. Emission and absorption intensities of the f–f transitions were calculated by integrating their bands. Absorption intensities were determined as oscillator strengths (*P*) by using eqn (4):

$$P = 4.32 \times 10^{-9} (cd)^{-1} \int A(\sigma) \, \mathrm{d}\sigma \tag{4}$$

where: *c* is the concentration of the Eu^{III} ion in M, *d* is the length of the optical pathlength in cm and $A(\sigma)$ is the absorbance as the function of the wavenumber in cm⁻¹.

The following eqn (5) was used for the dissociation constant $K_{\rm D}$ calculation:

$$2[\text{EuL}] \frac{X - X_{\text{EuL}}}{X_{\text{EuLA}} - X_{\text{EuL}}} = [\text{EuL}] + [\text{A}] + K_{\text{D}}$$
$$-\sqrt{([\text{EuL}] + [\text{A}] + K_{\text{D}})^2 - 4[\text{EuL}][\text{A}]}$$
(5)

where: [EuL] is the complex concentration, [A] is the HCO₃⁻ concentration, X is the measured quantity: oscillator strength value of the ${}^{7}F_{0} \rightarrow {}^{5}D_{2}$ transition, intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition scaled to the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ intensity, k is the luminescence decay rate in ms⁻¹ equal to τ^{-1} and τ is the luminescence lifetime in ms. The X_{EuLA} values were determined for the EuL solution saturated by NaHCO₃, while the X_{EuL} values were determined for the solution of which the pH adjusted by NaOH. The curves $X = f([NaHCO_3])$ were fitted by an iterative least-squares procedure in the Microsoft Excel programme. All data were well fitted to the linear dependence with the coefficients of determination ($R^{2} \ge 0.996$).

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