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Polyhedron 26 (2007) 845-850

POLYHEDRON

Structural and spectroscopic investigations of the Eu^{III}–CDTA system

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Received 20 July 2006; accepted 14 September 2006 Available online 27 September 2006

Abstract

Two crystal structures of Eu^{III} complexes with CDTA (*trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetate), $[C(NH_2)_3]_3[Eu_2-(CDTA)_2(H_2O)_2]ClO_4 \cdot 7H_2O$ (I) and $[C(NH_2)_3][Eu(CDTA)(H_2O)] \cdot 2.375H_2O$ (II), are presented. Both structures are polymeric and the central metal ions are eight-coordinate. The first coordination sphere of each Eu^{III} cation contains five carboxylate oxygen atoms, two nitrogen ones and a water molecule. For I, as well as for water solutions of the Eu^{III} -CDTA complex at various pH values, the spectroscopic (UV–Vis) properties were investigated. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Europium(III); CDTA; Structure; UV-Vis spectroscopy

1. Introduction

Lanthanide polyaminopolycarboxylate chelates play an important role both in fundamental investigations and in several areas of practical applications. They are used, among others, as shift reagents in NMR spectroscopy [1], contrast agents in MRI imaging [2], structural probes [3] and luminescent tags in immunoassays [4]. This family of compounds has been epitomized by complexes of Ln^{III} with the ethylenediaminetetraacetate (EDTA) anion, which have been extensively studied both in solution e.g. [5] and in the solid state e.g. [6] and now may serve as a kind of standard when the structure, spectroscopic and/or thermodynamic properties of lanthanide polyaminopolycarboxylates are discussed. It is therefore of interest to find how the properties are altered when the EDTA⁴⁻ skeleton is modified. In this work we present a study of two Eu^{III} complexes with such a ligand, i.e. trans-1.2-diaminocyclohexane-N, N, N', N'-tetraacetate (CDTA). The investigations of Ln^{III}-CDTA complexes carried out so far have been focused to a great part on their properties in aqueous solutions and included thermodynamic as well as spectroscopic

aspects. Their stability constants are higher by an order or two of magnitude, depending on the lanthanide, than those of the EDTA complexes [7], and generally saying, they are thermodynamically stable [8]. The spectroscopic studies have revealed that in solutions of Eu^{III}–CDTA complexes an equilibrium exists between two different species, nine- and eight-coordinate, the dissimilarity between them consisting of a different number of coordinated water molecules (three or two) [9]. The average number of these molecules has been found to be 2.3–2.6 and is a little lower than that found in water solutions of the EDTA complexes (2.6–2.8) [5f,5h].

Because of difficulties connected with growing of monocrystals of adequate quality, structural data for Ln^{III} – CDTA complexes are scarce. To the best of the authors' knowledge only three crystal structures of these complexes have been published. Two of them, $NH_4[Ln(CDTA)-(H_2O)_2] \cdot 4.5H_2O$ ($Ln = Gd^{III}$, Ho^{III}), are monomeric and isostructural [10,11] whereas in the third one, $Na[Eu-(CDTA)(H_2O)] \cdot 4H_2O$ [12], dimeric anions of $[Eu(CDTA)-\mu-(H_2O)_2-Eu(CDTA)]^{2-}$ are formed. For the last system luminescence properties were also reported. In all these complexes the Ln^{III} ions are eight-coordinate.

In the crystal, the coordination surrounding of Ln^{III} ion is unambiguously defined, therefore the spectra of the

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^{0277-5387/\$ -} see front matter @ 2006 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2006.09.031

crystals may be a good starting point for interpretation of spectral data of solution systems. The paucity of such data has motivated us to attempt the preparation of Eu^{III}– CDTA complexes in the crystalline state, to study their crystal structures and spectroscopic properties and to compare the latter with the analogous properties of Eu^{III}– CDTA complexes in solution.

2. Experimental

2.1. Materials

Solutions for spectroscopic measurements: A stock solution of europium chloride was prepared by dissolving Eu_2O_3 (99.99%; Standford materials) in 2 mol dm⁻³ hydrochloric acid. The Eu^{III} ion concentration was determined complexometrically using xylenol orange as an indicator. The stock solution of H₄CDTA (98%; Lancaster) was prepared by half-neutralization with NaOH. The pH of the 1:1.1 Eu^{III}–CDTA solutions was adjusted by a carbonate-free NaOH water solution.

Crystal preparations: An aqueous solution of equimolar quantities of europium perchlorate and H_4CDTA was heated at ca. 80 °C. Next, solid $[C(NH_2)_3]_2CO_3$ was added until the pH value was 5. Large colourless crystals of $[C(NH_2)_3]_3[Eu_2(CDTA)_2(H_2O)_2]ClO_4 \cdot 7H_2O$ (I) were

Table 1

Crystal	data	and	structure	refinement	for	both	crystals
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formed during slow evaporation. The other crystals, $[C(NH_2)_3][Eu(CDTA)(H_2O)] \cdot 2.375H_2O$ (II), were obtained as follows: a suspension of Eu_2O_3 and H_4CDTA was heated at ca. 80 °C. After dissolution of the substrates, the solution was alkalized with $[C(NH_2)_3]_2CO_3$ to a final pH value of 3, and left for crystallization.

2.2. X-ray study

Appropriate crystals were cut from larger ones and mounted on a Kuma KM4 diffractometer equipped with a CCD counter. The collected data were corrected for polarization, Lorentz and absorption, the last calculated from the crystal habit captured from photo scans. Both crystals turned out to be twinned. The twinning of crystal I was pseudo-merohedral; this was brought about by the fact that the unit cells spanned by vectors **a**, **b**, **c**, and **a**, **a-b**, **a-c** have very similar lattice constants. The fraction of the first twin component found from the refinement was 0.676(1). The twinning matrix in II was (-1/2 - 1/2 0/-3/2 1/2 0/-1/2 1/2 -1) with the result that only reflections with h + k even overlapped. The structure of I was solved and refined against all reflections, while that of II was solved using one twin component and refined against both. The positions of Eu were found from Patterson maps, the rest of the non-H atoms from difference Fourier

Crystal	I	П
Empirical formula	$C_{31}H_{72}ClEu_2N_{13}O_{29}$	$C_{15}H_{30,25}EuN_5O_{11,38}$
Formula weight	1430.39	614.65
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	triclinic, P1	triclinic, $P\overline{1}$
Unit cell dimensions		
<i>a</i> (Å)	10.652(8)	12.09(9)
b (Å)	16.075(13)	18.83(2)
<i>c</i> (Å)	17.943(14)	23.328(15)
α (°)	69.31(7)	66.82(14)
β (°)	73.24(7)	77.15(12)
γ (°)	70.86(7)	77.47(12)
Volume ($Å^3$)	2663(4)	4712(36)
Z, Calculated density (Mg/m^3)	2, 1.784	8, 1.733
Absorption coefficient (mm^{-1})	2.484	2.727
F(000)	1448	2474
Crystal size (mm)	$0.27 \times 0.20 \times 0.15$	$0.27 \times 0.18 \times 0.11$
Theta range for data collection (°)	3.03-28.43	2.25-29.07
Index ranges	$-9 \leq h \leq 14, -21 \leq k \leq 21, -23 \leq 1 \leq 23$	$-15 \leq h \leq 16, -25 \leq k \leq 23, -31 \leq 1 \leq 31$
Reflections collected/unique (R_{int})	18077/11545 (0.0341)	25498/25498
Completeness to 2θ	86.0%	69.1%
Absorption correction	analytical, from the shape	analytical, from the crystal shape
Maximum and minimum transmission	0.710 and 0.520	0.768 and 0.529
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	11 545/0/686	25498/0/1176
Goodness-of-fit on F^2	1.063	0.998
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R(F) = 0.0434, Rw(F^2) = 0.1031$	$R(F) = 0.0790, Rw(F^2) = 0.1403$
R indices (all data)	$R(F) = 0.0484, Rw(F^2) = 0.1059$	$R(F) = 0.1388, Rw(F^2) = 0.1620$
Largest differences in peak and hole ($e \text{ Å}^{-3}$)	2.654 and -2.604	1.800 and -1.616

maps. The positions of the C- and N-bonded hydrogen atoms were calculated geometrically. The refinement was full-matrix with all ordered non-H atoms anisotropic. The oxygen atoms from disordered water molecules (in II) were refined isotropically and C- and N-bonded H atoms were constrained to 1.2 times the factors of the relevant C atoms. Because of twinning and partial overlapping of some reflections the precision of the structure determination of II unfortunately deteriorated. Our several attempts to find an untwinned sample failed and therefore we decided to solve and refine the structure against the twin data. The large volume of the asymmetric part seems upsetting. However we could not find a cell with smaller volume and herein we present the best model of twinning and the crystal structure which we have been able to find. Both structures were solved and refined by SHELXS97 [13] and SHELXL97 [14], respectively, and the program DIAMOND [15] was used for the molecular graphics. The data concerning the crystal parameters, data collection and refinement details are presented in Table 1.

3. Spectroscopy

3.1. UV-Vis measurements

Electronic absorption spectra were recorded on a Cary 500 UV–VIS–near-IR spectrophotometer. The solutions were measured at room temperature. Only spectra of I were recorded because we could not obtain a good sample of II. The absorption spectra of I were measured at 293 and 30 K (in an Oxford CF 1204 continuous flow helium cryostat). The oscillator strengths (P) were determined using the equation:

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

where c is the concentration of the Eu^{III} ion in M, d is the length of the optical way in cm and $A(\sigma)$ is the absorbance as the function of the wavenumber in cm⁻¹. The P values were not corrected for the population of the ⁷F₁ state at room temperature. Corrected emission spectra were measured on a SLM Aminco 500 spectrofluorometer at 293 and 77 K. For luminescence, the Eu^{III} ion was excited with a wavelength of 394 nm.

4. Results and discussion

4.1. Structure

Both structures are built up from polymeric complex chains, guanidinium cations, water of crystallization (partially disordered in II), and, in the case of I, also perchlorate anions. The polymeric chains are composed of europium cations, *trans*-1,2-diaminocyclohexane-N,N,N',N'-tetraacetate (CDTA) anions and water molecules coordinated to europium. Each polymer unit (mer) contains a Eu^{III} cation and a CDTA anion which is coordinated to the metal

through its four carboxylate oxygen atoms and two nitrogen atoms, filling thus six coordinate sites. The seventh site is occupied by a water molecule. Apart from that each mer donates one of its carboxylate oxygen atoms to the first coordination sphere of an Eu^{III} ion in a neighbouring mer (accepting at the same time an analogous O atom from the other neighbour). In this way infinite polymeric chains are formed and the europium cations are eight-coordinate. In I there are two symmetry independent Eu sites, and accordingly two different mers. In II the number of symmetry independent Eu sites is 4. Nevertheless, superimposition of all six mers (Fig. 1) shows that their conformations are very similar, the difference being only in small variations of bond lengths and angles. The Eu-O and Eu-N distances (see Table 2) are similar to those found in the europium dimeric complex with CDTA, Na[Eu(CDTA)H₂O] · 4H₂O [12], however the Eu– OH_2 bond distances are significantly longer in the present structures. The Eu-OH₂ average distances are 0.125 Å (compound I) and 0.103 Å (compound **II**) longer than in the quoted dimer. These variations may be caused by different modes of interaction of guanidinium and sodium cations with the CDTA moiety, because these cations induce different hydrogen bond networks. In both presented structures the shortest bonds are those involving carboxylate O atoms, the Eu-OH₂ ones are longer, and the



Fig. 1. Superimposed Eu coordination environments in I and II. The shortened atomic labels stand: OA for O1 and O11 in I, O13, O23, O31, O41 in II; OB-O2, O12 (I), O14, O24, O32, O42 (II); OC-O4, O14 (I), O11, O21, O33, O43 (II); OD-O3, O13 (I), O12, O22, O34, O44 (II); OE-O7, O16 (I), O17, O27, O37, O47 (II); OF-O8, O15 (I), O18, O28, O38, O48 (II); OG-O5, O17 (I), O15, O25, O35, O45 (II); OH-O6, O18 (I), O16, O26, O36, O46 (II); OI-O8, O15ⁱ (I), O48^j, O18, O28, O38 (II); OW-OW1, OW2 (I), OW1, OW2, OW3, OW4 (II); NA-N12, N21 (I), N11, N21, N31, N41 (II); NB-N11, N22 (I), N12, N22, N32, N42 (II); CA-C1, C21 (I), C13, C33, C51, C71 (II); CB-C2, C22 (I), C14, C34, C52, C72 (II); CC-C4, C24 (I), C11, C31, C53, C73 (II); CD-C3, C23 (I), C12, C32, C54, C74 (II); CE-C5, C25 (I), C15, C35, C55, C75 (II); CF-C10, C30 (I), C16, C36, C56, C76 (II); CG-C9, C29 (I), C17, C37, C57, C77 (II); CH-C8, C28 (I), C18, C38, C58, C78 (II); CI-C7, C27 (I), C19, C39, C59, C79 (II); CJ-C6, C26 (I), C20, c40, C60, C80 (II); CK-C11, C33 (I), C24, C44, C64, C84 (II); CL-C12, C34 (I), C23, C43, C63, C83 (II); CM-C13, C31 (I), C22, C42, C62, C82 (II); CN-C14, C32 (I), C21, C41, C61, C81 (II).

Table 2 The Eu–O,N distances in I and II (Å)

I		II	
Eu(1)-O(1)	2.314(6)	Eu(1)-O(48 ^j)	2.327(8)
$Eu(1) - O(15^{i})$	2.339(5)	Eu(1)–O(17)	2.353(9)
Eu(1)–O(7)	2.343(6)	Eu(1)-O(13)	2.374(7)
Eu(1)–O(4)	2.362(6)	Eu(1)-O(15)	2.387(8)
Eu(1)–O(5)	2.364(5)	Eu(1)–O(11)	2.398(11)
Eu(1)-OW1	2.469(6)	Eu(1)-OW1	2.464(16)
Eu(1)-N(11)	2.615(6)	Eu(1) - N(12)	2.602(8)
Eu(1)-N(12)	2.626(6)	Eu(1) - N(11)	2.613(19)
Eu(2)–O(8)	2.311(6)	Eu(2)–O(18)	2.317(13)
Eu(2)–O(11)	2.364(5)	Eu(2)-O(23)	2.354(8)
Eu(2)–O(14)	2.363(5)	Eu(2)-O(27)	2.356(7)
Eu(2)-O(17)	2.369(5)	Eu(2)-O(25)	2.378(8)
Eu(2)-O(16)	2.407(5)	Eu(2)–O(21)	2.387(8)
Eu(2)–OW2	2.458(6)	Eu(2)-OW2	2.429(12)
Eu(2)-N(21)	2.597(6)	Eu(2)-N(21)	2.607(11)
Eu(2)-N(22)	2.604(6)	Eu(2)-N(22)	2.608(19)
		Eu(3)-O(28)	2.301(9)
		Eu(3)–O(31)	2.341(10)
		Eu(3)-O(37)	2.350(11)
		Eu(3)–O(35)	2.395(7)
		Eu(3)–O(33)	2.415(10)
		Eu(3)-OW3	2.429(15)
		Eu(3)–N(31)	2.596(19)
		Eu(3)-N(32)	2.667(9)
		Eu(4)–O(38)	2.297(12)
		Eu(4)-O(45)	2.370(8)
		Eu(4)–O(43)	2.374(10)
		Eu(4)–O(41)	2.375(9)
		Eu(4)–O(47)	2.388(7)
		Eu(4)–OW4	2.444(12)
		Eu(4)-N(42)	2.595(17)
		Eu(4) - N(41)	2.642(14)

Symmetry transformations used to generate equivalent atoms: i-x - 1, y, z; j-x + 1, y - 1, z.

Eu-N ones are the longest. As far as the conformation of the ligand is concerned, two subsets of methylenecarboxylate groups may be discerned. In each CDTA ligand two such groups are almost parallel. In II the angles between the least-squares fitted planes of such planes (namely C13 and C23, C33 and C43, C51 and C63, C71 and C83; the methylenecarboxylate groups are labelled after their central C atoms) are in the range 0.6–10.0°. In I the relevant angles differ more: the planes of the groups C1 and C12 are mutually twisted by 21.0°, whereas the groups C21 and C34 are twisted by only 4.5°. The other pairs are twisted by 54.9° and 59.7° in I, and 60.1-70.5° in II. Apart from that it may be noticed that the C-O bonds are generally longer when the O atom is coordinated to Eu, although the difference between the C-O lengths with O atoms coordinated and uncoordinated falls often within the range of experimental error. The approximate symmetry of all Eu first coordination spheres in both structures is C₂ (after neglecting the difference between the water and the bridging carboxylate O atoms); the axis passes through the center of the cyclohexyl ring. Eu and the bisector of the relevant water-Eu-bridging O atom angle. It is noteworthy that in the presented crystals the CDTA ligand behaves in a way



Fig. 2. A fragment of the polymeric chain in I.



Fig. 3. A fragment of the polymeric chain in II.

different to that of its analogue, i.e. ethylenediaminetetracetate (EDTA). The Eu^{III}–EDTA complexes are monomeric, and the europium cation is nine-coordinate [6d,6e,6f], contrary to the polymeric structures with eight-coordinate Eu ions in the present structures. Fragments of the polymeric complex chains are presented in Figs. 2 and 3.

5. Spectroscopic results

For the ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$ transition in I we were able to observe one peak at 17245 cm⁻¹ at room temperature while at 30 K two components at 17241 and 17234 cm^{-1} appeared. The ground $({}^{7}F_{0})$ and emitting $({}^{5}D_{0})$ states of the europium ion are non-degenerate, therefore the number of peaks observed in the range 578-582 nm indicates the number of various chemical surroundings of the Eu^{III} ion. Accordingly we may assume existence of two different europium sites at 30 K and of one site at room temperature. In the absorption spectrum of a related compound, $[C(NH_2)_3][Eu(EDTA)(H_2O)_3]$, only one ${}^7F_0 \rightarrow {}^5D_0$ peak was observed at a very similar energy, 17252 cm^{-1} at room temperature [16] and 17243 cm⁻¹ at 77 K. Also in the ${}^{7}F_{0} \rightarrow {}^{5}D_{1}$ and ${}^{7}F_{0} \rightarrow {}^{5}D_{2}$ transitions the number of components in the spectrum recorded at 77 K is greater than that found in the spectrum taken at 293 K. For the low local symmetry of the Eu^{III} ion in each symmetry independent site the number of the components should be 3 and 5, respectively. At room temperature the number of crystal

field levels in the absorption spectrum for ${}^{7}F_{0} \rightarrow {}^{5}D_{1}$ and ${}^{7}F_{0} \rightarrow {}^{5}D_{2}$ are actually 3 and 5, whereas in the low temperature (30 K) transitions 5 and 7 crystal field components in the range 19050–19120 and 21390–21550 cm⁻¹, respectively, may be seen (Fig. 4). This may suggest that between 293 and 100 K (taking into account the structural data reported above) a phase transition occurs. The oscillator strengths found in I at 293 and 30 K are presented in Table 3. Inspection of these data reveals somewhat anomalous behaviour of these quantities. Namely, the intensities of all the presented transitions increase on lowering the temperature. Such a change might be attributed to a phase transition in the case of ${}^7F_0 \rightarrow {}^5D_0$ and ${}^7F_0 \rightarrow {}^5D_2$. The most surprising thing is, however, the anomalous growth of the intensity of the ${}^{7}F_{0} \rightarrow {}^{5}D_{1}$ transition, which is more than twice as intense as theoretically predicted [17]. Such an increase cannot be explained by thermal population of the ${}^{7}F_{1}$ state, which would account only for the loss of approximately 20 % of the intensity at room temperature. The reasons for this phenomenon are unclear, and perhaps need more detailed investigations, which however lie outside the scope of the present paper.

The splitting of the bands may also be observed in emission spectra at 77 K. At room temperature the transition ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ was unsplit, whereas the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions had 3 and 4 discernible components. At 77 K the number of observed components was 2 for ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$, 6 for ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and 7 for ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$.

The results presented above may serve as a background for the interpretation of the spectroscopic properties of water solutions of the Eu^{III}–CDTA system. These properties remain essentially the same in the pH range between

Oscillator strength values ((P)	of the Eu	^{III} complexes	with	CDTA
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Complex	${}^7\mathrm{F}_0 \rightarrow {}^5\mathrm{D}_0$	$^7F_0 \rightarrow {}^5D_1$	$^7F_0 \rightarrow {}^5D_2$
-	$P \times 10^8$	$P \times 10^8$	$P \times 10^8$
Eu-CDTA pH 5.26	1.20	1.61	5.90
Eu-CDTA pH 7.40	1.25	1.62	5.34
Eu-CDTA pH 9.16	1.18	1.52	6.20
Eu-CDTA pH 11.0	0.59	1.50	11.4
Crystal $T = 293$ K	0.50	1.44	3.35
Crystal $T = 30$ K	1.38	3.20	11.0

3.5 and 9. The most significant changes in the absorption spectra are observed above pH 10. In Fig. 4 the absorption spectra of Eu^{III}-CDTA solutions at pH 7.40 and 11.0 have been juxtaposed. For both solutions two maxima at 17250 and 17239 cm⁻¹ may be observed for the ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$ transition, which confirms the equilibrium of nine- and eightcoordinate isomers, as was previously reported at pH = 6.0 [9]. These values are similar both to the maximum found in the crystal at room temperature and to the analogous maxima found in solutions of the Eu^{III}-EDTA complex $(17254 \text{ and } 17240 \text{ cm}^{-1})$ [16]. There is another similarity that perhaps should be mentioned. Namely, the most intense crystal field components in the ${}^7F_0 \rightarrow {}^5D_2$ transition in both solutions very closely match the analogous components in the spectrum of I at room temperature.

The most remarkable changes may be observed in the values of the oscillator strengths (Table 3). The *P* value of the transition ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$ remains practically constant up to approximately pH = 9 and then decreases by about half, reaching a value very similar to that calculated for **I**



Fig. 4. Absorption spectra of the ${}^{7}F_{0} \rightarrow {}^{5}D_{0,1,2}$ transitions of Eu^{III} complexes with CDTA in solution: $c_{Eu} = 44.1$ mM, d = 5 cm and in the monocrystal $c_{Eu} = 2.49$ M, d = 0.102 cm.

at room temperature. The magnetic-dipole allowed transition ${}^{7}F_{0} \rightarrow {}^{5}D_{1}$ in the solutions and in I at 293 K is constant with the P value close to the theoretical value [17]. The intensity of the hypersensitive ${}^{7}F_{0} \rightarrow {}^{5}D_{2}$ transition is, out of the three presented ones, the most affected by changes in the europium ion first coordination sphere. The oscillator strength of this band, like that of ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$, does not change essentially up to pH \approx 9, and then, contrary to the latter transition, doubles at pH = 11. These changes may reflect the alterations within the first coordination sphere of the Eu^{III} ion, consisting of partial substitution of coordinated water molecules by hydroxy anions [5c,5d] and/or formation of a polymeric species [18]. The P values for the solutions are greater than in I at 293 K, because of molecular dynamics around the metal ion in solutions.

6. Conclusions

The presented results suggest that the CDTA anion behaves in a somewhat different way in comparison to EDTA as far as the structural aspects are concerned. Namely CDTA shows a more pronounced tendency to form polymeric structures with lanthanides. Apart from that the coordination numbers of all Eu^{III}-CDTA complexes are eight while in all known crystal structures of Eu^{III}–EDTA systems the Eu^{III} ion is nine-coordinate. The spectroscopic properties of the presented Eu^{III}-CDTA systems in water solutions rather closely resemble those of related Eu^{III}-EDTA ones. For instance for Eu^{III} complexes with both ligands the ${}^{7}F_{0} \rightarrow {}^{5}D_{0,1,2}$ transitions lie at very similar energies. The [Eu(CDTA)(H₂O)_{3 or 2}]⁻ species remain stable up to $pH \approx 9$, then partial hydrolysis and/or polymerization take place. The spectra of $[C(NH_2)_3]_3[Eu_2(CDTA)_2(H_2O)_2]ClO_4 \cdot 7H_2O$ at various temperatures reveal a phase transition in the crystal.

Acknowledgements

The authors would like to thank Ing. Halina Trelińska-Nowak for the spectroscopic measurements and Dr. Andrzej Kochel for help in the X-ray data collection.

Appendix A. Supplementary material

CCDC 615028 and 615027 contain the supplementary crystallographic data for I and II. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallo-graphic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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